## General, Organic, and Biological Chemistry: A Cellular Perspective

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## 1 | THE STRUCTURE OF ATOMS



**Figure 1.1** Atoms are the building blocks of molecules found in the universe—air, soil, water, rocks . . . and also the cells of all living organisms. In this model of an organic molecule, the atoms of carbon (black), hydrogen (white), nitrogen (blue), oxygen (red), and sulfur (yellow) are shown in proportional atomic size. The silver rods indicate chemical bonds. (credit: modification of work by Christian Guthier)

## **Chapter Outline**

- 1.1: Phases and Classification of Matter
- 1.2: Atoms, Isotopes, Ions, and Molecules: The Building Blocks
- 1.3: The Periodic Table

## Introduction

Elements in various combinations comprise all matter, including living things. Some of the most abundant elements in living organisms include carbon, hydrogen, nitrogen, oxygen, sulfur, and phosphorus. These form the nucleic acids, proteins, carbohydrates, and lipids that are the fundamental components of living matter. Biologists must understand these important building blocks and the unique structures of the atoms that make up molecules, allowing for the formation of cells, tissues, organ systems, and entire organisms.

All biological processes follow the laws of physics and chemistry, so in order to understand how biological systems work, it is important to understand the underlying physics and chemistry. For example, the flow of blood within the circulatory system follows the laws of physics that regulate the modes of fluid flow. The breakdown of the large, complex molecules of food into smaller molecules—and the conversion of these to release energy to be stored in adenosine triphosphate (ATP)—is a series of chemical reactions that follow chemical laws. The properties of water and the formation of hydrogen bonds are key to understanding living processes. Recognizing the properties of acids and bases is important, for example, to our understanding of the digestive process. Therefore, the fundamentals of physics and chemistry are important for gaining insight into biological processes.

## 1.1 | Phases and Classification of Matter

By the end of this section, you will be able to:

- · Describe the basic properties of each physical state of matter: solid, liquid, and gas
- Define and give examples of atoms and molecules
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition
- · Distinguish between mass and weight
- Apply the law of conservation of matter

**Matter** is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure 1.2). A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A gas takes both the shape and volume of its container.



Figure 1.2 The three most common states or phases of matter are solid, liquid, and gas.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A **plasma** is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure 1.3). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.



Figure 1.3 A plasma torch can be used to cut metal. (credit: "Hypertherm"/Wikimedia Commons)



In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see. Watch this **video (http://openstax.org/l/16plasma)** to learn more about plasma and the places you encounter it.

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The **mass** of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. **Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon's gravity is only

one-sixth that of the earth's. She may feel "weightless" during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never "massless."

The **law of conservation of matter** summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change).* Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure 1.4). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.



**Figure 1.4** (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

## Atoms and Molecules

An **atom** is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning "indivisible") (**Figure 1.5**). This atom would no longer be gold if it were divided any further.



**Figure 1.5** (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by "Erwinrossen"/Wikimedia Commons)

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry. Other aspects of Dalton's atomic theory are still used but with minor revisions (details of Dalton's theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom "dimes" to cover it. (Figure 1.6) shows increasingly close microscopic and atomic level views of ordinary cotton.



**Figure 1.6** These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by "Featheredtar"/Wikimedia Commons)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about  $3 \times 10^{-13}$  grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or  $3 \times 10^{14}$ ) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms

(Figure 1.7). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A **molecule** consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.



**Figure 1.7** The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

## **Classifying Matter**

We can classify matter into several categories. Two broad categories are mixtures and pure substances. A **pure substance** has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called **elements**. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called **compounds**. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen (Figure 1.8). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).



Figure 1.8 (a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)



Many compounds break down when heated. This **site (http://openstax.org/l/16mercury)** shows the breakdown of mercury oxide, HgO. You can also view an example of the **photochemical decomposition of silver chloride (http://openstax.org/l/16silvchloride)** (AgCl), the basis of early photography.

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A **mixture** is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a **heterogeneous mixture**. Italian dressing is an example of a heterogeneous mixture (Figure 1.9). Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A **homogeneous mixture**, also called a **solution**, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly (Figure 1.9). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



**Figure 1.9** (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a "left": modification of work by John Mayer; credit a "right": modification of work by Umberto Salvagnin; credit b "left: modification of work by Jeff Bedford)

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties by which we can distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in (Figure 1.10).



Figure 1.10 Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth's crust and atmosphere (**Table 1.1**). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Element	Symbol	Percent Mass	Element	Symbol	Percent Mass
oxygen	0	49.20	chlorine	CI	0.19
silicon	Si	25.67	phosphorus	Р	0.11
aluminum	Al	7.50	manganese	Mn	0.09
iron	Fe	4.71	carbon	С	0.08
calcium	Са	3.39	sulfur	S	0.06
sodium	Na	2.63	barium	Ва	0.04
potassium	к	2.40	nitrogen	N	0.03
magnesium	Mg	1.93	fluorine	F	0.03
hydrogen	н	0.87	strontium	Sr	0.02
titanium	Ti	0.58	all others	-	0.47

### **Elemental Composition of Earth**

Table 1.1

Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in (Figure 1.11).



**Figure 1.11** The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H<sub>2</sub>O separates into H<sub>2</sub> and O<sub>2</sub> gases.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs,  $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ , will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline (Figure 1.12). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.



Figure 1.12 A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

### Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure 1.13) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Figure 1.13 Almost one-third of naturally occurring elements are used to make a cell phone. (credit: modification of work by John Taylor)

## **Chemistry End of Chapter Exercises**

### Exercise 1.1

Why do we use an object's mass, rather than its weight, to indicate the amount of matter it contains?

#### Exercise 1.2

What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

### Solution

Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

### Exercise 1.3

How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

### Exercise 1.4

How does a homogeneous mixture differ from a pure substance? How are they similar?

### Solution

The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

### Exercise 1.5

How does an element differ from a compound? How are they similar?

### Exercise 1.6

How do molecules of elements and molecules of compounds differ? In what ways are they similar?

### Solution

Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

Exercise 1.7

How does an atom differ from a molecule? In what ways are they similar?

### Exercise 1.8

Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds.

### Solution

Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

### Exercise 1.9

Classify each of the following as an element, a compound, or a mixture:

(a) copper

(b) water

(c) nitrogen

(d) sulfur

(e) air

(f) sucrose

(g) a substance composed of molecules each of which contains two iodine atoms

(h) gasoline

Exercise 1.10

Classify each of the following as an element, a compound, or a mixture:

(a) iron

(b) oxygen

(c) mercury oxide

(d) pancake syrup

(e) carbon dioxide

(f) a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom

(g) baking soda

(h) baking powder

### Solution

(a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture

Exercise 1.11

A sulfur atom and a sulfur molecule are not identical. What is the difference?

### Exercise 1.12

How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

### Solution

In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

### Exercise 1.13

We refer to astronauts in space as weightless, but not without mass. Why?

### Exercise 1.14

As we drive an automobile, we don't think about the chemicals consumed and produced. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.

### Solution

Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

### Exercise 1.15

Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.

### Exercise 1.16

When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide which we call rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?

### Solution

(a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 0.9 g

### Exercise 1.17

As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:

(a) Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.

(b) When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.

(c) Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

### Exercise 1.18

Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

### glucose $\longrightarrow$ ethanol + carbon dioxide

(a) If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?

(b) If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.

(c) If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

### Solution

(a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

# **1.2** Atoms, Isotopes, Ions, and Molecules: The Building Blocks

By the end of this section, you will be able to:

- Define matter and elements
- · Describe the interrelationship between protons, neutrons, and electrons
- · Compare the ways in which electrons can be donated or shared between atoms
- Explain the ways in which naturally occurring elements combine to create molecules, cells, tissues, organ systems, and organisms

At its most fundamental level, life is made up of matter. **Matter** is any substance that occupies space and has mass. **Elements** are unique forms of matter with specific chemical and physical properties that cannot be broken down into smaller substances by ordinary chemical reactions. There are 118 elements, but only 92 occur naturally. The remaining elements are synthesized in laboratories and are unstable.

Each element is designated by its chemical symbol, which is a single capital letter or, when the first letter is already "taken" by another element, a combination of two letters. Some elements follow the English term for the element, such as C for carbon and Ca for calcium. Other elements' chemical symbols derive from their Latin names; for example, the symbol for sodium is Na, referring to *natrium*, the Latin word for sodium.

The four elements common to all living organisms are oxygen (O), carbon (C), hydrogen (H), and nitrogen (N). In the non-living world, elements are found in different proportions, and some elements common to living organisms are relatively rare on the earth as a whole, as shown in Table 1.2. For example, the atmosphere is rich in nitrogen and oxygen but contains little carbon and hydrogen, while the earth's crust, although it contains oxygen and a small amount of hydrogen, has little nitrogen and carbon. In spite of their differences in abundance, all elements and the chemical reactions between them obey the same chemical and physical laws regardless of whether they are a part of the living or non-living world.

## Approximate Percentage of Elements in Living Organisms (Humans) Compared to the Non-living World

Element	Life (Humans)	Atmosphere	Earth's Crust
Oxygen (O)	65%	21%	46%
Carbon (C)	18%	trace	trace
Hydrogen (H)	10%	trace	0.1%
Nitrogen (N)	3%	78%	trace

Table 1.2

## The Structure of the Atom

To understand how elements come together, we must first discuss the smallest component or building block of an element, the atom. An **atom** is the smallest unit of matter that retains all of the chemical properties of an element. For example, one gold atom has all of the properties of gold in that it is a solid metal at room temperature. A gold coin is simply a very large number of gold atoms molded into the shape of a coin and containing small amounts of other elements known as impurities. Gold atoms cannot be broken down into anything smaller while still retaining the properties of gold.

An atom is composed of two regions: the **nucleus**, which is in the center of the atom and contains protons and neutrons, and the outermost region of the atom which holds its electrons in orbit around the nucleus, as illustrated in **Figure 1.14**. Atoms contain protons, electrons, and neutrons, among other subatomic particles. The

only exception is hydrogen (H), which is made of one proton and one electron with no neutrons.



Figure 1.14 Elements, such as helium, depicted here, are made up of atoms. Atoms are made up of protons and neutrons located within the nucleus, with electrons in orbitals surrounding the nucleus.

Protons and neutrons have approximately the same mass, about  $1.67 \times 10^{-24}$  grams. Scientists arbitrarily define this amount of mass as one atomic mass unit (amu) or one Dalton, as shown in **Table 1.3**. Although similar in mass, protons and neutrons differ in their electric charge. A **proton** is positively charged whereas a **neutron** is uncharged. Therefore, the number of neutrons in an atom contributes significantly to its mass, but not to its charge. **Electrons** are much smaller in mass than protons, weighing only  $9.11 \times 10^{-28}$  grams, or about 1/1800 of an atomic mass unit. Hence, they do not contribute much to an element's overall atomic mass. Therefore, when considering atomic mass, it is customary to ignore the mass of any electrons and calculate the atom's mass based on the number of protons and neutrons alone. Although not significant contributors to mass, electrons do contribute greatly to the atom's charge, as each electron has a negative charge equal to the positive charge of a proton. In uncharged, neutral atoms, the number of electrons orbiting the nucleus is equal to the number of protons inside the nucleus. In these atoms, the positive and negative charges cancel each other out, leading to an atom with no net charge.

Accounting for the sizes of protons, neutrons, and electrons, most of the volume of an atom—greater than 99 percent—is, in fact, empty space. With all this empty space, one might ask why so-called solid objects do not just pass through one another. The reason they do not is that the electrons that surround all atoms are negatively charged and negative charges repel each other.

	Charge	Mass (amu)	Location
Proton	+1	1	nucleus
Neutron	0	1	nucleus
Electron	-1	0	orbitals

### Protons, Neutrons, and Electrons

Table 1.3

## **Atomic Number and Mass**

Atoms of each element contain a characteristic number of protons and electrons. The number of protons determines an element's **atomic number** and is used to distinguish one element from another. The number of neutrons is variable, resulting in isotopes, which are different forms of the same atom that vary only in the number of neutrons they possess. Together, the number of protons and the number of neutrons determine an element's **mass number**, as illustrated in **Figure 1.15**. Note that the small contribution of mass from electrons is disregarded in calculating the mass number. This approximation of mass can be used to easily calculate how many neutrons an element has by simply subtracting the number of protons from the mass number. Since an element's isotopes will have slightly different mass numbers, scientists also determine the **atomic mass**, which is the calculated mean of the mass number for its naturally occurring isotopes. Often, the resulting number

contains a fraction. For example, the atomic mass of chlorine (Cl) is 35.45 because chlorine is composed of several isotopes, some (the majority) with atomic mass 35 (17 protons and 18 neutrons) and some with atomic mass 37 (17 protons and 20 neutrons).



thirteen, respectively. Its relative atomic mass is 12.011

How many neutrons do carbon-12 and carbon-13 have, respectively?

## Isotopes

**Isotopes** are different forms of an element that have the same number of protons but a different number of neutrons. Some elements—such as carbon, potassium, and uranium—have naturally occurring isotopes. Carbon-12 contains six protons, six neutrons, and six electrons; therefore, it has a mass number of 12 (six protons and six neutrons). Carbon-14 contains six protons, eight neutrons, and six electrons; its atomic mass is 14 (six protons and eight neutrons). These two alternate forms of carbon are isotopes. Some isotopes may emit neutrons, protons, and electrons, and attain a more stable atomic configuration (lower level of potential energy); these are radioactive isotopes, or **radioisotopes**. Radioactive decay (carbon-14 decaying to eventually become nitrogen-14) describes the energy loss that occurs when an unstable atom's nucleus releases radiation.

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## **Carbon Dating**

Carbon is normally present in the atmosphere in the form of gaseous compounds like carbon dioxide and methane. Carbon-14 (<sup>14</sup>C) is a naturally occurring radioisotope that is created in the atmosphere from atmospheric <sup>14</sup>N (nitrogen) by the addition of a neutron and the loss of a proton because of cosmic rays. This is a continuous process, so more <sup>14</sup>C is always being created. As a living organism incorporates <sup>14</sup>C initially as carbon dioxide fixed in the process of photosynthesis, the relative amount of <sup>14</sup>C in its body is equal to the concentration of <sup>14</sup>C in the atmosphere. When an organism dies, it is no longer ingesting <sup>14</sup>C, so the ratio between <sup>14</sup>C and <sup>12</sup>C will decline as <sup>14</sup>C decays gradually to <sup>14</sup>N by a process called beta decay—the emission of electrons or positrons. This decay gives off energy in a slow process.

After approximately 5,730 years, half of the starting concentration of <sup>14</sup>C will have been converted back to <sup>14</sup>N. The time it takes for half of the original concentration of an isotope to decay back to its more stable form is called its half-life. Because the half-life of <sup>14</sup>C is long, it is used to date formerly living objects such as old bones or wood. Comparing the ratio of the <sup>14</sup>C concentration found in an object to the amount of <sup>14</sup>C detected in the atmosphere, the amount of the isotope that has not yet decayed can be determined. On the basis of this amount, the age of the material, such as the pygmy mammoth shown in Figure 1.16, can be calculated with accuracy if it is not much older than about 50,000 years. Other elements have isotopes with different half lives. For example, <sup>40</sup>K (potassium-40) has a half-life of 1.25 billion years, and <sup>235</sup>U (Uranium 235) has a half-life of about 700 million years. Through the use of radiometric dating, scientists can study the age of fossils or other remains of extinct organisms to understand how organisms have evolved from earlier species.



**Figure 1.16** The age of carbon-containing remains less than about 50,000 years old, such as this pygmy mammoth, can be determined using carbon dating. (credit: Bill Faulkner, NPS)

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To learn more about atoms, isotopes, and how to tell one isotope from another, run the simulation. (This media type is not supported in this reader. Click to open media in browser.) (http://legacy.cnx.org/content/m44390/1.21/#eip-id1165071748010)

## **The Periodic Table**

The different elements are organized and displayed in the **periodic table**. Devised by Russian chemist Dmitri Mendeleev (1834–1907) in 1869, the table groups elements that, although unique, share certain chemical properties with other elements. The properties of elements are responsible for their physical state at room temperature: they may be gases, solids, or liquids. Elements also have specific **chemical reactivity**, the ability to combine and to chemically bond with each other.

In the periodic table, shown in **Figure 1.17**, the elements are organized and displayed according to their atomic number and are arranged in a series of rows and columns based on shared chemical and physical properties. In addition to providing the atomic number for each element, the periodic table also displays the element's atomic mass. Looking at carbon, for example, its symbol (C) and name appear, as well as its atomic number of six (in the upper left-hand corner) and its atomic mass of 12.11.



Figure 1.17 The periodic table shows the atomic mass and atomic number of each element. The atomic number appears above the symbol for the element and the approximate atomic mass appears below it.

The periodic table groups elements according to chemical properties. The differences in chemical reactivity between the elements are based on the number and spatial distribution of an atom's electrons. Atoms that chemically react and bond to each other form molecules. **Molecules** are simply two or more atoms chemically bonded together. Logically, when two atoms chemically bond to form a molecule, their electrons, which form the outermost region of each atom, come together first as the atoms form a chemical bond.

## **Electron Shells and the Bohr Model**

It should be stressed that there is a connection between the number of protons in an element, the atomic number that distinguishes one element from another, and the number of electrons it has. In all electrically neutral atoms,

the number of electrons is the same as the number of protons. Thus, each element, at least when electrically neutral, has a characteristic number of electrons equal to its atomic number.

An early model of the atom was developed in 1913 by Danish scientist Niels Bohr (1885–1962). The Bohr model shows the atom as a central nucleus containing protons and neutrons, with the electrons in circular **orbitals** at specific distances from the nucleus, as illustrated in **Figure 1.18**. These orbits form electron shells or energy levels, which are a way of visualizing the number of electrons in the outermost shells. These energy levels are designated by a number and the symbol "n." For example, 1n represents the first energy level located closest to the nucleus.



**Figure 1.18** The Bohr model was developed by Niels Bohrs in 1913. In this model, electrons exist within principal shells. An electron normally exists in the lowest energy shell available, which is the one closest to the nucleus. Energy from a photon of light can bump it up to a higher energy shell, but this situation is unstable, and the electron quickly decays back to the ground state. In the process, a photon of light is released.

Electrons fill orbitals in a consistent order: they first fill the orbitals closest to the nucleus, then they continue to fill orbitals of increasing energy further from the nucleus. If there are multiple orbitals of equal energy, they will be filled with one electron in each energy level before a second electron is added. The electrons of the outermost energy level determine the energetic stability of the atom and its tendency to form chemical bonds with other atoms to form molecules.

Under standard conditions, atoms fill the inner shells first, often resulting in a variable number of electrons in the outermost shell. The innermost shell has a maximum of two electrons but the next two electron shells can each have a maximum of eight electrons. This is known as the **octet rule**, which states, with the exception of the innermost shell, that atoms are more stable energetically when they have eight electrons in their **valence shell**, the outermost electron shell. Examples of some neutral atoms and their electron configurations are shown in **Figure 1.19**. Notice that in this **Figure 1.19**, helium has a complete outer electron shell, with two electrons filling its first and only shell. Similarly, neon has a complete outer 2n shell containing eight electrons. In contrast, chlorine and sodium have seven and one in their outer shells, respectively, but theoretically they would be more energetically stable if they followed the octet rule and had eight.



**Figure 1.19** Bohr diagrams indicate how many electrons fill each principal shell. Group 18 elements (helium, neon, and argon are shown) have a full outer, or valence, shell. A full valence shell is the most stable electron configuration. Elements in other groups have partially filled valence shells and gain or lose electrons to achieve a stable electron configuration.

An atom may give, take, or share electrons with another atom to achieve a full valence shell, the most stable electron configuration. Looking at this figure, how many electrons do elements in group 1 need to lose in order to achieve a stable electron configuration? How many electrons do elements in groups 14 and 17 need to gain to achieve a stable configuration?

Understanding that the organization of the periodic table is based on the total number of protons (and electrons) helps us know how electrons are distributed among the outer shell. The periodic table is arranged in columns and rows based on the number of electrons and where these electrons are located. Take a closer look at the some of the elements in the table's far right column in Figure 1.17. The group 18 atoms helium (He), neon (Ne), and argon (Ar) all have filled outer electron shells, making it unnecessary for them to share electrons with other atoms to attain stability; they are highly stable as single atoms. Their non-reactivity has resulted in their being named the **inert gases** (or **noble gases**). Compare this to the group 1 elements in the left-hand column. These elements, including hydrogen (H), lithium (Li), and sodium (Na), all have one electron in their outermost shells. That means that they can achieve a stable configuration and a filled outer shell by donating or sharing one electron with another atom or a molecule such as water. Hydrogen will donate or share its electron to achieve this configuration, while lithium and sodium will donate their electron to become stable. As a result of losing a negatively charged electron, they become positively charged ions. Group 17 elements, including fluorine and chlorine, have seven electrons in their outmost shells, so they tend to fill this shell with an electron from other atoms or molecules, making them negatively charged ions. Group 14 elements, of which carbon is the most important to living systems, have four electrons in their outer shell allowing them to make several covalent bonds (discussed below) with other atoms. Thus, the columns of the periodic table represent the potential shared state of these elements' outer electron shells that is responsible for their similar chemical characteristics.

## **Electron Orbitals**

Although useful to explain the reactivity and chemical bonding of certain elements, the Bohr model of the atom does not accurately reflect how electrons are spatially distributed surrounding the nucleus. They do not circle the nucleus like the earth orbits the sun, but are found in **electron orbitals**. These relatively complex shapes result from the fact that electrons behave not just like particles, but also like waves. Mathematical equations from

quantum mechanics known as wave functions can predict within a certain level of probability where an electron might be at any given time. The area where an electron is most likely to be found is called its orbital.

Recall that the Bohr model depicts an atom's electron shell configuration. Within each electron shell are subshells, and each subshell has a specified number of orbitals containing electrons. While it is impossible to calculate exactly where an electron is located, scientists know that it is most probably located within its orbital path. Subshells are designated by the letter s, p, d, and f. The s subshell is spherical in shape and has one orbital. Principal shell 1n has only a single s orbital, which can hold two electrons. Principal shell 2n has one s and one p subshell, and can hold a total of eight electrons. The p subshell has three dumbbell-shaped orbitals, as illustrated in Figure 1.20. Subshells d and f have more complex shapes and contain five and seven orbitals, respectively. These are not shown in the illustration. Principal shell 3n has s, p, and d subshells and can hold 18 electrons. Principal shell 4n has s, p, d and f orbitals and can hold 32 electrons. Moving away from the nucleus, the number of electrons and orbitals found in the energy levels increases. Progressing from one atom to the next in the periodic table, the electron structure can be worked out by fitting an extra electron into the next available orbital.



**Figure 1.20** The *s* subshells are shaped like spheres. Both the 1n and 2n principal shells have an *s* orbital, but the size of the sphere is larger in the 2n orbital. Each sphere is a single orbital. *p* subshells are made up of three dumbbell-shaped orbitals. Principal shell 2n has a *p* subshell, but shell 1 does not.

The closest orbital to the nucleus, called the 1s orbital, can hold up to two electrons. This orbital is equivalent to the innermost electron shell of the Bohr model of the atom. It is called the 1s orbital because it is spherical around the nucleus. The 1s orbital is the closest orbital to the nucleus, and it is always filled first, before any other orbital can be filled. Hydrogen has one electron; therefore, it has only one spot within the 1s orbital occupied. This is designated as  $1s^1$ , where the superscripted 1 refers to the one electron within the 1s orbital. Helium has two electrons; therefore, it can completely fill the 1s orbital. On the periodic table Figure 1.17, hydrogen and helium are the only two elements in the first row (period); this is because they only have electrons in their first shell, the 1s orbital. Hydrogen and helium are the only two elements that have the 1s and no other electron orbitals in the electrically neutral state.

The second electron shell may contain eight electrons. This shell contains another spherical *s* orbital and three "dumbbell" shaped *p* orbitals, each of which can hold two electrons, as shown in **Figure 1.20**. After the 1*s* orbital is filled, the second electron shell is filled, first filling its 2*s* orbital and then its three *p* orbitals. When filling the *p* orbitals, each takes a single electron; once each *p* orbital has an electron, a second may be added. Lithium (Li) contains three electrons that occupy the first and second shells. Two electrons fill the 1*s* orbital, and the third electron then fills the 2*s* orbital. Its **electron configuration** is  $1s^22s^1$ . Neon (Ne), on the other hand, has a total

of ten electrons: two are in its innermost 1s orbital and eight fill its second shell (two each in the 2s and three *p* orbitals); thus, it is an inert gas and energetically stable as a single atom that will rarely form a chemical bond with other atoms. Larger elements have additional orbitals, making up the third electron shell. While the concepts of electron shells and orbitals are closely related, orbitals provide a more accurate depiction of the electron configuration of an atom because the orbital model specifies the different shapes and special orientations of all the places that electrons may occupy.

Link to Learning



Watch this visual animation to see the spatial arrangement of the p and s orbitals. (This media type is not supported in this reader. Click to open media in browser.) (http://legacy.cnx.org/content/m44390/ 1.21/#eip-id5846277)

## **Chemical Reactions and Molecules**

All elements are most stable when their outermost shell is filled with electrons according to the octet rule. This is because it is energetically favorable for atoms to be in that configuration and it makes them stable. However, since not all elements have enough electrons to fill their outermost shells, atoms form **chemical bonds** with other atoms thereby obtaining the electrons they need to attain a stable electron configuration. When two or more atoms chemically bond with each other, the resultant chemical structure is a molecule. The familiar water molecule, H<sub>2</sub>O, consists of two hydrogen atoms and one oxygen atom; these bond together to form water, as illustrated in Figure 1.21. Atoms can form molecules by donating, accepting, or sharing electrons to fill their outer shells.



Figure 1.21 Two or more atoms may bond with each other to form a molecule. When two hydrogens and an oxygen share electrons via covalent bonds, a water molecule is formed.

**Chemical reactions** occur when two or more atoms bond together to form molecules or when bonded atoms are broken apart. The substances used in the beginning of a chemical reaction are called the **reactants** (usually found on the left side of a chemical equation), and the substances found at the end of the reaction are known as the **products** (usually found on the right side of a chemical equation). An arrow is typically drawn between the reactants and products to indicate the direction of the chemical reaction; this direction is not always a "one-way street." For the creation of the water molecule shown above, the chemical equation would be:

$$2H + O \rightarrow H_2O$$

An example of a simple chemical reaction is the breaking down of hydrogen peroxide molecules, each of which

consists of two hydrogen atoms bonded to two oxygen atoms (H<sub>2</sub>O<sub>2</sub>). The reactant hydrogen peroxide is broken down into water, containing one oxygen atom bound to two hydrogen atoms (H<sub>2</sub>O), and oxygen, which consists of two bonded oxygen atoms (O<sub>2</sub>). In the equation below, the reaction includes two hydrogen peroxide molecules and two water molecules. This is an example of a **balanced chemical equation**, wherein the number of atoms of each element is the same on each side of the equation. According to the law of conservation of matter, the number of atoms before and after a chemical reaction should be equal, such that no atoms are, under normal circumstances, created or destroyed.

$$2H_2O_2$$
 (hydrogen peroxide)  $\rightarrow 2H_2O$  (water) +  $O_2$  (oxygen)

Even though all of the reactants and products of this reaction are molecules (each atom remains bonded to at least one other atom), in this reaction only hydrogen peroxide and water are representatives of **compounds**: they contain atoms of more than one type of element. Molecular oxygen, on the other hand, as shown in Figure 1.22, consists of two doubly bonded oxygen atoms and is not classified as a compound but as a homonuclear molecule.



Figure 1.22 The oxygen atoms in an O<sub>2</sub> molecule are joined by a double bond.

Some chemical reactions, such as the one shown above, can proceed in one direction until the reactants are all used up. The equations that describe these reactions contain a unidirectional arrow and are **irreversible**. **Reversible reactions** are those that can go in either direction. In reversible reactions, reactants are turned into products, but when the concentration of product goes beyond a certain threshold (characteristic of the particular reaction), some of these products will be converted back into reactants; at this point, the designations of products and reactants are reversed. This back and forth continues until a certain relative balance between reactants and products occurs—a state called **equilibrium**. These situations of reversible reactions are often denoted by a chemical equation with a double headed arrow pointing towards both the reactants and products.

For example, in human blood, excess hydrogen ions  $(H^+)$  bind to bicarbonate ions  $(HCO_3^-)$  forming an equilibrium state with carbonic acid  $(H_2CO_3)$ . If carbonic acid were added to this system, some of it would be converted to bicarbonate and hydrogen ions.

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3$$

In biological reactions, however, equilibrium is rarely obtained because the concentrations of the reactants or products or both are constantly changing, often with a product of one reaction being a reactant for another. To return to the example of excess hydrogen ions in the blood, the formation of carbonic acid will be the major direction of the reaction. However, the carbonic acid can also leave the body as carbon dioxide gas (via exhalation) instead of being converted back to bicarbonate ion, thus driving the reaction to the right by the chemical law known as **law of mass action**. These reactions are important for maintaining the homeostasis of our blood.

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$$

### lons and lonic Bonds

Some atoms are more stable when they gain or lose an electron (or possibly two) and form ions. This fills their outermost electron shell and makes them energetically more stable. Because the number of electrons does not equal the number of protons, each ion has a net charge. **Cations** are positive ions that are formed by losing electrons. Negative ions are formed by gaining electrons and are called anions. **Anions** are designated by their elemental name being altered to end in "-ide": the anion of chlorine is called chloride, and the anion of sulfur is called sulfide, for example.

This movement of electrons from one element to another is referred to as **electron transfer**. As **Figure 1.23** illustrates, sodium (Na) only has one electron in its outer electron shell. It takes less energy for sodium to donate that one electron than it does to accept seven more electrons to fill the outer shell. If sodium loses an electron, it now has 11 protons, 11 neutrons, and only 10 electrons, leaving it with an overall charge of +1. It is now referred

to as a sodium ion. Chlorine (CI) in its lowest energy state (called the ground state) has seven electrons in its outer shell. Again, it is more energy-efficient for chlorine to gain one electron than to lose seven. Therefore, it tends to gain an electron to create an ion with 17 protons, 17 neutrons, and 18 electrons, giving it a net negative (-1) charge. It is now referred to as a chloride ion. In this example, sodium will donate its one electron to empty its shell, and chlorine will accept that electron to fill its shell. Both ions now satisfy the octet rule and have complete outermost shells. Because the number of electrons is no longer equal to the number of protons, each is now an ion and has a +1 (sodium cation) or -1 (chloride anion) charge. Note that these transactions can normally only take place simultaneously: in order for a sodium atom to lose an electron, it must be in the presence of a suitable recipient like a chlorine atom.



Figure 1.23 In the formation of an ionic compound, metals lose electrons and nonmetals gain electrons to achieve an octet.

**lonic bonds** are formed between ions with opposite charges. For instance, positively charged sodium ions and negatively charged chloride ions bond together to make crystals of sodium chloride, or table salt, creating a crystalline molecule with zero net charge.

Certain salts are referred to in physiology as **electrolytes** (including sodium, potassium, and calcium), ions necessary for nerve impulse conduction, muscle contractions and water balance. Many sports drinks and dietary supplements provide these ions to replace those lost from the body via sweating during exercise.

### **Covalent Bonds and Other Bonds and Interactions**

Another way the octet rule can be satisfied is by the sharing of electrons between atoms to form **covalent bonds**. These bonds are stronger and much more common than ionic bonds in the molecules of living organisms. Covalent bonds are commonly found in carbon-based organic molecules, such as our DNA and proteins. Covalent bonds are also found in inorganic molecules like H<sub>2</sub>O, CO<sub>2</sub>, and O<sub>2</sub>. One, two, or three pairs of electrons may be shared, making single, double, and triple bonds, respectively. The more covalent bonds between two atoms, the stronger their connection. Thus, triple bonds are the strongest.

The strength of different levels of covalent bonding is one of the main reasons living organisms have a difficult time in acquiring nitrogen for use in constructing their molecules, even though molecular nitrogen, N<sub>2</sub>, is the most abundant gas in the atmosphere. Molecular nitrogen consists of two nitrogen atoms triple bonded to each other and, as with all molecules, the sharing of these three pairs of electrons between the two nitrogen atoms allows for the filling of their outer electron shells, making the molecule more stable than the individual nitrogen atoms. This strong triple bond makes it difficult for living systems to break apart this nitrogen in order to use it as constituents of proteins and DNA.

The formation of water molecules provides an example of covalent bonding. The hydrogen and oxygen atoms that combine to form water molecules are bound together by covalent bonds, as shown in **Figure 1.21**. The electron from the hydrogen splits its time between the incomplete outer shell of the hydrogen atoms and the incomplete outer shell of the oxygen atoms. To completely fill the outer shell of oxygen, which has six electrons in its outer shell but which would be more stable with eight, two electrons (one from each hydrogen atom) are needed: hence the well-known formula  $H_2O$ . The electrons are shared between the two elements to fill the outer shell of each, making both elements more stable.

Link to Learning



View this short video to see an animation of ionic and covalent bonding. (This media type is not supported in this reader. Click to open media in browser.) (http://legacy.cnx.org/content/m44390/1.21/#eip-id1166283807593)

### **Polar Covalent Bonds**

There are two types of covalent bonds: polar and nonpolar. In a **polar covalent bond**, shown in **Figure 1.24**, the electrons are unequally shared by the atoms and are attracted more to one nucleus than the other. Because of the unequal distribution of electrons between the atoms of different elements, a slightly positive ( $\delta$ +) or slightly negative ( $\delta$ -) charge develops. This partial charge is an important property of water and accounts for many of its characteristics.

Water is a polar molecule, with the hydrogen atoms acquiring a partial positive charge and the oxygen a partial negative charge. This occurs because the nucleus of the oxygen atom is more attractive to the electrons of the hydrogen atoms than the hydrogen nucleus is to the oxygen's electrons. Thus oxygen has a higher **electronegativity** than hydrogen and the shared electrons spend more time in the vicinity of the oxygen nucleus than they do near the nucleus of the hydrogen atoms, giving the atoms of oxygen and hydrogen slightly negative and positive charges, respectively. Another way of stating this is that the probability of finding a shared electron near an oxygen nucleus is more likely than finding it near a hydrogen nucleus. Either way, the atom's relative electronegativity contributes to the development of partial charges whenever one element is significantly more electronegative than the other, and the charges generated by these polar bonds may then be used for the formation of hydrogen bonds based on the attraction of opposite partial charges. (Hydrogen bonds, which are discussed in detail below, are weak bonds between slightly positively charged hydrogen atoms to slightly negatively charged atoms in other molecules.) Since macromolecules often have atoms within them that differ in electronegativity, polar bonds are often present in organic molecules.

### Nonpolar Covalent Bonds

**Nonpolar covalent bonds** form between two atoms of the same element or between different elements that share electrons equally. For example, molecular oxygen (O<sub>2</sub>) is nonpolar because the electrons will be equally distributed between the two oxygen atoms.

Another example of a nonpolar covalent bond is methane (CH<sub>4</sub>), also shown in **Figure 1.24**. Carbon has four electrons in its outermost shell and needs four more to fill it. It gets these four from four hydrogen atoms, each atom providing one, making a stable outer shell of eight electrons. Carbon and hydrogen do not have the same electronegativity but are similar; thus, nonpolar bonds form. The hydrogen atoms each need one electron for their outermost shell, which is filled when it contains two electrons. These elements share the electrons equally among the carbons and the hydrogen atoms, creating a nonpolar covalent molecule.



Figure 1.24 Whether a molecule is polar or nonpolar depends both on bond type and molecular shape. Both water and carbon dioxide have polar covalent bonds, but carbon dioxide is linear, so the partial charges on the molecule cancel each other out.

### Hydrogen Bonds and Van Der Waals Interactions

Ionic and covalent bonds between elements require energy to break. Ionic bonds are not as strong as covalent, which determines their behavior in biological systems. However, not all bonds are ionic or covalent bonds. Weaker bonds can also form between molecules. Two weak bonds that occur frequently are hydrogen bonds and van der Waals interactions. Without these two types of bonds, life as we know it would not exist. Hydrogen bonds provide many of the critical, life-sustaining properties of water and also stabilize the structures of proteins and DNA, the building block of cells.

When polar covalent bonds containing hydrogen form, the hydrogen in that bond has a slightly positive charge because hydrogen's electron is pulled more strongly toward the other element and away from the hydrogen. Because the hydrogen is slightly positive, it will be attracted to neighboring negative charges. When this happens, a weak interaction occurs between the  $\delta^+$  of the hydrogen from one molecule and the  $\delta_-$  charge on the more electronegative atoms of another molecule, usually oxygen or nitrogen, or within the same molecule. This interaction is called a **hydrogen bond**. This type of bond is common and occurs regularly between water molecules. Individual hydrogen bonds are weak and easily broken; however, they occur in very large numbers in water and in organic polymers, creating a major force in combination. Hydrogen bonds are also responsible for zipping together the DNA double helix.

Like hydrogen bonds, **van der Waals interactions** are weak attractions or interactions between molecules. Van der Waals attractions can occur between any two or more molecules and are dependent on slight fluctuations of the electron densities, which are not always symmetrical around an atom. For these attractions to happen, the molecules need to be very close to one another. These bonds—along with ionic, covalent, and hydrogen bonds—contribute to the three-dimensional structure of the proteins in our cells that is necessary for their proper function.

## caleer connection

## **Pharmaceutical Chemist**

Pharmaceutical chemists are responsible for the development of new drugs and trying to determine the mode of action of both old and new drugs. They are involved in every step of the drug development process. Drugs can be found in the natural environment or can be synthesized in the laboratory. In many cases, potential drugs found in nature are changed chemically in the laboratory to make them safer and more effective, and sometimes synthetic versions of drugs substitute for the version found in nature.

After the initial discovery or synthesis of a drug, the chemist then develops the drug, perhaps chemically altering it, testing it to see if the drug is toxic, and then designing methods for efficient large-scale production. Then, the process of getting the drug approved for human use begins. In the United States, drug approval is handled by the Food and Drug Administration (FDA) and involves a series of large-scale experiments using human subjects to make sure the drug is not harmful and effectively treats the condition it aims to treat. This process often takes several years and requires the participation of physicians and scientists, in addition to chemists, to complete testing and gain approval.

An example of a drug that was originally discovered in a living organism is Paclitaxel (Taxol), an anti-cancer drug used to treat breast cancer. This drug was discovered in the bark of the pacific yew tree. Another example is aspirin, originally isolated from willow tree bark. Finding drugs often means testing hundreds of samples of plants, fungi, and other forms of life to see if any biologically active compounds are found within them. Sometimes, traditional medicine can give modern medicine clues to where an active compound can be found. For example, the use of willow bark to make medicine has been known for thousands of years, dating back to ancient Egypt. It was not until the late 1800s, however, that the aspirin molecule, known as acetylsalicylic acid, was purified and marketed for human use.

Occasionally, drugs developed for one use are found to have unforeseen effects that allow these drugs to be used in other, unrelated ways. For example, the drug minoxidil (Rogaine) was originally developed to treat high blood pressure. When tested on humans, it was noticed that individuals taking the drug would grow new hair. Eventually the drug was marketed to men and women with baldness to restore lost hair.

The career of the pharmaceutical chemist may involve detective work, experimentation, and drug development, all with the goal of making human beings healthier.

## **1.3 | The Periodic Table**

By the end of this section, you will be able to:

- · State the periodic law and explain the organization of elements in the periodic table
- · Predict the general properties of elements based on their location within the periodic table
- · Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (CI), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables

with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 1.25).



Figure 1.25 (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (**Figure 1.26**). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.



Figure 1.26 Elements in the periodic table are organized according to their properties.

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); **nonmetals** (elements that appear dull, poor conductors of heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12; and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**; **Figure 1.27**). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and the **noble gases** (group 18, also known as **inert gases**). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.



Figure 1.27 The periodic table organizes elements with similar properties into groups.



Click on this link (http://openstax.org/l/16Periodic) for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this **one** that shows photos of all the elements.

### Example 1.1

### Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

- (a) chlorine
- (b) calcium
- (c) sodium
- (d) sulfur

### Solution

The family names are as follows:

- (a) halogen
- (b) alkaline earth metal
- (c) alkali metal
- (d) chalcogen

### **Check Your Learning**

Give the group name for each of the following elements:

- (a) krypton
- (b) selenium
- (c) barium
- (d) lithium
  - Answer:

(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (an approximate atomic mass) of the most stable isotope of that element.

## **Chemistry End of Chapter Exercises**

### Exercise 1.19

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

- (a) uranium
- (b) bromine
- (c) strontium
- (d) neon
- (e) gold
- (f) americium
- (g) rhodium
- (h) sulfur
- (i) carbon

(j) potassium

### Solution

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element; (k) metal, representative element; (k) nonmetal, representativ

Exercise 1.20

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

- (a) cobalt
- (b) europium
- (c) iodine
- (d) indium
- (e) lithium
- (f) oxygen
- (g) cadmium

(h) terbium

(i) rhenium

Exercise 1.21

Using the periodic table, identify the lightest member of each of the following groups:

(a) noble gases

(b) alkaline earth metals

(c) alkali metals

(d) chalcogens

**Solution** (a) He; (b) Be; (c) Li; (d) O

Exercise 1.22

Using the periodic table, identify the heaviest member of each of the following groups:

- (a) alkali metals
- (b) chalcogens
- (c) noble gases
- (d) alkaline earth metals

Exercise 1.23

Use the periodic table to give the name and symbol for each of the following elements:

- (a) the noble gas in the same period as germanium
- (b) the alkaline earth metal in the same period as selenium
- (c) the halogen in the same period as lithium
- (d) the chalcogen in the same period as cadmium

### Solution

(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

Exercise 1.24

Use the periodic table to give the name and symbol for each of the following elements:

- (a) the halogen in the same period as the alkali metal with 11 protons
- (b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
- (c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
- (d) the noble gas in the same period as gold

### Exercise 1.25

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

- (a) the alkali metal with 11 protons and a mass number of 23
- (b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom
- (c) the isotope with 33 protons and 40 neutrons in its nucleus
- (d) the alkaline earth metal with 88 electrons and 138 neutrons

### Solution

(a)  $^{23}_{11}$ Na; (b)  $^{129}_{54}$ Xe; (c)  $^{73}_{33}$ As; (d)  $^{226}_{88}$ Ra

### Exercise 1.26
Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

- (a) the chalcogen with a mass number of 125
- (b) the halogen whose longest-lived isotope is radioactive
- (c) the noble gas, used in lighting, with 10 electrons and 10 neutrons
- (d) the lightest alkali metal with three neutrons

## **KEY TERMS**

actinide inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal element in group 1

alkaline earth metal element in group 2

anion negative ion that is formed by an atom gaining one or more electrons

atom smallest particle of an element that can enter into a chemical combination

atom the smallest unit of matter that retains all of the chemical properties of an element

atomic mass calculated mean of the mass number for an element's isotopes

atomic number total number of protons in an atom

**balanced chemical equation** statement of a chemical reaction with the number of each type of atom equalized for both the products and reactants

cation positive ion that is formed by an atom losing one or more electrons

chalcogen element in group 16

**chemical bond** interaction between two or more of the same or different atoms that results in the formation of molecules

chemical reaction process leading to the rearrangement of atoms in molecules

chemical reactivity the ability to combine and to chemically bond with each other

compound pure substance that can be decomposed into two or more elements

compound substance composed of molecules consisting of atoms of at least two different elements

covalent bond type of strong bond formed between two of the same or different elements; forms when electrons are shared between atoms

electrolyte ion necessary for nerve impulse conduction, muscle contractions and water balance

electron negatively charged subatomic particle that resides outside of the nucleus in the electron orbital; lacks functional mass and has a negative charge of -1 unit

electron configuration arrangement of electrons in an atom's electron shell (for example, 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>)

electron orbital how electrons are spatially distributed surrounding the nucleus; the area where an electron is most likely to be found

electron transfer movement of electrons from one element to another; important in creation of ionic bonds

- electronegativity ability of some elements to attract electrons (often of hydrogen atoms), acquiring partial negative charges in molecules and creating partial positive charges on the hydrogen atoms
- element substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change
- element one of 118 unique substances that cannot be broken down into smaller substances; each element has unique properties and a specified number of protons
- equilibrium steady state of relative reactant and product concentration in reversible chemical reactions in a closed system

gas state in which matter has neither definite volume nor shape

group vertical column of the periodic table

halogen element in group 17

heterogeneous mixture combination of substances with a composition that varies from point to point

- **homogeneous mixture** (also, solution) combination of substances with a composition that is uniform throughout
- **hydrogen bond** weak bond between slightly positively charged hydrogen atoms to slightly negatively charged atoms in other molecules

inert gas (also, noble gas) element with filled outer electron shell that is unreactive with other atoms

- inert gas (also, noble gas) element in group 18
- inner transition metal (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

ion atom or chemical group that does not contain equal numbers of protons and electrons

ionic bond chemical bond that forms between ions with opposite charges (cations and anions)

irreversible chemical reaction chemical reaction where reactants proceed uni-directionally to form products

isotope one or more forms of an element that have different numbers of neutrons

**lanthanide** inner transition metal in the top of the bottom two rows of the periodic table

**law of conservation of matter** when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

law of mass action chemical law stating that the rate of a reaction is proportional to the concentration of the reacting substances

liquid state of matter that has a definite volume but indefinite shape

main-group element (also, representative element) element in columns 1, 2, and 12-18

mass fundamental property indicating amount of matter

mass number total number of protons and neutrons in an atom

matter anything that occupies space and has mass

matter anything that has mass and occupies space

**metal** element that is shiny, malleable, good conductor of heat and electricity

metalloid element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

mixture matter that can be separated into its components by physical means

**molecule** bonded collection of two or more atoms of the same or different elements

molecule two or more atoms chemically bonded together

**neutron** uncharged particle that resides in the nucleus of an atom; has a mass of one amu

noble gas see inert gas

noble gas (also, inert gas) element in group 18

nonmetal element that appears dull, poor conductor of heat and electricity

- **nonpolar covalent bond** type of covalent bond that forms between atoms when electrons are shared equally between them
- nucleus core of an atom; contains protons and neutrons
- octet rule rule that atoms are most stable when they hold eight electrons in their outermost shells
- orbital region surrounding the nucleus; contains electrons
- period (also, series) horizontal row of the periodic table
- **periodic law** properties of the elements are periodic function of their atomic numbers.
- **periodic table** organizational chart of elements indicating the atomic number and atomic mass of each element; provides key information about the properties of the elements
- periodic table table of the elements that places elements with similar chemical properties close together
- plasma gaseous state of matter containing a large number of electrically charged atoms and/or molecules
- pnictogen element in group 15
- **polar covalent bond** type of covalent bond that forms as a result of unequal sharing of electrons, resulting in the creation of slightly positive and slightly negative charged regions of the molecule
- product molecule found on the right side of a chemical equation
- proton positively charged particle that resides in the nucleus of an atom; has a mass of one amu and a charge of +1
- pure substance homogeneous substance that has a constant composition
- radioisotope isotope that emits radiation composed of subatomic particles to form more stable elements
- reactant molecule found on the left side of a chemical equation
- representative element (also, main-group element) element in columns 1, 2, and 12–18
- reversible chemical reaction chemical reaction that functions bi-directionally, where products may turn into reactants if their concentration is great enough
- series (also, period) horizontal row of the period table
- solid state of matter that is rigid, has a definite shape, and has a fairly constant volume
- transition metal element in columns 3-11
- valence shell outermost shell of an atom
- van der Waals interaction very weak interaction between molecules due to temporary charges attracting atoms that are very close together

weight force that gravity exerts on an object

## CHAPTER SUMMARY

## 1.1 Phases and Classification of Matter

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the

smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

## 1.2 Atoms, Isotopes, Ions, and Molecules: The Building Blocks

Matter is anything that occupies space and has mass. It is made up of elements. All of the 92 elements that occur naturally have unique qualities that allow them to combine in various ways to create molecules, which in turn combine to form cells, tissues, organ systems, and organisms. Atoms, which consist of protons, neutrons, and electrons, are the smallest units of an element that retain all of the properties of that element. Electrons can be transferred, shared, or cause charge disparities between atoms to create bonds, including ionic, covalent, and hydrogen bonds, as well as van der Waals interactions.

## **1.3 The Periodic Table**

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

## ART CONNECTION QUESTIONS

**27. Figure 1.15** How many neutrons do carbon-12 and carbon-13 have, respectively?

**28. Figure 1.19** An atom may give, take, or share electrons with another atom to achieve a full valence shell, the most stable electron configuration. Looking

## **REVIEW QUESTIONS**

**29.** If xenon has an atomic number of 54 and a mass number of 108, how many neutrons does it have?

- a. 54
- b. 27
- c. 100
- d. 108

**30.** Atoms that vary in the number of neutrons found in their nuclei are called

- a. ions
- b. neutrons
- c. neutral atoms
- d. isotopes

**31.** Potassium has an atomic number of 19. What is its electron configuration?

at this figure, how many electrons do elements in group 1 need to lose in order to achieve a stable electron configuration? How many electrons do elements in groups 14 and 17 need to gain to achieve a stable configuration?

- a. shells 1 and 2 are full, and shell 3 has nine electrons
- b. shells 1, 2 and 3 are full and shell 4 has three electrons
- c. shells 1, 2 and 3 are full and shell 4 has one electron
- d. shells 1, 2 and 3 are full and no other electrons are present

**32.** Which type of bond represents a weak chemical bond?

- a. hydrogen bond
- b. atomic bond
- c. covalent bond
- d. nonpolar covalent bond

## **CRITICAL THINKING QUESTIONS**

**33.** What makes ionic bonds different from covalent bonds?

**34.** Why are hydrogen bonds and van der Waals interactions necessary for cells?

# 2 | MEASUREMENT

# 2.1 | Measurements

By the end of this section, you will be able to:

- · Explain the process of measurement
- · Identify the three basic parts of a quantity
- Describe the properties and units of length, mass, volume, density, temperature, and time
- · Perform basic unit calculations and conversions in the metric and other unit systems

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. (Scientific notation is also known as exponential notation; a review of this topic can be found in **Appendix B (https://legacy.cnx.org/content/m51211/latest/)**.) For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as  $2.98 \times 10^5$  kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as  $2.5 \times 10^{-6}$  kg.

**Units**, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect that the volume of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. 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.

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in **Table 2.1**. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the **International System of Units** or **SI Units** (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Property Measured	Name of Unit	Symbol of Unit
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	К
electric current	ampere	A
amount of substance	mole	mol

## Base Units of the SI System

Table 2.1

Symbol of Unit
d

**Base Units of the SI System** 

Table 2.1

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is  $10^3$  (1 kilometer = 1000 m =  $10^3$  m). The prefixes used and the powers to which 10 are raised are listed in Table 2.2.

## **Common Unit Prefixes**

Prefix	Symbol	Factor	Example
femto	f	10 <sup>-15</sup>	1 femtosecond (fs) = $1 \times 10^{-15}$ s (0.0000000000000000000000000000000000
pico	р	10 <sup>-12</sup>	1 picometer (pm) = $1 \times 10^{-12}$ m (0.000000000001 m)
nano	n	10 <sup>-9</sup>	4 nanograms (ng) = $4 \times 10^{-9}$ g (0.000000004 g)
micro	μ	10 <sup>-6</sup>	1 microliter ( $\mu$ L) = 1 $\times$ 10 <sup>-6</sup> L (0.000001 L)
milli	m	10 <sup>-3</sup>	2 millimoles (mmol) = $2 \times 10^{-3}$ mol (0.002 mol)
centi	с	10 <sup>-2</sup>	7 centimeters (cm) = $7 \times 10^{-2}$ m (0.07 m)
deci	d	10 <sup>-1</sup>	1 deciliter (dL) = $1 \times 10^{-1}$ L (0.1 L)
kilo	k	10 <sup>3</sup>	1 kilometer (km) = $1 \times 10^3$ m (1000 m)
mega	М	10 <sup>6</sup>	3 megahertz (MHz) = 3 $\times$ 10 <sup>6</sup> Hz (3,000,000 Hz)
giga	G	10 <sup>9</sup>	8 gigayears (Gyr) = $8 \times 10^9$ yr (8,000,000,000 yr)
tera	Т	10 <sup>12</sup>	5 terawatts (TW) = 5 $\times$ 10 <sup>12</sup> W (5,000,000,000,000 W)

Table 2.2



Need a refresher or more practice with scientific notation? Visit this **site (http://openstax.org/l/16notation)** to go over the basics of scientific notation.

## **SI Base Units**

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

## Length

The standard unit of **length** in both the SI and original metric systems is the **meter (m)**. A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure 2.1); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers (1 km =  $1000 \text{ m} = 10^3 \text{ m}$ ), whereas shorter distances can be reported in centimeters (1 cm =  $0.01 \text{ m} = 10^{-2} \text{ m}$ ) or millimeters (1 mm =  $0.001 \text{ m} = 10^{-3} \text{ m}$ ).



Figure 2.1 The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

#### Mass

The standard unit of mass in the SI system is the **kilogram (kg)**. A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France (Figure 2.2). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram ( $10^{-3}$  kg).



Figure 2.2 This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology)

## Temperature

Temperature is an intensive property. The SI unit of temperature is the **kelvin (K)**. The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word "degree" nor the degree symbol (°). The degree **Celsius (°C)** is also allowed in the SI system, with both the word "degree" and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

## Time

The SI base unit of time is the **second (s)**. Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds =  $0.000003 \text{ s} = 3 \times 10^{-6}$  and 5 megaseconds =  $5,000,000 \text{ s} = 5 \times 10^{6}$  s. Alternatively, hours, days, and years can be used.

## **Derived SI Units**

We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

## Volume

**Volume** is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 2.3). The standard volume is a **cubic meter (m<sup>3</sup>)**, a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths

of exactly one decimeter contains a volume of one cubic decimeter (dm<sup>3</sup>). A **liter (L)** is the more common name for the cubic decimeter. One liter is about 1.06 quarts.

A cubic centimeter (cm<sup>3</sup>) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation cc (for cubic centimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.



**Figure 2.3** (a) The relative volumes are shown for cubes of  $1 \text{ m}^3$ ,  $1 \text{ dm}^3$  (1 L), and  $1 \text{ cm}^3$  (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm<sup>3</sup> (1-mL) cube.

## Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The **density** of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m<sup>3</sup>). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimeter (g/cm<sup>3</sup>) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm<sup>3</sup> (the density of gasoline) to 19 g/cm<sup>3</sup> (the density of gold). The density of air is about 1.2 g/L. Table 2.3 shows the densities of some common substances.

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm <sup>3</sup>	water 1.0 g/cm <sup>3</sup>	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm <sup>3</sup>	ethanol 0.79 g/cm <sup>3</sup>	oxygen 1.31 g/L
iron 7.9 g/cm <sup>3</sup>	acetone 0.79 g/cm <sup>3</sup>	nitrogen 1.14 g/L
copper 9.0 g/cm <sup>3</sup>	glycerin 1.26 g/cm <sup>3</sup>	carbon dioxide 1.80 g/L
lead 11.3 g/cm <sup>3</sup>	olive oil 0.92 g/cm <sup>3</sup>	helium 0.16 g/L
silver 10.5 g/cm <sup>3</sup>	gasoline 0.70–0.77 g/cm <sup>3</sup>	neon 0.83 g/L
gold 19.3 g/cm <sup>3</sup>	mercury 13.6 g/cm <sup>3</sup>	radon 9.1 g/L

## **Densities of Common Substances**

## Table 2.3

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

density =  $\frac{\text{mass}}{\text{volume}}$ 

## Example 2.1

## **Calculation of Density**

Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold, 19.3 g/cm<sup>3</sup>. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

## Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

volume of lead cube = 2.00 cm × 2.00 cm × 2.00 cm = 8.00 cm<sup>3</sup>  
density = 
$$\frac{\text{mass}}{\text{volume}} = \frac{90.7 \text{ g}}{8.00 \text{ cm}^3} = \frac{11.3 \text{ g}}{1.00 \text{ cm}^3} = 11.3 \text{ g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

## **Check Your Learning**

- (a) To three decimal places, what is the volume of a cube  $(cm^3)$  with an edge length of 0.843 cm?
- (b) If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?
  - Answer:
  - (a)  $0.599 \text{ cm}^3$ ; (b)  $8.91 \text{ g/cm}^3$



To learn more about the relationship between mass, volume, and density, use this **interactive simulator** (http://openstax.org/l/16phetmasvolden) to explore the density of different materials, like wood, ice, brick, and aluminum.

#### Example 2.2

## Using Displacement of Water to Determine Density

This **PhET simulation (http://openstax.org/l/16phetmasvolden)** illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

#### Solution

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than

water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/ L), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

density = 
$$\frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{1.25 \text{ L}} = 4.00 \text{ kg/L}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

density = 
$$\frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{10.00 \text{ L}} = 0.500 \text{ kg/L}$$

## **Check Your Learning**

Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank. Determine the density of the green block.

Answer:

2.00 kg/L

## **Key Concepts and Summary**

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and g/cm<sup>3</sup> (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10<sup>-6</sup> seconds) and megahertz (10<sup>6</sup> hertz), respectively.

## **Key Equations**

• density =  $\frac{\text{mass}}{\text{volume}}$ 

## **Chemistry End of Chapter Exercises**

Exercise 2.1 Is one liter about an ounce, a pint, a quart, or a gallon?

Exercise 2.2 Is a meter about an inch, a foot, a yard, or a mile?

Solution about a yard

Exercise 2.3

Indicate the SI base units or derived units that are appropriate for the following measurements:

- (a) the length of a marathon race (26 miles 385 yards)
- (b) the mass of an automobile
- (c) the volume of a swimming pool
- (d) the speed of an airplane
- (e) the density of gold

- (f) the area of a football field
- (g) the maximum temperature at the South Pole on April 1, 1913

## Exercise 2.4

Indicate the SI base units or derived units that are appropriate for the following measurements:

- (a) the mass of the moon
- (b) the distance from Dallas to Oklahoma City
- (c) the speed of sound
- (d) the density of air
- (e) the temperature at which alcohol boils
- (f) the area of the state of Delaware
- (g) the volume of a flu shot or a measles vaccination

#### Solution

(a) kilograms; (b) meters; (c) kilometers/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

Exercise 2.5

Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.

(a) 10<sup>3</sup>

(b) 10<sup>-2</sup>

(c) 0.1

- (d)  $10^{-3}$
- (e) 1,000,000

(f) 0.000001

## Exercise 2.6

Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

(a) c

(b) d

(c) G

(d) k

(e) m

(f) n

(g) p

(h) T

## Solution

(a) centi-,  $\times 10^{-2}$ ; (b) deci-,  $\times 10^{-1}$ ; (c) Giga-,  $\times 10^{9}$ ; (d) kilo-,  $\times 10^{3}$ ; (e) milli-,  $\times 10^{-3}$ ; (f) nano-,  $\times 10^{-9}$ ; (g) pico-,  $\times 10^{-12}$ ; (h) tera-,  $\times 10^{12}$ 

## Exercise 2.7

A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

(a) Determine the density of this piece of jewelry.

(b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

## Exercise 2.8

Visit this **PhET density simulation (http://openstax.org/l/16phetmasvolden)** and select the Same Volume Blocks.

- (a) What are the mass, volume, and density of the yellow block?
- (b) What are the mass, volume and density of the red block?
- (c) List the block colors in order from smallest to largest mass.
- (d) List the block colors in order from lowest to highest density.
- (e) How are mass and density related for blocks of the same volume?

## Solution

(a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

## Exercise 2.9

Visit this **PhET density simulation (http://openstax.org/l/16phetmasvolden)** and select Custom Blocks and then My Block.

(a) Enter mass and volume values for the block such that the mass in kg is *less than* the volume in L. What does the block do? Why? Is this always the case when mass < volume?

(b) Enter mass and volume values for the block such that the mass in kg is *more than* the volume in L. What does the block do? Why? Is this always the case when mass > volume?

(c) How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?

(d) How would (a) and (b) be different if the liquid in the tank were mercury instead of water?

## Exercise 2.10

Visit this PhET density simulation (http://openstax.org/l/16phetmasvolden) and select Mystery Blocks.

(a) Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.

(b) Pick a different Mystery Block and determine its mass, volume, density, and its likely identity.

(c) Order the Mystery Blocks from least dense to most dense. Explain.

## Solution

(a) (b) Answer is one of the following. A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold. B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple. C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline. D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond. (c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L) < D/red/ice (0.920 kg/L) < E/purple/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

# **2.2 | Mathematical Treatment of Measurement Results**

By the end of this section, you will be able to:

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities
- Use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For

example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:

speed = 
$$\frac{\text{distance}}{\text{time}}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of

$$\frac{100 \text{ m}}{10 \text{ s}} = 10 \text{ m/s}$$

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity (100/10 = 10) and likewise dividing the units of each measured quantity to yield the unit of the computed quantity (m/s = m/s). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation between the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:

time = 
$$\frac{\text{distance}}{\text{speed}}$$

The time can then be computed as:

$$\frac{25 \text{ m}}{10 \text{ m/s}} = 2.5 \text{ s}$$

Again, arithmetic on the numbers (25/10 = 2.5) was accompanied by the same arithmetic on the units (m/m/s = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is "1"—or, as commonly phrased, the units "cancel."

These calculations are examples of a versatile mathematical approach known as **dimensional analysis** (or the **factor-label method**). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

## **Conversion Factors and Dimensional Analysis**

A ratio of two equivalent quantities expressed with different measurement units can be used as a **unit conversion factor**. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

$$\frac{2.54 \text{ cm}}{1 \text{ in.}}$$
 (2.54 cm = 1 in.) or 2.54  $\frac{\text{cm}}{\text{in.}}$ 

Several other commonly used conversion factors are given in Table 2.4.

Length	Volume	Mass
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft <sup>3</sup> = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

## **Common Conversion Factors**

When we multiply a quantity (such as distance given in inches) by an appropriate unit conversion factor, we convert the quantity to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

Table 2.4

$$34 \text{ in.} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} = 86 \text{ cm}$$

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield  $\frac{\text{in.} \times \text{cm}}{\text{in.}}$ . Just as for numbers, a ratio of identical units is

also numerically equal to one,  $\frac{\text{in.}}{\text{in.}} = 1$ , and the unit product thus simplifies to *cm*. (When identical units divide to

yield a factor of 1, they are said to "cancel.") Using dimensional analysis, we can determine that a unit conversion factor has been set up correctly by checking to confirm that the original unit will cancel, and the result will contain the sought (converted) unit.

## Example 2.3

## Using a Unit Conversion Factor

The mass of a competition frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table 2.4).

## Solution

If we have the conversion factor, we can determine the mass in kilograms using an equation similar the one used for converting length from inches to centimeters.

 $x \text{ oz} = 125 \text{ g} \times \text{unit conversion factor}$ 

We write the unit conversion factor in its two forms:

$$\frac{1 \text{ oz}}{28.349 \text{ g}}$$
 and  $\frac{28.349 \text{ g}}{1 \text{ oz}}$ 

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.

$$x \text{ oz} = 125 \text{ g} \times \frac{1 \text{ oz}}{28.349 \text{ g}}$$
$$= \left(\frac{125}{28.349}\right) \text{ oz}$$
$$= 4.41 \text{ oz (three significant figures)}$$

## **Check Your Learning**

Convert a volume of 9.345 qt to liters.

Answer:

8.844 L

Beyond simple unit conversions, the factor-label method can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to insure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. This is why it is referred to as the factor-label method. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

## Example 2.4

#### Computing Quantities from Measurement Results and Known Mathematical Relations

What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

#### Solution

Since density =  $\frac{\text{mass}}{\text{volume}}$ , we need to divide the mass in grams by the volume in milliliters. In general: the

number of units of B = the number of units of A  $\times$  unit conversion factor. The necessary conversion factors are given in Table 2.4: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams

in one step:

$$9.26 \frac{\text{tb}}{\text{tb}} \times \frac{453.59 \text{ g}}{1 \frac{\text{tb}}{\text{tb}}} = 4.20 \times 10^3 \text{ g}$$

We need to use two steps to convert volume from quarts to milliliters.

1. Convert quarts to liters.

$$4.00 \frac{\text{qt}}{\text{qt}} \times \frac{1 \text{ L}}{1.0567 \frac{\text{qt}}{\text{qt}}} = 3.78 \text{ L}$$

2. Convert liters to milliliters.

$$3.78 \pm \times \frac{1000 \text{ mL}}{1 \pm} = 3.78 \times 10^3 \text{ mL}$$

Then,

density = 
$$\frac{4.20 \times 10^3 \text{ g}}{3.78 \times 10^3 \text{ mL}} = 1.11 \text{ g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:

$$\frac{9.26 \text{ tb}}{4.00 \text{ ct}} \times \frac{453.59 \text{ g}}{1 \text{ tb}} \times \frac{1.0567 \text{ ct}}{1 \text{ t}} \times \frac{1 \text{ t}}{1000 \text{ mL}} = 1.11 \text{ g/mL}$$

#### **Check Your Learning**

What is the volume in liters of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

Answer:

 $2.956 \times 10^{-2}$  L

## Example 2.5

#### Computing Quantities from Measurement Results and Known Mathematical Relations

While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.

(a) What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?

(b) If gasoline costs \$3.80 per gallon, what was the fuel cost for this trip?

## Solution

(a) We first convert distance from kilometers to miles:

$$1250 \text{ km} \times \frac{0.62137 \text{ mi}}{1 \text{ km}} = 777 \text{ mi}$$

and then convert volume from liters to gallons:

$$213 \pm \times \frac{1.0567 \text{ qt}}{1 \pm} \times \frac{1 \text{ gal}}{4 \text{ qt}} = 56.3 \text{ gal}$$

Then,

(average) mileage = 
$$\frac{777 \text{ mi}}{56.3 \text{ gal}}$$
 = 13.8 miles/gallon = 13.8 mpg

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:

$$\frac{1250 \text{ km}}{213 \text{ L}} \times \frac{0.62137 \text{ mi}}{1 \text{ km}} \times \frac{1 \text{ L}}{1.0567 \text{ qt}} \times \frac{4 \text{ qt}}{1 \text{ gal}} = 13.8 \text{ mpg}$$

(b) Using the previously calculated volume in gallons, we find:

$$56.3 \text{ gal} \times \frac{\$3.80}{1 \text{ gal}} = \$214$$

## **Check Your Learning**

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

- (a) What (average) fuel economy, in miles per gallon, did the Prius get during this trip?
- (b) If gasoline costs \$3.90 per gallon, what was the fuel cost for this trip?

Answer:

(a) 51 mpg; (b) \$62

## **Conversion of Temperature Units**

We use the word temperature to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes. Because the volume of the liquid changes more than the volume of the glass, we can see the liquid expand when it gets warmer and contract when it gets cooler.

To mark a scale on a thermometer, we need a set of reference values: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the **Fahrenheit** scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

Defining the Celsius and Fahrenheit temperature scales as described in the previous paragraph results in a slightly more complex relationship between temperature values on these two scales than for different units of measure for other properties. Most measurement units for a given property are directly proportional to one another (y = mx). Using familiar length units as one example:

length in feet = 
$$\left(\frac{1 \text{ ft}}{12 \text{ in.}}\right) \times$$
 length in inches

where y = length in feet, x = length in inches, and the proportionality constant, m, is the conversion factor. The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one (y = mx + b). Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor, m, it also must take into account differences in the scales' zero points (b).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as *x* and the Fahrenheit temperature as *y*, the slope, *m*, is computed to be:

$$m = \frac{\Delta y}{\Delta x} = \frac{212 \text{ }^{\circ}\text{F} - 32 \text{ }^{\circ}\text{F}}{100 \text{ }^{\circ}\text{C} - 0 \text{ }^{\circ}\text{C}} = \frac{180 \text{ }^{\circ}\text{F}}{100 \text{ }^{\circ}\text{C}} = \frac{9 \text{ }^{\circ}\text{F}}{5 \text{ }^{\circ}\text{C}}$$

The y-intercept of the equation, b, is then calculated using either of the equivalent temperature pairs, (100 °C, 212 °F) or (0 °C, 32 °F), as:

$$b = y - mx = 32 \text{ °F} - \frac{9 \text{ °F}}{5 \text{ °C}} \times 0 \text{ °C} = 32 \text{ °F}$$

The equation relating the temperature scales is then:

$$T_{\circ F} = \left(\frac{9 \circ F}{5 \circ C} \times T_{\circ C}\right) + 32 \circ C$$

An abbreviated form of this equation that omits the measurement units is:

$$T_{^{\circ}\mathrm{F}} = \left(\frac{9}{5} \times T_{^{\circ}\mathrm{C}}\right) + 32$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

$$T_{^{\circ}\mathrm{C}} = \frac{5}{9}(T_{^{\circ}\mathrm{F}} - 32)$$

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at -273.15 °C. In 1848, British physicist William Thompson, who later adopted the title of Lord Kelvin, proposed an absolute temperature scale based on this concept (further treatment of this topic is provided in this text's chapter on gases).

The freezing temperature of water on this scale is 273.15 K and its boiling temperature 373.15 K. Notice the numerical difference in these two reference temperatures is 100, the same as for the Celsius scale, and so the linear relation between these two temperature scales will exhibit a slope of  $1 \frac{K}{°C}$ . Following the same approach,

the equations for converting between the kelvin and Celsius temperature scales are derived to be:

$$T_{\rm K} = T_{^{\circ}\rm C} + 273.15$$
  
 $T_{^{\circ}\rm C} = T_{\rm K} - 273.15$ 

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 2.4 shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.



Figure 2.4 The Fahrenheit, Celsius, and kelvin temperature scales are compared.

Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for nonscience contexts in almost all areas of the world. Very few countries (the U.S. and its territories, the Bahamas, Belize, Cayman Islands, and Palau) still use Fahrenheit for weather, medicine, and cooking.

## Example 2.6

#### **Conversion from Celsius**

Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the kelvin scale and on

#### the Fahrenheit scale?

## Solution

$$K = {}^{\circ}C + 273.15 = 37.0 + 273.2 = 310.2 \text{ K}$$
$${}^{\circ}F = \frac{9}{5} {}^{\circ}C + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6 {}^{\circ}F$$

## **Check Your Learning**

Convert 80.92 °C to K and °F.

Answer:

354.07 K, 177.7 °F

## Example 2.7

## **Conversion from Fahrenheit**

Baking a ready-made pizza calls for an oven temperature of 450 °F. If you are in Europe, and your oven thermometer uses the Celsius scale, what is the setting? What is the kelvin temperature?

## Solution

°C = 
$$\frac{5}{9}$$
(°F - 32) =  $\frac{5}{9}$ (450 - 32) =  $\frac{5}{9}$  × 418 = 232 °C → set oven to 230 °C (two significant figures)  
K = °C + 273.15 = 230 + 273 = 503 K → 5.0 × 10<sup>2</sup> K (two significant figures)

## **Check Your Learning**

Convert 50 °F to °C and K.

Answer: 10 °C, 280 K

## **Key Concepts and Summary**

Measurements are made using a variety of units. It is often useful or necessary to convert a measured quantity from one unit into another. These conversions are accomplished using unit conversion factors, which are derived by simple applications of a mathematical approach called the factor-label method or dimensional analysis. This strategy is also employed to calculate sought quantities using measured quantities and appropriate mathematical relations.

## **Key Equations**

- $T_{\circ C} = \left(\frac{5}{9} \times T_{\circ F}\right) 32$
- $T_{\circ F} = \left(\frac{9}{5} \times T_{\circ C}\right) + 32$
- $T_{\rm K} = {}^{\circ}{\rm C} + 273.15$
- $T_{\circ C} = K 273.15$

## **Chemistry End of Chapter Exercises**

Exercise 2.11 Write conversion factors (as ratios) for the number of: (a) yards in 1 meter (b) liters in 1 liquid quart (c) pounds in 1 kilogram

## Solution

(a)  $\frac{1.0936 \text{ yd}}{1 \text{ m}}$ ; (b)  $\frac{0.94635 \text{ L}}{1 \text{ qt}}$ ; (c)  $\frac{2.2046 \text{ lb}}{1 \text{ kg}}$ 

Exercise 2.12

Write conversion factors (as ratios) for the number of:

(a) kilometers in 1 mile

(b) liters in 1 cubic foot

(c) grams in 1 ounce

## Exercise 2.13

The label on a soft drink bottle gives the volume in two units: 2.0 L and 67.6 fl oz. Use this information to derive a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

## Solution

 $\frac{2.0 \text{ L}}{67.6 \text{ fl oz}} = \frac{0.030 \text{ L}}{1 \text{ fl oz}}$ Only two significant figures are justified.

## Exercise 2.14

The label on a box of cereal gives the mass of cereal in two units: 978 grams and 34.5 oz. Use this information to find a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

Exercise 2.15

Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimeters and grams?

## Solution

68–71 cm; 400–450 g

Exercise 2.16

A woman's basketball has a circumference between 28.5 and 29.0 inches and a maximum weight of 20 ounces (two significant figures). What are these specifications in units of centimeters and grams?

## Exercise 2.17

How many milliliters of a soft drink are contained in a 12.0-oz can?

## Solution

355 mL

## Exercise 2.18

A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?

## Exercise 2.19

The diameter of a red blood cell is about  $3 \times 10^{-4}$  in. What is its diameter in centimeters?

## Solution

 $8 \times 10^{-4} \, \text{cm}$ 

Exercise 2.20

The distance between the centers of the two oxygen atoms in an oxygen molecule is  $1.21 \times 10^{-8}$  cm. What is this distance in inches?

Exercise 2.21

Is a 197-Ib weight lifter light enough to compete in a class limited to those weighing 90 kg or less?

## Solution

yes; weight = 89.4 kg

## Exercise 2.22

A very good 197-lb weight lifter lifted 192 kg in a move called the clean and jerk. What was the mass of the weight lifted in pounds?

## Exercise 2.23

Many medical laboratory tests are run using 5.0 µL blood serum. What is this volume in milliliters?

## Solution

 $5.0 \times 10^{-3} \, \text{mL}$ 

## Exercise 2.24

If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?

## Exercise 2.25

Use scientific (exponential) notation to express the following quantities in terms of the SI base units in Table 2.2:

- (a) 0.13 g
- (b) 232 Gg
- (c) 5.23 pm
- (d) 86.3 mg
- (e) 37.6 cm
- (f) 54 µm

(g) 1 Ts

- (h) 27 ps
- (i) 0.15 mK

## Solution

(a)  $1.3 \times 10^{-4}$  kg; (b)  $2.32 \times 10^{8}$  kg; (c)  $5.23 \times 10^{-12}$  m; (d)  $8.63 \times 10^{-5}$  kg; (e)  $3.76 \times 10^{-1}$  m; (f)  $5.4 \times 10^{-5}$  m; (g)  $1 \times 10^{12}$  s; (h)  $2.7 \times 10^{-11}$  s; (i)  $1.5 \times 10^{-4}$  K

Exercise 2.26

Complete the following conversions between SI units.

(a) 612 g = \_\_\_\_ mg

- (b) 8.160 m = \_\_\_\_ cm
- (c) 3779 µg = \_\_\_\_\_ g
- (d) 781 mL = L
- (e) 4.18 kg = \_\_\_\_\_ g
- (f) 27.8 m = \_\_\_\_\_ km
- (g) 0.13 mL = \_\_\_\_\_ L
- (h) 1738 km = \_\_\_\_\_ m

## (i) 1.9 Gg = \_\_\_\_\_ g

Exercise 2.27

Gasoline is sold by the liter in many countries. How many liters are required to fill a 12.0-gal gas tank?

## Solution

45.4 L

Exercise 2.28

Milk is sold by the liter in many countries. What is the volume of exactly 1/2 gal of milk in liters?

Exercise 2.29

A long ton is defined as exactly 2240 lb. What is this mass in kilograms?

## Solution

 $1.0160 \times 10^3 \, \text{kg}$ 

Exercise 2.30

Make the conversion indicated in each of the following:

- (a) the men's world record long jump, 29 ft 41/4 in., to meters
- (b) the greatest depth of the ocean, about 6.5 mi, to kilometers
- (c) the area of the state of Oregon, 96,981 mi<sup>2</sup>, to square kilometers
- (d) the volume of 1 gill (exactly 4 oz) to milliliters
- (e) the estimated volume of the oceans, 330,000,000 mi<sup>3</sup>, to cubic kilometers.
- (f) the mass of a 3525-lb car to kilograms
- (g) the mass of a 2.3-oz egg to grams

## Exercise 2.31

Make the conversion indicated in each of the following:

- (a) the length of a soccer field, 120 m (three significant figures), to feet
- (b) the height of Mt. Kilimanjaro, at 19,565 ft the highest mountain in Africa, to kilometers
- (c) the area of an 8.5  $\times$  11-inch sheet of paper in cm<sup>2</sup>
- (d) the displacement volume of an automobile engine, 161 in.<sup>3</sup>, to liters
- (e) the estimated mass of the atmosphere,  $5.6 \times 10^{15}$  tons, to kilograms
- (f) the mass of a bushel of rye, 32.0 lb, to kilograms
- (g) the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)

## Solution

- (a) 394 ft (b) 5.9634 km (c)  $6.0 \times 10^2$ (d) 2.64 L (e)  $5.1 \times 10^{18}$  kg
- (f) 14.5 kg
- (g) 324 mg

## Exercise 2.32

Many chemistry conferences have held a 50-Trillion Angstrom Run (two significant figures). How long is this run

in kilometers and in miles? (1 Å = 1  $\times$  10<sup>-10</sup> m)

## Exercise 2.33

A chemist's 50-Trillion Angstrom Run (see Exercise 2.32) would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? (1 Å =  $1 \times 10^{-8}$  cm)

## Solution

0.46 m; 1.5 ft/cubit

Exercise 2.34

The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is 0.8206 g/mL, determine the mass in kilograms and pounds of the fuel in a full tank.

Exercise 2.35

As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?

## Solution

Yes, the acid's volume is 123 mL.

## Exercise 2.36

To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing 1/4 lb is available. Did the student have enough of the compound?

Exercise 2.37

A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?

## Solution

62.6 in (about 5 ft 3 in.) and 101 lb

## Exercise 2.38

In a recent Grand Prix, the winner completed the race with an average speed of 229.8 km/h. What was his speed in miles per hour, meters per second, and feet per second?

## Exercise 2.39

Solve these problems about lumber dimensions.

(a) To describe to a European how houses are constructed in the US, the dimensions of "two-by-four" lumber must be converted into metric units. The thickness  $\times$  width  $\times$  length dimensions are 1.50 in.  $\times$  3.50 in.  $\times$  8.00 ft in the US. What are the dimensions in cm  $\times$  cm  $\times$  m?

(b) This lumber can be used as vertical studs, which are typically placed 16.0 in. apart. What is that distance in centimeters?

## Solution

(a)  $3.81 \text{ cm} \times 8.89 \text{ cm} \times 2.44 \text{ m}$ ; (b) 40.6 cm

## Exercise 2.40

The mercury content of a stream was believed to be above the minimum considered safe—1 part per billion (ppb) by weight. An analysis indicated that the concentration was 0.68 parts per billion. What quantity of mercury in grams was present in 15.0 L of the water, the density of which is 0.998 g/ml? (1 ppb Hg =  $\frac{1 \text{ ng Hg}}{1 \text{ g water}}$ )

Exercise 2.41

Calculate the density of aluminum if 27.6 cm<sup>3</sup> has a mass of 74.6 g.

#### Solution

 $2.70 \text{ g/cm}^3$ 

Exercise 2.42

Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm<sup>3</sup>?

Exercise 2.43

Calculate these masses.

(a) What is the mass of 6.00 cm<sup>3</sup> of mercury, density = 13.5939 g/cm<sup>3</sup>?

(b) What is the mass of 25.0 mL octane, density =  $0.702 \text{ g/cm}^3$ ?

## Solution

(a) 81.6 g; (b) 17.6 g

Exercise 2.44

Calculate these masses.

(a) What is the mass of 4.00 cm<sup>3</sup> of sodium, density =  $0.97 \text{ g/cm}^3$ ?

(b) What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

Exercise 2.45

Calculate these volumes.

(a) What is the volume of 25 g iodine, density =  $4.93 \text{ g/cm}^3$ ?

(b) What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

## Solution

(a) 5.1 mL; (b) 37 L

Exercise 2.46

Calculate these volumes.

(a) What is the volume of 11.3 g graphite, density =  $2.25 \text{ g/cm}^3$ ?

(b) What is the volume of 39.657 g bromine, density = 2.928 g/cm<sup>3</sup>?

Exercise 2.47

Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.

#### Solution

5371 °F, 3239 K

## Exercise 2.48

Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.

#### Exercise 2.49

Convert the temperature of the coldest area in a freezer, -10 °F, to degrees Celsius and kelvin.

## Solution

−23 °C, 250 K

Exercise 2.50

Convert the temperature of dry ice, -77 °C, into degrees Fahrenheit and kelvin.

Exercise 2.51

Convert the boiling temperature of liquid ammonia, -28.1 °F, into degrees Celsius and kelvin.

## Solution

–33.4 °C, 239.8 K

Exercise 2.52

The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?

Exercise 2.53

The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45  $^{\circ}$ C. What was the temperature on the Fahrenheit scale?

Solution

113 °F

## **KEY TERMS**

Celsius (°C) unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm<sup>3</sup> or cc) volume of a cube with an edge length of exactly 1 cm

cubic meter (m<sup>3</sup>) SI unit of volume

density ratio of mass to volume for a substance or object

**dimensional analysis** (also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Fahrenheit unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

kelvin (K) SI unit of temperature; 273.15 K = 0 °C

kilogram (kg) standard SI unit of mass; 1 kg = approximately 2.2 pounds

length measure of one dimension of an object

liter (L) (also, cubic decimeter) unit of volume;  $1 L = 1,000 \text{ cm}^3$ 

- meter (m) standard metric and SI unit of length; 1 m = approximately 1.094 yards
- milliliter (mL) 1/1,000 of a liter; equal to 1 cm<sup>3</sup>

second (s) SI unit of time

SI units (International System of Units) standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

unit standard of comparison for measurements

unit conversion factor ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

volume amount of space occupied by an object

# 3 | THE STRUCTURE OF MOLECULES

# **3.1 | Chemical Formulas**

By the end of this section, you will be able to:

- · Symbolize the composition of molecules using molecular formulas and empirical formulas
- · Represent the bonding arrangement of atoms within molecules using structural formulas

A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The **structural formula** for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure 3.1). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.



**Figure 3.1** A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-andstick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas  $H_2$ ,  $O_2$ , and  $N_2$ , respectively. Other elements commonly found as diatomic molecules are fluorine ( $F_2$ ), chlorine ( $Cl_2$ ), bromine ( $Br_2$ ), and iodine ( $I_2$ ). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is  $S_8$  (Figure 3.2).



**Figure 3.2** 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.

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<sub>2</sub> and 2H represent distinctly different species. H<sub>2</sub> 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<sub>2</sub> represents two molecules of diatomic hydrogen (Figure 3.3).



Figure 3.3 The symbols H, 2H, H<sub>2</sub>, and 2H<sub>2</sub> represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an **empirical formula**, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO<sub>2</sub>. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (**Figure 3.4**).



**Figure 3.4** (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO<sub>2</sub>, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by "osseous"/Flickr)

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular

formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C<sub>6</sub>H<sub>6</sub> (Figure 3.5).



**Figure 3.5** Benzene, C<sub>6</sub>H<sub>6</sub>, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is  $C_2H_4O_2$ . This formula indicates that a molecule of acetic acid (Figure 3.6) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is  $CH_2O$ . Note that a molecular formula is always a whole-number multiple of an empirical formula.



**Figure 3.6** (a) Vinegar contains acetic acid, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, which has an empirical formula of CH<sub>2</sub>O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

## Example 3.1

## **Empirical and Molecular Formulas**

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

## Solution

The molecular formula is  $C_6H_{12}O_6$  because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is  $CH_2O$ .

## **Check Your Learning**

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

## Answer:

Molecular formula, C<sub>8</sub>H<sub>16</sub>O<sub>4</sub>; empirical formula, C<sub>2</sub>H<sub>4</sub>O



You can explore molecule building (http://openstax.org/l/16molbuilding) using an online simulation.

## Lee Cronin

What is it that chemists do? According to Lee Cronin (Figure 3.7), chemists make very complicated molecules by "chopping up" small molecules and "reverse engineering" them. He wonders if we could "make a really cool universal chemistry set" by what he calls "app-ing" chemistry. Could we "app" chemistry?

In a 2012 TED talk, Lee describes one fascinating possibility: combining a collection of chemical "inks" with a 3D printer capable of fabricating a reaction apparatus (tiny test tubes, beakers, and the like) to fashion a "universal toolkit of chemistry." This toolkit could be used to create custom-tailored drugs to fight a new superbug or to "print" medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, "What Apple did for music, I'd like to do for the discovery and distribution of prescription drugs."<sup>[1]</sup> View his **full talk (http://openstax.org/l/16LeeCronin)** at the TED website.

1. Lee Cronin, "Print Your Own Medicine," Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.



**Figure 3.7** Chemist Lee Cronin has been named one of the UK's 10 most inspirational scientists. The youngest chair at the University of Glasgow, Lee runs a large research group, collaborates with many scientists worldwide, has published over 250 papers in top scientific journals, and has given more than 150 invited talks. His research focuses on complex chemical systems and their potential to transform technology, but also branches into nanoscience, solar fuels, synthetic biology, and even artificial life and evolution. (credit: image courtesy of Lee Cronin)

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form a methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of **isomers**—compounds with the same chemical formula but different molecular structures (**Figure 3.8**). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.



**Figure 3.8** Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 3.9). Acetic acid and methyl formate are **structural isomers**, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of **spatial isomers**, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(–)-carvone smells like spearmint.



**Figure 3.9** Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)



Select this link (http://openstax.org/l/16isomers) to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled "Mirror Molecule: Carvone").

## **Key Concepts and Summary**

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

## **Chemistry End of Chapter Exercises**

## Exercise 3.1

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

## Solution

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O<sub>2</sub>, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

## Exercise 3.2

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

## Exercise 3.3

Write the molecular and empirical formulas of the following compounds:





## Solution

(a) molecular CO<sub>2</sub>, empirical CO<sub>2</sub>; (b) molecular C<sub>2</sub>H<sub>2</sub>, empirical CH; (c) molecular C<sub>2</sub>H<sub>4</sub>, empirical CH<sub>2</sub>; (d) molecular H<sub>2</sub>SO<sub>4</sub>, empirical H<sub>2</sub>SO<sub>4</sub>

## Exercise 3.4

Write the molecular and empirical formulas of the following compounds:



Exercise 3.5

Determine the empirical formulas for the following compounds:

- (a) caffeine, C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>
- (b) fructose, C12H22O11
- (c) hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>
- (d) glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>
- (e) ascorbic acid (vitamin C), C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>

## Solution

(a) C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>O; (b) C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>; (c) HO; (d) CH<sub>2</sub>O; (e) C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>
### Exercise 3.6

Determine the empirical formulas for the following compounds:

(a) acetic acid, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>

(b) citric acid, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>

- (c) hydrazine, N<sub>2</sub>H<sub>4</sub>
- (d) nicotine, C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>
- (e) butane, C<sub>4</sub>H<sub>10</sub>

Exercise 3.7

Write the empirical formulas for the following compounds:

(a)







#### Solution

(a) CH<sub>2</sub>O; (b) C<sub>2</sub>H<sub>4</sub>O

### Exercise 3.8

Open the **Build a Molecule simulation (http://openstax.org/l/16molbuilding)** and select the "Larger Molecules" tab. Select an appropriate atoms "Kit" to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the "Kit" to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on "3D" to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms in any way to make a different compound?

#### Exercise 3.9

Use the **Build a Molecule simulation (http://openstax.org/l/16molbuilding)** to repeat **Exercise 3.8**, but build a molecule with two carbons, six hydrogens, and one oxygen.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).

### Solution

(a) ethanol



(b) methoxymethane, more commonly known as dimethyl ether



(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

### Exercise 3.10

Use the **Build a Molecule simulation (http://openstax.org/l/16molbuilding)** to repeat **Exercise 3.8**, but build a molecule with three carbons, seven hydrogens, and one chlorine.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

# 3.2 | Molecular and Ionic Compounds

By the end of this section, you will be able to:

- · Define ionic and molecular (covalent) compounds
- · Predict the type of compound formed from elements based on their location within the periodic table
- · Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 3.10).





You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized  $Ca^{2+}$ . The name of a metal ion is the same as the name of the metal atom from which it forms, so  $Ca^{2+}$  is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1– charge; atoms of group 16 gain two electrons and form ions with a 2– charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1– charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized  $Br^-$ . (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 3.11). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1– ions; group 16 elements (two groups left) form 2– ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.



Figure 3.11 Some elements exhibit a regular pattern of ionic charge when they form ions.

### Example 3.2

### **Composition of lons**

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

### Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as AI (aluminum). The AI atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, AI<sup>3+</sup>.

### **Check Your Learning**

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer:

 $\mathrm{Se}^{2-}$ , the selenide ion

### Example 3.3

### Formation of lons

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

### Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg<sup>2+</sup>, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3–. The symbol for the ion is  $N^{3-}$ , and it is called a nitride ion.

#### **Check Your Learning**

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer:

Al will form a cation with a charge of 3+: Al<sup>3+</sup>, an aluminum ion. Carbon will form an anion with a charge of 4-: C<sup>4-</sup>, a carbide ion.

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in **Table 3.1**. **Oxyanions** are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Name	Formula	<b>Related Acid</b>	Formula
ammonium	$\mathrm{NH_4}^+$		
hydronium	$H_3O^+$		
peroxide	02 <sup>2-</sup>		
hydroxide	OH-		
acetate	CH <sub>3</sub> COO <sup>-</sup>	acetic acid	CH3COOH
cyanide	CN⁻	hydrocyanic acid	HCN
azide	N <sub>3</sub> <sup>-</sup>	hydrazoic acid	HN <sub>3</sub>
carbonate	CO <sub>3</sub> <sup>2-</sup>	carbonic acid	H <sub>2</sub> CO <sub>3</sub>
bicarbonate	HCO <sub>3</sub> -		
nitrate	NO <sub>3</sub> <sup>-</sup>	nitric acid	HNO3
nitrite	NO <sub>2</sub> <sup>-</sup>	nitrous acid	HNO <sub>2</sub>
sulfate	SO <sub>4</sub> <sup>2–</sup>	sulfiric acid	H <sub>2</sub> SO <sub>4</sub>
hydrogen sulfate	HSO <sub>4</sub> <sup>-</sup>		
sulfite	SO <sub>3</sub> <sup>2–</sup>	sulfurous acid	H <sub>2</sub> SO <sub>3</sub>
hydrogen sulfite	HSO <sub>3</sub> <sup>-</sup>		
phosphate	PO <sub>4</sub> <sup>3-</sup>	phosphoric acid	H3PO4
hydrogen phosphate	HPO <sub>4</sub> <sup>2–</sup>		
dihydrogen phosphate	$H_2PO_4^-$		

### **Common Polyatomic Ions**

Table 3.1

Name	Formula	<b>Related Acid</b>	Formula
perchlorate	ClO <sub>4</sub> <sup>-</sup>	perchloric acid	HCIO <sub>4</sub>
chlorate	ClO <sub>3</sub> <sup>-</sup>	chloric acid	HCIO <sub>3</sub>
chlorite	ClO <sub>2</sub> <sup>-</sup>	chlorous acid	HCIO <sub>2</sub>
hypochlorite	CIO	hypochlorous acid	HCIO
chromate	CrO <sub>4</sub> <sup>2–</sup>	chromic acid	H <sub>2</sub> Cr <sub>2</sub> O <sub>4</sub>
dichromate	Cr <sub>2</sub> O <sub>7</sub> <sup>2–</sup>	dichromic acid	H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
permanganate	MnO <sub>4</sub> <sup>-</sup>	permanganic acid	HMnO <sub>4</sub>

**Common Polyatomic Ions** 

Table 3.1

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for "hyper") and *hypo-* (meaning "under") are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is  $CIO_4^-$ , chlorate is  $CIO_3^-$ , chlorite is  $CIO_2^-$  and hypochlorite is  $CIO^-$ . Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is  $NO_3^-$  while sulfate is  $SO_4^{-2-}$ . This will be covered in more detail in the next module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

# **Ionic Compounds**

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na<sup>+</sup>, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl<sup>-</sup>, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na<sup>+</sup> ion for each Cl<sup>-</sup> ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form CaCl<sub>2</sub>, which is composed of Ca<sup>2+</sup> and Cl<sup>-</sup> ions in the ratio of one Ca<sup>2+</sup> ion to two Cl<sup>-</sup> ions.

A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, AlCl<sub>3</sub>, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move

### freely through the liquid (Figure 3.12).



Figure 3.12 Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)



Watch this video (http://openstax.org/l/16moltensalt) to see a mixture of salts melt and conduct electricity.

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

### Example 3.4

### Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 3.13) is mostly a compound of aluminum and oxygen that contains aluminum cations,  $Al^{3+}$ , and oxygen anions,  $O^{2-}$ . What is the formula of this compound?



Figure 3.13 Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

### Solution

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

### Check Your Learning

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

Answer:

Na<sub>2</sub>S

Many ionic compounds contain polyatomic ions (**Table 3.1**) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is  $Ca_3(PO_4)_2$ . This formula indicates that there are three calcium ions ( $Ca^{2+}$ ) for every two phosphate ( $PO_4^{3-}$ ) groups. The

 $PO_4^{3-}$  groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3–. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

### Example 3.5

### Predicting the Formula of a Compound with a Polyatomic Anion

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

### Solution

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

### **Check Your Learning**

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion,  $O_2^{2-}$  (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer:

Li<sub>2</sub>O<sub>2</sub>

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as CaSO<sub>4</sub>), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na<sup>+</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>

ions combined in a 2:1 ratio, and its formula is written as Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, NaCO<sub>2</sub>. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion,  $C_2 O_4^{2-}$ .

# **Molecular Compounds**

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These **molecular compounds** (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

### Example 3.6

### Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

- (a) KI, the compound used as a source of iodine in table salt
- (b) H<sub>2</sub>O<sub>2</sub>, the bleach and disinfectant hydrogen peroxide
- (c) CHCl<sub>3</sub>, the anesthetic chloroform
- (d) Li<sub>2</sub>CO<sub>3</sub>, a source of lithium in antidepressants

### Solution

(a) Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.

(b) Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H<sub>2</sub>O<sub>2</sub> is predicted to be molecular.

(c) Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; CHCl<sub>3</sub> is predicted to be molecular.

(d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li<sub>2</sub>CO<sub>3</sub> is predicted to be ionic.

### **Check Your Learning**

Using the periodic table, predict whether the following compounds are ionic or covalent:

(a) SO<sub>2</sub>

(b) CaF<sub>2</sub>

- (c) N<sub>2</sub>H<sub>4</sub>
- (d) Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

#### Answer:

(a) molecular; (b) ionic; (c) molecular; (d) ionic

# **Key Concepts and Summary**

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

# **Chemistry End of Chapter Exercises**

### Exercise 3.11

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl<sub>3</sub>, ICl, MgCl<sub>2</sub>, PCl<sub>5</sub>, and CCl<sub>4</sub>.

### Solution

Ionic: KCl, MgCl<sub>2</sub>; Covalent: NCl<sub>3</sub>, ICl, PCl<sub>5</sub>, CCl<sub>4</sub>

Exercise 3.12

Using the periodic table, predict whether the following chlorides are ionic or covalent: SiCl<sub>4</sub>, PCl<sub>3</sub>, CaCl<sub>2</sub>, CsCl, CuCl<sub>2</sub>, and CrCl<sub>3</sub>.

Exercise 3.13

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

(a) NF3

(b) BaO

(c) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>

(d) Sr(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>

(e) IBr

(f) Na<sub>2</sub>O

### Solution

(a) covalent; (b) ionic,  $Ba^{2+}$ ,  $O^{2-}$ ; (c) ionic,  $NH_4^+$ ,  $CO_3^{2-}$ ; (d) ionic,  $Sr^{2+}$ ,  $H_2PO_4^-$ ; (e) covalent; (f) ionic,  $Na^+$ ,  $O^{2-}$ 

### Exercise 3.14

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

(a) KClO4

(b) Mg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>

(c) H<sub>2</sub>S

(d) Ag<sub>2</sub>S (e) N<sub>2</sub>Cl<sub>4</sub> (f) Co(NO<sub>3</sub>)<sub>2</sub>

Exercise 3.15

For each of the following pairs of ions, write the formula of the compound they will form:

(a) Ca<sup>2+</sup>, S<sup>2-</sup>

(b)  $NH_4^+$ ,  $SO_4^{2-}$ 

(c) Al<sup>3+</sup>, Br<sup>-</sup>

(d) Na<sup>+</sup>, HPO<sub>4</sub>  $^{2-}$ 

```
(e) Mg^{2+}, PO_4^{3-}
```

### Solution

(a) CaS; (b) (NH4)2SO4; (c) AlBr3; (d) Na2HPO4; (e) Mg3 (PO4)2

Exercise 3.16

For each of the following pairs of ions, write the formula of the compound they will form:

(a) K<sup>+</sup>, O<sup>2–</sup>

- (b)  $NH_4^+$ ,  $PO_4^{3-}$
- (c) Al<sup>3+</sup>, O<sup>2-</sup>
- (d) Na<sup>+</sup>,  $CO_3^{2-}$

(e)  $Ba^{2+}$ ,  $PO_4^{3-}$ 

# 3.3 | Covalent Bonding

By the end of this section, you will be able to:

- · Describe the formation of covalent bonds
- · Define electronegativity and assess the polarity of covalent bonds

lonic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called **covalent bonds**. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H<sub>2</sub> molecule; each hydrogen atom in the H<sub>2</sub> molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds 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. 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 are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

# **Formation of Covalent Bonds**

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H<sub>2</sub>, contains a covalent bond between its two hydrogen atoms. **Figure 3.14** illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The **bond length** is determined by the distance at which the lowest potential energy is achieved.



**Figure 3.14** The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H<sub>2</sub>, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 436 \, \text{kJ}$$

Conversely, the same amount of energy is released when one mole of H<sub>2</sub> molecules forms from two moles of H atoms:

$$2H(g) \longrightarrow H_2(g)$$
  $\Delta H = -436 \text{ kJ}$ 

## Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H<sub>2</sub>, Cl<sub>2</sub>, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **pure covalent bond**. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl<sub>2</sub>, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$Cl + Cl \longrightarrow Cl_2$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl<sub>2</sub> also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent bond**, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. **Figure 3.15** shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to **Figure 3.14**, which shows the even distribution of electrons in the H<sub>2</sub> nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta,"  $\delta$ , with a plus sign or minus sign to indicate whether the atom has a partial positive charge ( $\delta$ +) or a partial negative charge ( $\delta$ -). This symbolism is shown for the H–Cl molecule in Figure 3.15.



**Figure 3.15** (a) The distribution of electron density in the HCI molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols  $\delta$ + and  $\delta$ - indicate the polarity of the H–Cl bond.

### Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrones in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 3.16 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 3.17). In general, electronegativity increases from left to right

across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as  $XeO_2$  do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)



Figure 3.16 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

### Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

#### Linus Pauling

Linus Pauling, shown in **Figure 3.17**, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.



Figure 3.17 Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

#### Electronegativity and Bond Type

The absolute value of the difference in electronegativity ( $\Delta$ EN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 3.18 shows the relationship between electronegativity difference and bond type.



Figure 3.18 As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in **Figure 3.18**. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH<sub>3</sub> a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in Mnl<sub>2</sub> have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH<sup>-</sup>, NO<sub>3</sub><sup>-</sup>,

and NH4<sup>+</sup>, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds

by combining with ions of opposite charge. For example, potassium nitrate, KNO<sub>3</sub>, contains the  $K^+$  cation and the polyatomic NO<sub>3</sub><sup>-</sup> anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction

between the ions  $K^+$  and  $NO_3^-$ , as well as covalent between the nitrogen and oxygen atoms in  $NO_3^-$ .

### Example 3.7

#### **Electronegativity and Bond Polarity**

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in **Figure 3.16**, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols  $\delta$ + and  $\delta$ -:

C-H, C-N, C-O, N-H, O-H, S-H

### Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the  $\delta$ - designation is the more electronegative of the two. Table 3.2 shows these bonds in order of increasing polarity.

· · · · · · · · · · · · · · · · · · ·		J
Bond	ΔΕΝ	Polarity
C–H	0.4	$\overset{\delta-}{\mathrm{C-H}}\overset{\delta+}{\mathrm{H}}$
S–H	0.4	$\stackrel{\delta-}{\operatorname{S}}\stackrel{\delta+}{\operatorname{-H}}$
C–N	0.5	$\overset{\delta+}{\mathrm{C}}\overset{\delta-}{-}\mathrm{N}$
N–H	0.9	$\stackrel{\delta-}{\mathrm{N-H}}\stackrel{\delta+}{\mathrm{H}}$
C–O	1.0	$\overset{\delta + \ \delta -}{\mathrm{C} - \mathrm{O}}$
O_H	1.4	$\stackrel{\delta-}{\mathrm{O-H}}^{\delta+}$

### Bond Polarity and Electronegativity Difference

Table 3.2

#### **Check Your Learning**

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 3.16, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols  $\delta$ + and  $\delta$ –.

### Answer:

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{\mathrm{C}}\overset{\delta+}{-\mathrm{H}}$
Si–C	0.7	$\stackrel{\delta +  \delta -}{\operatorname{Si} - \operatorname{C}}$
Si–O	1.7	$\stackrel{\delta +  \delta -}{\text{Si-O}}$

# **Key Concepts and Summary**

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

# **Chemistry End of Chapter Exercises**

### Exercise 3.17

Why is it incorrect to speak of a molecule of solid NaCl?

### Solution

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

### Exercise 3.18

What information can you use to predict whether a bond between two atoms is covalent or ionic?

### Exercise 3.19

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

- (a) Cl<sub>2</sub>CO
- (b) MnO
- (c) NCl<sub>3</sub>
- (d) CoBr<sub>2</sub>
- (e) K<sub>2</sub>S
- (f) CO
- (g) CaF<sub>2</sub>
- (h) HI
- (i) CaO
- (j) IBr
- (k) CO<sub>2</sub>

### Solution

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

Exercise 3.20

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

Exercise 3.21

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) Br or Cl

(b) N or O

(c) S or O

(d) P or S

(e) Si or N

(f) Ba or P

(g) N or K

#### Solution

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

Exercise 3.22

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) N or P

(b) N or Ge

(c) S or F

(d) CI or S

(e) H or C

(f) Se or P

(g) C or Si

Exercise 3.23

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, H, N, O

(b) Br, Cl, F, H, I

(c) F, H, O, P, S

(d) Al, H, Na, O, P

(e) Ba, H, N, O, As

### Solution

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

Exercise 3.24

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) As, H, N, P, Sb
(b) Cl, H, P, S, Si
(c) Br, Cl, Ge, H, Sr
(d) Ca, H, K, N, Si

### (e) Cl, Cs, Ge, H, Sr

Exercise 3.25

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

### Solution

N, O, F, and Cl

Exercise 3.26

Which is the most polar bond?

(a) C–C

(b) C–H

(c) N–H

(d) O–H

(e) Se-H

Exercise 3.27

Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCI

(b) NO or CO

(c) SH or OH

(d) PCI or SCI

(e) CH or NH

(f) SO or PO

(g) CN or NN

### Solution

(a) HF; (b) CO; (c) OH; (d) PCI; (e) NH; (f) PO; (g) CN

Exercise 3.28

Which of the following molecules or ions contain polar bonds?

(a) O3

(b) S<sub>8</sub>

(c)  $O_2^{2-}$ 

(d)  $NO_3^-$ 

(e) CO<sub>2</sub>

(f) H<sub>2</sub>S

(g)  $BH_4^-$ 

# 3.4 | Lewis Symbols and Structures

By the end of this section, you will be able to:

- · Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

# **Lewis Symbols**

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons:

# •Ca•

Figure 3.19 shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	[Ne]3s <sup>1</sup>	Na •
magnesium	[Ne]3s <sup>2</sup>	۰Mg・
aluminum	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	٠ÅI٠
silicon	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	٠si٠
phosphorus	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	 •P•
sulfur	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	::: ::::::::::::::::::::::::::::::::::
chlorine	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	:ci•
argon	[Ne]3s <sup>2</sup> 3p <sup>6</sup>	: Ar :

Figure 3.19 Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



MetalNonmetalIonic CompoundNa ·+:::· $\longrightarrow$ Na<sup>+</sup>[::::]<sup>-</sup>sodium atomchlorine atomsodium chloride<br/>(sodium ion and chloride ion)·Mg ·+::· $\longrightarrow$ Mg<sup>2+</sup>[::::]<sup>2-</sup>

Figure 3.20 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

sodium atom		chlorine atom	sodium chloride (sodium ion and chloride ion)
• Mg •	+	:ö·	$\longrightarrow$ Mg <sup>2+</sup> $\left[: \vdots : \right]^{2^{-}}$
magnesium atom		oxygen atom	magnesium oxide (magnesium ion and oxide ion)
۰Ca・	+	2:F•	$\longrightarrow$ Ca <sup>2+</sup> $\left[ : \overrightarrow{F} : \right]_{2}^{-}$
calcium atom		fluorine atoms	calcium fluoride (calcium ion and two fluoride ions)

Figure 3.20 Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

# **Lewis Structures**

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each CI atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:



A single shared pair of electrons is called a **single bond**. Each CI atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

### The Octet Rule

The other halogen molecules (F<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, and At<sub>2</sub>) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl<sub>4</sub> (carbon tetrachloride) and silicon in SiH<sub>4</sub> (silane).

Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:



# carbon tetrachloride

silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH<sub>3</sub> (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



### **Double and Triple Bonds**

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH<sub>2</sub>O (formaldehyde) and between the two carbon atoms in C<sub>2</sub>H<sub>4</sub> (ethylene):



A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion  $(CN^{-})$ :



# carbon monoxide

cyanide ion

# Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



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

- 1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
- 2. 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).
- 3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
- 4. Place all remaining electrons on the central atom.
- 5. 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 SiH<sub>4</sub>,  $CHO_2^{-}$ ,  $NO^+$ , and  $OF_2$  as examples in following this procedure:

- 1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
  - $\circ~$  For a molecule, we add the number of valence electrons on each atom in the molecule:

SiH<sub>4</sub> Si: 4 valence electrons/atom  $\times$  1 atom = 4 + H: 1 valence electron/atom  $\times$  4 atoms = 4

= 8 valence electrons

• For a *negative ion*, such as  $CHO_2^-$ , we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

 $CHO_2^{-}$ C: 4 valence electrons/atom × 1 atom = 4 H: 1 valence electron/atom × 1 atom = 1 O: 6 valence electrons/atom × 2 atoms = 12 + 1 additional electron = 1 = 18 valence electrons

 For a *positive ion*, such as NO<sup>+</sup>, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

 $NO^+$ 

N: 5 valence electrons/atom  $\times$  1 atom = 5 O: 6 valence electron/atom  $\times$  1 atom = 6 + -1 electron (positive charge) = -1

= 10 valence electrons

• Since OF<sub>2</sub> is a neutral molecule, we simply add the number of valence electrons:

 $OF_2$ 

O: 6 valence electrons/atom  $\times$  1 atom = 6 + F: 7 valence electrons/atom  $\times$  2 atoms = 14

= 20 valence electrons

2. 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 we denote ions with brackets around the structure, indicating the charge outside the brackets:)



When several arrangements of atoms are possible, as for  $CHO_2^-$ , we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In  $CHO_2^-$ , the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in POCl<sub>3</sub>, S in SO<sub>2</sub>, and Cl in  $CIO_4^-$ . An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

- 3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
  - There are no remaining electrons on SiH<sub>4</sub>, so it is unchanged:



- 4. Place all remaining electrons on the central atom.
  - For SiH<sub>4</sub>, CHO<sub>2</sub><sup>-</sup>, and NO<sup>+</sup>, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
  - For OF<sub>2</sub>, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



- 5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
  - SiH4: Si already has an octet, so nothing needs to be done.
  - CHO<sub>2</sub><sup>-</sup>: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



 NO<sup>+</sup>: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



• In OF<sub>2</sub>, each atom has an octet as drawn, so nothing changes.

### Example 3.8

### Writing Lewis Structures

NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H<sub>3</sub>CCH<sub>3</sub>), acetylene (HCCH), and ammonia (NH<sub>3</sub>). What are the Lewis structures of these molecules?

#### Solution

 Calculate the number of valence electrons. HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10 H<sub>3</sub>CCH<sub>3</sub>: (1 × 3) + (2 × 4) + (1 × 3) = 14 HCCH:  $(1 \times 1) + (2 \times 4) + (1 \times 1) = 10$ NH<sub>3</sub>:  $(5 \times 1) + (3 \times 1) = 8$ 

2. Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



3. Where needed, distribute electrons to the terminal atoms:

$$H - C - \stackrel{\cdots}{N}: H - \stackrel{H}{C} - \stackrel{H}{C} - H H - C - C - H H - C - C - H H - N - H$$

HCN: six electrons placed on N H<sub>3</sub>CCH<sub>3</sub>: no electrons remain HCCH: no terminal atoms capable of accepting electrons NH<sub>3</sub>: no terminal atoms capable of accepting electrons

4. Where needed, place remaining electrons on the central atom:



HCN: no electrons remain H<sub>3</sub>CCH<sub>3</sub>: no electrons remain HCCH: four electrons placed on carbon NH<sub>3</sub>: two electrons placed on nitrogen

 Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom: HCN: form two more C–N bonds H<sub>3</sub>CCH<sub>3</sub>: all atoms have the correct number of electrons HCCH: form a triple bond between the two carbon atoms NH<sub>3</sub>: all atoms have the correct number of electrons



#### **Check Your Learning**

Both carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO<sub>2</sub> has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer:



#### **Fullerene Chemistry**

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 3.21), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C<sub>60</sub> buckminsterfullerene molecule (m51046 (https://legacy.cnx.org/content/m51046/latest/#CNX\_Chem\_07\_00\_Bucky) ). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C<sub>60</sub>. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.



**Figure 3.21** Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

## Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

· Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired

electron.

- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

#### **Odd-electron Molecules**

We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

- Determine the total number of valence (outer shell) electrons. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
- Draw a skeleton structure of the molecule. We can easily draw a skeleton with an N–O single bond: N–O
- 3. Distribute the remaining electrons as lone pairs on the terminal atoms. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

- 4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
- 5. Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible. We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

#### **Electron-deficient Molecules**

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH<sub>2</sub>, and boron trifluoride, BF<sub>3</sub>, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF<sub>3</sub>, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF<sub>3</sub>, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH<sub>3</sub> reacts with BF<sub>3</sub> because the lone pair on nitrogen can be shared with the boron atom:



### Hypervalent Molecules

Elements in the second period of the periodic table (n = 2) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2s and three 2p orbitals). Elements in the third and higher periods ( $n \ge 3$ ) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules**. Figure 3.22 shows the Lewis structures for two hypervalent molecules, PCl<sub>5</sub> and SF<sub>6</sub>.



Figure 3.22 In PCl<sub>5</sub>, the central atom phosphorus shares five pairs of electrons. In SF<sub>6</sub>, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF<sub>5</sub> and XeF<sub>4</sub>, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

### Example 3.9

#### Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined  $XeF_4$  earlier. What are the Lewis structures of  $XeF_2$  and  $XeF_6$ ?

#### Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

- Calculate the number of valence electrons: XeF<sub>2</sub>: 8 + (2 × 7) = 22 XeF<sub>6</sub>: 8 + (6 × 7) = 50
- 2. *Draw a skeleton joining the atoms by single bonds.* Xenon will be the central atom because fluorine cannot be a central atom:



3. Distribute the remaining electrons.

XeF<sub>2</sub>: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF<sub>2</sub> shows two bonding pairs and three lone pairs of electrons around the Xe atom:

XeF<sub>6</sub>: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



### **Check Your Learning**

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to

Answer:



# **Key Concepts and Summary**

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

;

# **Chemistry End of Chapter Exercises**

Exercise 3.29

Write the Lewis symbols for each of the following ions:

(a)  $As^{3-}$ (b)  $I^-$ (c)  $Be^{2+}$ (d)  $O^{2-}$ (e)  $Ga^{3+}$ (f)  $Li^+$ (g)  $N^{3-}$ Solution (a) eight electrons: (b) eight electrons: (c) no electrons  $Be^{2+}$ ; (d) eight electrons:



(e) no electrons
Ga<sup>3+</sup>;
(f) no electrons
Li<sup>+</sup>;
(g) eight electrons:



Exercise 3.30

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

;

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

Exercise 3.31

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b) Al<sub>2</sub>O<sub>3</sub>

(c) GaCl<sub>3</sub>

(d) K<sub>2</sub>O

(e) Li<sub>3</sub>N

(f) KF

Solution

(a)

(b)

(C)





### Exercise 3.32

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

(a)

(b)

(C)

(d)

$$\left[\mathsf{M}^{3+}\right]_{2}\left[::::]_{3}^{2-}$$

### Exercise 3.33

Write the Lewis structure for the diatomic molecule P<sub>2</sub>, an unstable form of phosphorus found in high-temperature phosphorus vapor.

Solution



Exercise 3.34

Write Lewis structures for the following:

(a) H<sub>2</sub>

(b) HBr

(c) PCl<sub>3</sub>

(d) SF<sub>2</sub>

(e) H<sub>2</sub>CCH<sub>2</sub>

(f) HNNH

(g) H<sub>2</sub>CNH

(h) NO<sup>-</sup>

(i) N<sub>2</sub>

(j) CO

(k) CN<sup>-</sup>

Exercise 3.35

Write Lewis structures for the following:

(a) O2

(b) H<sub>2</sub>CO

(c) AsF3

(d) CINO

(e) SiCl<sub>4</sub>

(f) H<sub>3</sub>O<sup>+</sup>

(g)  $\mathrm{NH_4}^+$ 

(h)  $BF_4^-$ 

(i) HCCH

(j) CICN

(k)  $C_2^{2+}$ 

Solution

(a)

:0=0:

In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

(b)



(f)



;

;

;

(g)



(h)





Write Lewis structures for the following:

(a) CIF3

(b) PCI<sub>5</sub>

(c) BF3

(d)  $PF_6^-$ 

Exercise 3.37

Write Lewis structures for the following:

(a) SeF<sub>6</sub>

(b) XeF4

(c)  $SeCl_3^+$ 

(d) Cl<sub>2</sub>BBCl<sub>2</sub> (contains a B-B bond)

Solution

(a) SeF<sub>6</sub>:



(b) XeF4:

;


(c)  $SeCl_3^+$ :



(d) Cl<sub>2</sub>BBCl<sub>2</sub>:



Exercise 3.38

Write Lewis structures for:

- (a)  $PO_4^{3-}$
- (b)  $ICl_4^-$
- (c)  $SO_3^{2-}$
- (d) HONO

Exercise 3.39

Correct the following statement: "The bonds in solid  $PbCl_2$  are ionic; the bond in a HCI molecule is covalent. Thus, all of the valence electrons in  $PbCl_2$  are located on the  $CI^-$  ions, and all of the valence electrons in a HCI molecule are shared between the H and CI atoms."

;

### Solution

Two valence electrons per Pb atom are transferred to Cl atoms; the resulting  $Pb^{2+}$  ion has a  $6s^2$  valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

Exercise 3.40

Write Lewis structures for the following molecules or ions:

(a) SbH<sub>3</sub>

#### (b) XeF<sub>2</sub>

(c) Se<sub>8</sub> (a cyclic molecule with a ring of eight Se atoms)

### Exercise 3.41

Methanol,  $H_3COH$ , is used as the fuel in some race cars. Ethanol,  $C_2H_5OH$ , is used extensively as motor fuel in Brazil. Both methanol and ethanol produce  $CO_2$  and  $H_2O$  when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

### Solution



#### Exercise 3.42

Many planets in our solar system contain organic chemicals including methane (CH<sub>4</sub>) and traces of ethylene (C<sub>2</sub>H<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), propyne (H<sub>3</sub>CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

#### Exercise 3.43

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl<sub>2</sub>CO. Write the Lewis structures for carbon tetrachloride and phosgene.

### Solution



Exercise 3.44

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

(a)  $1s^2 2s^2 2p^5$ 

(b) 
$$1s^2 2s^2 2p^6 3s^2$$

(c)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3q^{10}$ 

### Exercise 3.45

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

(a) the amino acid serine:



(b) urea:



(c) pyruvic acid:



(d) uracil:



(e) carbonic acid:



(b)



;



#### Exercise 3.46

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

### Exercise 3.47

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

# Solution



#### Exercise 3.48

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

#### Exercise 3.49

How are single, double, and triple bonds similar? How do they differ?

#### Solution

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

# 3.5 | Water

By the end of this section, you will be able to:

- Describe the properties of water that are critical to maintaining life
- · Explain why water is an excellent solvent
- · Provide examples of water's cohesive and adhesive properties
- Discuss the role of acids, bases, and buffers in homeostasis

Why do scientists spend time looking for water on other planets? Why is water so important? It is because water is essential to life as we know it. Water is one of the more abundant molecules and the one most critical to life on Earth. Approximately 60–70 percent of the human body is made up of water. Without it, life as we know it simply would not exist.

The polarity of the water molecule and its resulting hydrogen bonding make water a unique substance with special properties that are intimately tied to the processes of life. Life originally evolved in a watery environment, and most of an organism's cellular chemistry and metabolism occur inside the watery contents of the cell's cytoplasm. Special properties of water are its high heat capacity and heat of vaporization, its ability to dissolve polar molecules, its cohesive and adhesive properties, and its dissociation into ions that leads to the generation of pH. Understanding these characteristics of water helps to elucidate its importance in maintaining life.

# Water's Polarity

One of water's important properties is that it is composed of polar molecules: the hydrogen and oxygen within water molecules (H<sub>2</sub>O) form polar covalent bonds. While there is no net charge to a water molecule, the polarity of water creates a slightly positive charge on hydrogen and a slightly negative charge on oxygen, contributing to water's properties of attraction. Water's charges are generated because oxygen is more electronegative than hydrogen, making it more likely that a shared electron would be found near the oxygen nucleus than the hydrogen nucleus, thus generating the partial negative charge near the oxygen.

As a result of water's polarity, each water molecule attracts other water molecules because of the opposite charges between water molecules, forming hydrogen bonds. Water also attracts or is attracted to other polar molecules and ions. A polar substance that interacts readily with or dissolves in water is referred to as **hydrophilic** (hydro- = "water"; -philic = "loving"). In contrast, non-polar molecules such as oils and fats do not interact well with water, as shown in **Figure 3.23** and separate from it rather than dissolve in it, as we see in salad dressings containing oil and vinegar (an acidic water solution). These nonpolar compounds are called **hydrophobic** (hydro- = "water"; -phobic = "fearing").



Figure 3.23 Oil and water do not mix. As this macro image of oil and water shows, oil does not dissolve in water but forms droplets instead. This is due to it being a nonpolar compound. (credit: Gautam Dogra).

# Water's States: Gas, Liquid, and Solid

The formation of hydrogen bonds is an important quality of the liquid water that is crucial to life as we know it. As water molecules make hydrogen bonds with each other, water takes on some unique chemical characteristics compared to other liquids and, since living things have a high water content, understanding these chemical features is key to understanding life. In liquid water, hydrogen bonds are constantly formed and broken as the water molecules slide past each other. The breaking of these bonds is caused by the motion (kinetic energy) of the water molecules due to the heat contained in the system. When the heat is raised as water is boiled, the higher kinetic energy of the water molecules causes the hydrogen bonds to break completely and allows water molecules to escape into the air as gas (steam or water vapor). On the other hand, when the temperature of water is reduced and water freezes, the water molecules form a crystalline structure maintained by hydrogen bonding (there is not enough energy to break the hydrogen bonds) that makes ice less dense than liquid water, a phenomenon not seen in the solidification of other liquids.

Water's lower density in its solid form is due to the way hydrogen bonds are oriented as it freezes: the water molecules are pushed farther apart compared to liquid water. With most other liquids, solidification when the temperature drops includes the lowering of kinetic energy between molecules, allowing them to pack even more tightly than in liquid form and giving the solid a greater density than the liquid.

The lower density of ice, illustrated and pictured in **Figure 3.24**, an anomaly, causes it to float at the surface of liquid water, such as in an iceberg or in the ice cubes in a glass of ice water. In lakes and ponds, ice will form on the surface of the water creating an insulating barrier that protects the animals and plant life in the pond from freezing. Without this layer of insulating ice, plants and animals living in the pond would freeze in the solid block of ice and could not survive. The detrimental effect of freezing on living organisms is caused by the expansion of ice relative to liquid water. The ice crystals that form upon freezing rupture the delicate membranes essential for the function of living cells, irreversibly damaging them. Cells can only survive freezing if the water in them is temporarily replaced by another liquid like glycerol.



**Figure 3.24** Hydrogen bonding makes ice less dense than liquid water. The (a) lattice structure of ice makes it less dense than the freely flowing molecules of liquid water, enabling it to (b) float on water. (credit a: modification of work by Jane Whitney, image created using Visual Molecular Dynamics (VMD) software<sup>[2]</sup>; credit b: modification of work by Carlos Ponte)





Click here (http://openstaxcollege.org/l/ice\_lattice2) to see a 3-D animation of the structure of an ice lattice. (Image credit: Jane Whitney. Image created using Visual Molecular Dynamics VMD software.<sup>[3]</sup>)

# Water's High Heat Capacity

Water's high heat capacity is a property caused by hydrogen bonding among water molecules. Water has the highest **specific heat capacity** of any liquids. Specific heat is defined as the amount of heat one gram of a substance must absorb or lose to change its temperature by one degree Celsius. For water, this amount is one **calorie**. It therefore takes water a long time to heat and long time to cool. In fact, the specific heat capacity of water is about five times more than that of sand. This explains why the land cools faster than the sea. Due to its high heat capacity, water is used by warm blooded animals to more evenly disperse heat in their bodies: it acts in a similar manner to a car's cooling system, transporting heat from warm places to cool places, causing the body to maintain a more even temperature.

# Water's Heat of Vaporization

Water also has a high **heat of vaporization**, the amount of energy required to change one gram of a liquid substance to a gas. A considerable amount of heat energy (586 cal) is required to accomplish this change in water. This process occurs on the surface of water. As liquid water heats up, hydrogen bonding makes it difficult to separate the liquid water molecules from each other, which is required for it to enter its gaseous phase (steam). As a result, water acts as a heat sink or heat reservoir and requires much more heat to boil than does a liquid such as ethanol (grain alcohol), whose hydrogen bonding with other ethanol molecules is weaker than water's hydrogen bonding. Eventually, as water reaches its boiling point of 100° Celsius (212° Fahrenheit), the heat is able to break the hydrogen bonds between the water molecules, and the kinetic energy (motion) between the water molecules allows them to escape from the liquid as a gas. Even when below its boiling point, water's individual molecules acquire enough energy from other water molecules such that some surface water molecules can escape and vaporize: this process is known as **evaporation**.

The fact that hydrogen bonds need to be broken for water to evaporate means that a substantial amount of energy is used in the process. As the water evaporates, energy is taken up by the process, cooling the environment where the evaporation is taking place. In many living organisms, including in humans, the

<sup>2.</sup> W. Humphrey W., A. Dalke, and K. Schulten, "VMD—Visual Molecular Dynamics," Journal of Molecular Graphics 14 (1996): 33-38.

<sup>3.</sup> W. Humphrey W., A. Dalke, and K. Schulten, "VMD—Visual Molecular Dynamics," Journal of Molecular Graphics 14 (1996): 33-38.

evaporation of sweat, which is 90 percent water, allows the organism to cool so that homeostasis of body temperature can be maintained.

# Water's Solvent Properties

Since water is a polar molecule with slightly positive and slightly negative charges, ions and polar molecules can readily dissolve in it. Therefore, water is referred to as a **solvent**, a substance capable of dissolving other polar molecules and ionic compounds. The charges associated with these molecules will form hydrogen bonds with water, surrounding the particle with water molecules. This is referred to as a **sphere of hydration**, or a hydration shell, as illustrated in Figure 3.25 and serves to keep the particles separated or dispersed in the water.

When ionic compounds are added to water, the individual ions react with the polar regions of the water molecules and their ionic bonds are disrupted in the process of **dissociation**. Dissociation occurs when atoms or groups of atoms break off from molecules and form ions. Consider table salt (NaCl, or sodium chloride): when NaCl

crystals are added to water, the molecules of NaCl dissociate into Na<sup>+</sup> and Cl<sup>-</sup> ions, and spheres of hydration form around the ions, illustrated in Figure 3.25. The positively charged sodium ion is surrounded by the partially negative charge of the water molecule's oxygen. The negatively charged chloride ion is surrounded by the partially positive charge of the hydrogen on the water molecule.



Figure 3.25 When table salt (NaCl) is mixed in water, spheres of hydration are formed around the ions.

# Water's Cohesive and Adhesive Properties

Have you ever filled a glass of water to the very top and then slowly added a few more drops? Before it overflows, the water forms a dome-like shape above the rim of the glass. This water can stay above the glass because of the property of **cohesion**. In cohesion, water molecules are attracted to each other (because of hydrogen bonding), keeping the molecules together at the liquid-gas (water-air) interface, although there is no more room in the glass.

Cohesion allows for the development of **surface tension**, the capacity of a substance to withstand being ruptured when placed under tension or stress. This is also why water forms droplets when placed on a dry surface rather than being flattened out by gravity. When a small scrap of paper is placed onto the droplet of water, the paper floats on top of the water droplet even though paper is denser (heavier) than the water. Cohesion and surface tension keep the hydrogen bonds of water molecules intact and support the item floating on the top. It's even possible to "float" a needle on top of a glass of water if it is placed gently without breaking the surface tension, as shown in Figure 3.26.



**Figure 3.26** The weight of the needle is pulling the surface downward; at the same time, the surface tension is pulling it up, suspending it on the surface of the water and keeping it from sinking. Notice the indentation in the water around the needle. (credit: Cory Zanker)

These cohesive forces are related to water's property of **adhesion**, or the attraction between water molecules and other molecules. This attraction is sometimes stronger than water's cohesive forces, especially when the water is exposed to charged surfaces such as those found on the inside of thin glass tubes known as capillary tubes. Adhesion is observed when water "climbs" up the tube placed in a glass of water: notice that the water appears to be higher on the sides of the tube than in the middle. This is because the water molecules are attracted to the charged glass walls of the capillary more than they are to each other and therefore adhere to it. This type of adhesion is called **capillary action**, and is illustrated in **Figure 3.27**.



Figure 3.27 Capillary action in a glass tube is caused by the adhesive forces exerted by the internal surface of the glass exceeding the cohesive forces between the water molecules themselves. (credit: modification of work by Pearson-Scott Foresman, donated to the Wikimedia Foundation)

Why are cohesive and adhesive forces important for life? Cohesive and adhesive forces are important for the transport of water from the roots to the leaves in plants. These forces create a "pull" on the water column. This pull results from the tendency of water molecules being evaporated on the surface of the plant to stay connected to water molecules below them, and so they are pulled along. Plants use this natural phenomenon to help transport water from their roots to their leaves. Without these properties of water, plants would be unable to receive the water and the dissolved minerals they require. In another example, insects such as the water strider, shown in **Figure 3.28**, use the surface tension of water to stay afloat on the surface layer of water and even

mate there.



Figure 3.28 Water's cohesive and adhesive properties allow this water strider (*Gerris* sp.) to stay afloat. (credit: Tim Vickers)

# pH, Buffers, Acids, and Bases

The pH of a solution indicates its acidity or alkalinity.

$$H_2 O(I) \leftrightarrow H^+(aq) + OH^-(aq)$$

**litmus** or pH paper, filter paper that has been treated with a natural water-soluble dye so it can be used as a pH indicator, to test how much acid (acidity) or base (alkalinity) exists in a solution. You might have even used some to test whether the water in a swimming pool is properly treated. In both cases, the pH test measures the concentration of hydrogen ions in a given solution.

Hydrogen ions are spontaneously generated in pure water by the dissociation (ionization) of a small percentage of water molecules into equal numbers of hydrogen ( $H^+$ ) ions and hydroxide ( $OH^-$ ) ions. While the hydroxide ions are kept in solution by their hydrogen bonding with other water molecules, the hydrogen ions, consisting of naked protons, are immediately attracted to un-ionized water molecules, forming hydronium ions ( $H_30^+$ ). Still, by convention, scientists refer to hydrogen ions and their concentration as if they were free in this state in liquid water.

The concentration of hydrogen ions dissociating from pure water is  $1 \times 10^{-7}$  moles H<sup>+</sup> ions per liter of water. Moles (mol) are a way to express the amount of a substance (which can be atoms, molecules, ions, etc), with one mole being equal to  $6.02 \times 10^{23}$  particles of the substance. Therefore, 1 mole of water is equal to  $6.02 \times 10^{23}$  water molecules. The pH is calculated as the negative of the base 10 logarithm of this concentration. The log10 of  $1 \times 10^{-7}$  is -7.0, and the negative of this number (indicated by the "p" of "pH") yields a pH of 7.0, which is also known as neutral pH. The pH inside of human cells and blood are examples of two areas of the body where near-neutral pH is maintained.

Non-neutral pH readings result from dissolving acids or bases in water. Using the negative logarithm to generate positive integers, high concentrations of hydrogen ions yield a low pH number, whereas low levels of hydrogen ions result in a high pH. An **acid** is a substance that increases the concentration of hydrogen ions ( $H^+$ ) in a solution, usually by having one of its hydrogen atoms dissociate. A **base** provides either hydroxide ions ( $OH^-$ ) or other negatively charged ions that combine with hydrogen ions, reducing their concentration in the solution and thereby raising the pH. In cases where the base releases hydroxide ions, these ions bind to free hydrogen ions, generating new water molecules.

The stronger the acid, the more readily it donates  $H^+$ . For example, hydrochloric acid (HCl) completely dissociates into hydrogen and chloride ions and is highly acidic, whereas the acids in tomato juice or vinegar do not completely dissociate and are considered weak acids. Conversely, strong bases are those substances that readily donate  $OH^-$  or take up hydrogen ions. Sodium hydroxide (NaOH) and many household cleaners are highly alkaline and give up  $OH^-$  rapidly when placed in water, thereby raising the pH. An example of a weak basic solution is seawater, which has a pH near 8.0, close enough to neutral pH that marine organisms adapted to this saline environment are able to thrive in it.

The **pH scale** is, as previously mentioned, an inverse logarithm and ranges from 0 to 14 (Figure 3.29). Anything below 7.0 (ranging from 0.0 to 6.9) is acidic, and anything above 7.0 (from 7.1 to 14.0) is alkaline. Extremes in pH

in either direction from 7.0 are usually considered inhospitable to life. The pH inside cells (6.8) and the pH in the blood (7.4) are both very close to neutral. However, the environment in the stomach is highly acidic, with a pH of 1 to 2. So how do the cells of the stomach survive in such an acidic environment? How do they homeostatically maintain the near neutral pH inside them? The answer is that they cannot do it and are constantly dying. New stomach cells are constantly produced to replace dead ones, which are digested by the stomach acids. It is estimated that the lining of the human stomach is completely replaced every seven to ten days.



Figure 3.29 The pH scale measures the concentration of hydrogen ions (H<sup>+</sup>) in a solution. (credit: modification of work by Edward Stevens)

Link to Learning



Watch this video for a straightforward explanation of pH and its logarithmic scale. (This media type is not supported in this reader. Click to open media in browser.) (http://legacy.cnx.org/content/m44392/ 1.10/#eip-id1170503069363)

So how can organisms whose bodies require a near-neutral pH ingest acidic and basic substances (a human drinking orange juice, for example) and survive? Buffers are the key. **Buffers** readily absorb excess  $H^+$  or  $OH^-$ , keeping the pH of the body carefully maintained in the narrow range required for survival. Maintaining a constant blood pH is critical to a person's well-being. The buffer maintaining the pH of human blood involves carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate ion (HCO<sub>3</sub><sup>-</sup>), and carbon dioxide (CO<sub>2</sub>). When bicarbonate ions combine with free hydrogen ions and become carbonic acid, hydrogen ions are removed, moderating pH changes. Similarly, as shown in **Figure 3.30**, excess carbonic acid can be converted to carbon dioxide gas and exhaled through the lungs. This prevents too many free hydrogen ions from building up in the blood and dangerously reducing the blood's pH. Likewise, if too much OH<sup>-</sup> is introduced into the system, carbonic acid will combine with it to create bicarbonate, lowering the pH. Without this buffer system, the body's pH would fluctuate enough to put survival in jeopardy.



**Figure 3.30** This diagram shows the body's buffering of blood pH levels. The blue arrows show the process of raising pH as more CO<sub>2</sub> is made. The purple arrows indicate the reverse process: the lowering of pH as more bicarbonate is created.

Other examples of buffers are antacids used to combat excess stomach acid. Many of these over-the-counter medications work in the same way as blood buffers, usually with at least one ion capable of absorbing hydrogen and moderating pH, bringing relief to those that suffer "heartburn" after eating. The unique properties of water that contribute to this capacity to balance pH—as well as water's other characteristics—are essential to sustaining life on Earth.





To learn more about water. Visit the U.S. Geological Survey Water Science for Schools (http://openstaxcollege.org/l/all\_about\_water) All About Water! website.

# **Section Summary**

Water has many properties that are critical to maintaining life. It is a polar molecule, allowing for the formation of hydrogen bonds. Hydrogen bonds allow ions and other polar molecules to dissolve in water. Therefore, water is an excellent solvent. The hydrogen bonds between water molecules cause the water to have a high heat capacity, meaning it takes a lot of added heat to raise its temperature. As the temperature rises, the hydrogen bonds between water continually break and form anew. This allows for the overall temperature to remain stable, although energy is added to the system. Water also exhibits a high heat of vaporization, which is key to how organisms cool themselves by the evaporation of sweat. Water's cohesive forces allow for the property of surface tension, whereas its adhesive properties are seen as water rises inside capillary tubes. The pH value is a measure of hydrogen ion concentration in a solution and is one of many chemical characteristics that is highly regulated in living organisms through homeostasis. Acids and bases can change pH values, but buffers tend to moderate the changes they cause. These properties of water are intimately connected to the biochemical and physical processes performed by living organisms, and life would be very different if these properties were altered, if it could exist at all.

# **Review Questions**

Exercise 3.50

Which of the following statements is not true?

- a. Water is polar.
- b. Water stabilizes temperature.
- c. Water is essential for life.
- d. Water is the most abundant molecule in the Earth's atmosphere.

Solution

D

Exercise 3.51

When acids are added to a solution, the pH should \_\_\_\_\_

a. decrease

- b. increase
- c. stay the same
- d. cannot tell without testing

# Solution

А

# Exercise 3.52

A molecule that binds up excess hydrogen ions in a solution is called a(n) \_\_\_\_\_\_.

- a. acid
- b. isotope
- c. base
- d. donator

# Solution

С

Exercise 3.53

Which of the following statements is true?

- a. Acids and bases cannot mix together.
- b. Acids and bases will neutralize each other.
- c. Acids, but not bases, can change the pH of a solution.
- d. Acids donate hydroxide ions (OH<sup>-</sup>); bases donate hydrogen ions (H<sup>+</sup>).

# Solution

В

# **Free Response**

Exercise 3.54

Discuss how buffers help prevent drastic swings in pH.

# Solution

Buffers absorb the free hydrogen ions and hydroxide ions that result from chemical reactions. Because they can bond these ions, they prevent increases or decreases in pH. An example of a buffer system is the bicarbonate system in the human body. This system is able to absorb hydrogen and hydroxide ions to prevent changes in pH and keep cells functioning properly.

Exercise 3.55

Why can some insects walk on water?

# Solution

Some insects can walk on water, although they are heavier (denser) than water, because of the surface tension of water. Surface tension results from cohesion, or the attraction between water molecules at the surface of the body of water (the liquid-air/gas interface).

# 3.6 Brønsted-Lowry Acids and Bases

By the end of this section, you will be able to:

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- · Write equations for acid and base ionization reactions
- · Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO<sub>2</sub>), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions  $(H_3O^+)$  and a base as a compound that dissolves in water to yield hydronium is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton,  $H^+$ . A proton is what remains when the most common isotope of hydrogen,  $\frac{1}{1}H$ , loses an electron. A

compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H<sub>2</sub>SO<sub>4</sub>, organic acids like acetic acid (CH<sub>3</sub>COOH) or ascorbic acid (vitamin C), or H<sub>2</sub>O. Anions (such as HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HS<sup>-</sup>, and HCO<sub>3</sub><sup>-</sup>) and cations (such as H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>3</sub>NH<sub>2</sub>), anions (such as OH<sup>-</sup>, HS<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>), or cations (such as [Al(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup>). The most familiar bases are ionic compounds such as NaOH and Ca(OH)<sub>2</sub>, which contain the hydroxide ion, OH<sup>-</sup>. The hydroxide ion in these compounds accepts a proton

from acids to form water:

$$H^+ + OH^- \longrightarrow H_2O$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

acid 
$$\Rightarrow$$
 proton + conjugate base  
HF  $\Rightarrow$  H<sup>+</sup> + F<sup>-</sup>  
H<sub>2</sub>SO<sub>4</sub>  $\Rightarrow$  H<sup>+</sup> + HSO<sub>4</sub><sup>-</sup>  
H<sub>2</sub>O  $\Rightarrow$  H<sup>+</sup> + OH<sup>-</sup>  
HSO<sub>4</sub><sup>-</sup>  $\Rightarrow$  H<sup>+</sup> + SO<sub>4</sub><sup>2-</sup>  
NH<sub>4</sub><sup>+</sup>  $\Rightarrow$  H<sup>+</sup> + NH<sub>3</sub>

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

base + proton  $\Rightarrow$  conjugate acid OH<sup>-</sup> + H<sup>+</sup>  $\Rightarrow$  H<sub>2</sub>O H<sub>2</sub>O + H<sup>+</sup>  $\Rightarrow$  H<sub>3</sub>O<sup>+</sup> NH<sub>3</sub> + H<sup>+</sup>  $\Rightarrow$  NH<sub>4</sub><sup>+</sup> S<sup>2-</sup> + H<sup>+</sup>  $\Rightarrow$  HS<sup>-</sup> CO<sub>3</sub><sup>2-</sup> + H<sup>+</sup>  $\Rightarrow$  HCO<sub>3</sub><sup>-</sup> F<sup>-</sup> + H<sup>+</sup>  $\Rightarrow$  HF

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the *transfer* of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water,  $OH^-$ , and the conjugate acid of ammonia,  $NH_4^+$ :



The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



When we add a base to water, a **base ionization** reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**.

Pure water undergoes autoionization to a very slight extent. Only about two out of every  $10^9$  molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the **ion-product constant for water** ( $K_w$ ):

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-]$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C,  $K_W$  has a value of 1.0 × 10<sup>-14</sup>. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for  $K_W$  is about 5.6 × 10<sup>-13</sup>, roughly 50 times larger than the value at 25 °C.

### Example 3.10

#### Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

#### Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water,  $[H_3O^+] = [OH^-]$ . At 25 °C:

$$K_{\rm w} = [{\rm H}_3{\rm O}^+][{\rm O}{\rm H}^-] = [{\rm H}_3{\rm O}^+]^2 = [{\rm O}{\rm H}^-]^2 = 1.0 \times 10^{-14}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal  $1.0 \times 10^{-7} M$ .

### **Check Your Learning**

The ion product of water at 80 °C is  $2.4 \times 10^{-13}$ . What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer:

 $[H_3O^+] = [OH^-] = 4.9 \times 10^{-7} M$ 

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. **Example 3.11** demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

#### Example 3.11

# The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of  $2.0 \times 10^{-6}$  *M*. What is the concentration of hydroxide ion at 25 °C?

#### Solution

We know the value of the ion-product constant for water at 25 °C:

$$2H_2O(l) \Rightarrow H_3O^+(aq) + OH^-(aq)$$
  $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ 

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the  $K_w$  expression yields that [OH<sup>-</sup>] is directly proportional to the inverse of [H<sub>3</sub>O<sup>+</sup>]:

$$[OH^{-}] = \frac{K_{\rm w}}{[H_3O^{+}]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to  $5.0 \times 10^{-9}$  *M* as the hydronium ion concentration increases to  $2.0 \times 10^{-6}$  *M*. This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the [OH<sup>-</sup>] is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_{\rm w} = [{\rm H}_3 {\rm O}^+][{\rm O}{\rm H}^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

#### **Check Your Learning**

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M

at 25 °C?

Answer:

 $[H_3O^+] = 1 \times 10^{-11} M$ 

# **Amphiprotic Species**

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be **amphiprotic**. Another term used to describe such species is **amphoteric**, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO_{3}^{-}(aq) + H_{2}O(l) \rightleftharpoons CO_{3}^{2-}(aq) + H_{3}O^{+}(aq)$$
$$HCO_{3}^{-}(aq) + H_{2}O(l) \rightleftharpoons H_{2}CO_{3}(aq) + OH^{-}(aq)$$

### Example 3.12

### Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO3<sup>-</sup>

(a) as an acid with OH

(b) as a base with HI

#### Solution

(a)  $\text{HSO}_3^{-}(aq) + \text{OH}^{-}(aq) \rightleftharpoons \text{SO}_3^{2-}(aq) + \text{H}_2\text{O}(l)$ 

(b)  $\text{HSO}_3(aq) + \text{HI}(aq) \rightleftharpoons \text{H}_2\text{SO}_3(aq) + \text{I}^-(aq)$ 

### **Check Your Learning**

Write separate equations representing the reaction of  $H_2 PO_4$  <sup>-</sup>

(a) as a base with HBr

(b) as an acid with OH<sup>-</sup>

Answer:

(a) 
$$H_2 PO_4^{-}(aq) + HBr(aq) \approx H_3 PO_4(aq) + Br^{-}(aq);$$
 (b) 
$$H_2 PO_4^{-}(aq) + OH^{-}(aq) \approx HPO_4^{2-}(aq) + H_2 O(l)$$

# **Key Concepts and Summary**

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion,  $H_3O^+$ , and the hydroxide ion,  $OH^-$  when it undergoes autoionization:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water,  $K_{W}$  is the equilibrium constant for the autoionization reaction:

# **Key Equations**

•  $K_{\rm W} = [{\rm H}_3{\rm O}^+][{\rm OH}^-] = 1.0 \times 10^{-14} ({\rm at} 25 \,{}^{\circ}{\rm C})$ 

# **Chemistry End of Chapter Exercises**

### Exercise 3.56

Write equations that show NH<sub>3</sub> as both a conjugate acid and a conjugate base.

#### Solution

One example for NH<sub>3</sub> as a conjugate acid:  $NH_2^- + H^+ \longrightarrow NH_3$ ; as a conjugate base:  $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$ 

Exercise 3.57

Write equations that show  $H_2PO_4^-$  acting both as an acid and as a base.

Exercise 3.58

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a)  $H_{3}O^{+}$ 

(b) HCl

(c) NH3

- (d) CH<sub>3</sub>CO<sub>2</sub>H
- (e)  $NH_4^+$
- (f)  $HSO_4$  -

### Solution

(a)  $H_3O^+(aq) \longrightarrow H^+(aq) + H_2O(l);$  (b)  $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq);$  (c)  $NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq);$  (d)  $CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq);$  (e)  $NH_4^+(aq) \longrightarrow H^+(aq) + NH_3(aq);$  (f)  $HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{-2-}(aq)$ 

Exercise 3.59

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

- (a) HNO3
- (b)  $PH_4^+$
- (c) H<sub>2</sub>S
- (d) CH<sub>3</sub>CH<sub>2</sub>COOH
- (e)  $H_2PO_4^-$

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(f) HS<sup>-</sup>
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Exercise 3.60

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base: (a) H<sub>2</sub>O (b) OH<sup>-</sup>

(c) NH3

(d) CN<sup>-</sup>

(e) S<sup>2-</sup>

(f)  $H_2PO_4^-$ 

#### Solution

(a)  $H_2O(l) + H^+(aq) \longrightarrow H_3O^+(aq);$  (b)  $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l);$  (c)  $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq);$  (d)  $CN^-(aq) + H^+(aq) \longrightarrow HCN(aq);$  (e)  $S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq);$  (f)  $H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)$ 

Exercise 3.61

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) HS<sup>-</sup>

- (b)  $PO_4^{3-}$
- (c)  $NH_2^-$
- (d) C<sub>2</sub>H<sub>5</sub>OH
- (e) O<sup>2-</sup>
- (f)  $H_2PO_4^-$

Exercise 3.62

What is the conjugate acid of each of the following? What is the conjugate base of each?

- (a) OH<sup>-</sup>
- (b) H<sub>2</sub>O
- (c)  $HCO_3^-$
- (d) NH3
- (e)  $HSO_4^-$
- (f) H<sub>2</sub>O<sub>2</sub>
- (g) HS<sup>-</sup>
- (h)  $H_5 N_2^+$

### Solution

(a) H<sub>2</sub>O, O<sup>2-</sup>; (b) H<sub>3</sub>O<sup>+</sup>, OH<sup>-</sup>; (c) H<sub>2</sub>CO<sub>3</sub>, CO<sub>3</sub><sup>2-</sup>; (d) NH<sub>4</sub><sup>+</sup>, NH<sub>2</sub><sup>-</sup>; (e) H<sub>2</sub>SO<sub>4</sub>, SO<sub>4</sub><sup>2-</sup>; (f) H<sub>3</sub>O<sub>2</sub><sup>+</sup>, HO<sub>2</sub><sup>-</sup>; (g) H<sub>2</sub>S; S<sup>2-</sup>; (h) H<sub>6</sub>N<sub>2</sub><sup>2+</sup>, H<sub>4</sub>N<sub>2</sub>

Exercise 3.63

What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) H<sub>2</sub>S

(b)  $H_2PO_4^-$ 

(c) PH<sub>3</sub>

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# (d) HS<sup>-</sup>

(e)  $HSO_3^-$ 

(f)  $H_3O_2^+$ 

(g) H4N2

(h) CH<sub>3</sub>OH

# Exercise 3.64

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) 
$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$
  
(b)  $CN^- + H_2O \longrightarrow HCN + OH^-$   
(c)  $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$   
(d)  $HSO_4^- + OH^- \longrightarrow SO_4^{-2-} + H_2O$   
(e)  $O^{2-} + H_2O \longrightarrow 2OH^-$   
(f)  $[CP(H_1O_1) + OH_2]^+ + [A](H_1O_2)^{-3+} \longrightarrow [CP(H_1O_2)^{-2+} + [A](H_1O_2)^{-2+}]^{-3+}$ 

(f)  $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$ 

(g)  $H_2S + NH_2^- \longrightarrow HS^- + NH_3$ 

# Solution

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) HNO<sub>3</sub>(BA), H<sub>2</sub>O(BB), H<sub>3</sub>O<sup>+</sup>(CA), NO<sub>3</sub><sup>-</sup>(CB); (b) CN<sup>-</sup>(BB), H<sub>2</sub>O(BA), HCN(CA), OH<sup>-</sup>(CB); (c) H<sub>2</sub>SO<sub>4</sub>(BA), Cl<sup>-</sup>(BB), HCl(CA), HSO<sub>4</sub><sup>-</sup>(CB); (d) HSO<sub>4</sub><sup>-</sup>(BA), OH<sup>-</sup>(BB), SO<sub>4</sub><sup>2-</sup>(CB), H<sub>2</sub>O(CA); (e) O<sup>2-</sup>(BB), H<sub>2</sub>O(BA) OH<sup>-</sup>(CB and CA); (f) [Cu(H<sub>2</sub>O)<sub>3</sub>(OH)]<sup>+</sup>(BB), [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>(BA), [Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>(CA), [Al(H<sub>2</sub>O)<sub>5</sub>(OH)]<sup>2+</sup>(CB); (g) H<sub>2</sub>S(BA), NH<sub>2</sub><sup>-</sup>(BB), HS<sup>-</sup>(CB), NH<sub>3</sub>(CA)

# Exercise 3.65

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

- (a)  $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
- (b)  $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
- (c)  $HS^- + H_2O \longrightarrow H_2S + OH^-$
- (d)  $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
- (e)  $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$
- (f)  $[Fe(H_2O_5(OH)]^{2+} + [Al(H_2O_6)]^{3+} \longrightarrow [Fe(H_2O_6)]^{3+} + [Al(H_2O_5(OH))]^{2+}$
- (g)  $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

# Exercise 3.66

What are amphiprotic species? Illustrate with suitable equations.

# Solution

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid.

 $H_2O(aq) + NH_3(aq) \Rightarrow NH_4^+(aq) + OH^-(aq)$ . As a base:  $H_2O(aq) + HCl(aq) \Rightarrow H_3O^+(aq) + Cl^-(aq)$ 

Exercise 3.67

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

(a) H<sub>2</sub>O

- (b)  $H_2PO_4^-$
- (c) S<sup>2-</sup>
- (d)  $CO_3^{2-}$
- (e)  $HSO_4^-$

### Exercise 3.68

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

- (a) NH3
- (b)  $HPO_4^-$
- (c) Br
- (d)  $NH_4^+$
- (e)  $ASO_4^{3-}$

### Solution

amphiprotic: (a)  $NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$ ,  $NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH$ ; (b)  $HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$ ,  $HPO_4^{2-} + HCIO_4 \longrightarrow H_2PO_4^- + CIO_4^-$ ; not amphiprotic: (c) Br<sup>-</sup>; (d)  $NH_4^+$ ; (e)  $AsO_4^{3-}$ 

Exercise 3.69

Is the self ionization of water endothermic or exothermic? The ionization constant for water ( $K_W$ ) is 2.9  $\times$  10<sup>-14</sup> at 40 °C and 9.3  $\times$  10<sup>-14</sup> at 60 °C.

# 3.7 | pH and pOH

By the end of this section, you will be able to:

- · Explain the characterization of aqueous solutions as acidic, basic, or neutral
- · Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- · Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water ( $K_W$ ). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and

hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$pX = -\log X$$

The **pH** of a solution is therefore defined as shown here, where  $[H_3O^+]$  is the molar concentration of hydronium ion in the solution:

$$pH = -\log[H_3O^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[H_2 O^+] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH**:

$$pOH = -log[OH^-]$$

or

$$[OH^{-}] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the  $K_w$  expression:

$$K_{\rm w} = [{\rm H}_3 {\rm O}^+][{\rm OH}^-]$$
  
 $-\log K_{\rm w} = -\log([{\rm H}_3 {\rm O}^+][{\rm OH}^-]) = -\log[{\rm H}_3 {\rm O}^+] + -\log[{\rm OH}^-]$   
 $pK_{\rm w} = p{\rm H} + p{\rm OH}$ 

At 25 °C, the value of  $K_W$  is 1.0  $\times$  10<sup>-14</sup>, and so:

14.00 = pH + pOH

As was shown in **Example 3.10**, the hydronium ion molarity in pure water (or any neutral solution) is  $1.0 \times 10^{-7}$  *M* at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00$$
$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than  $1.0 \times 10^{-7}$  *M* and hydroxide ion molarities less than  $1.0 \times 10^{-7}$  *M* (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than  $1.0 \times 10^{-7}$  *M* and hydroxide ion molarities greater than  $1.0 \times 10^{-7}$  *M* (corresponding to pH values greater than 7.00 and pOH values less than  $1.0 \times 10^{-7}$  *M* (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant  $K_w$  is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the "Check Your Learning" exercise accompanying **Example 3.10** showed the hydronium molarity of pure water at 80 °C is 4.9  $\times 10^{-7}$  *M*, which corresponds to pH and pOH values of:

$$pH = -\log[H_3O^+] = -\log(4.9 \times 10^{-7}) = 6.31$$
$$pOH = -\log[OH^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as

enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 3.3).

Classification	<b>Relative Ion Concentrations</b>	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	[H <sub>3</sub> O <sup>+</sup> ] < [OH <sup>−</sup> ]	pH > 7

Table 3.3

**Figure 3.31** shows the relationships between [H<sub>3</sub>O<sup>+</sup>], [OH<sup>-</sup>], pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

[H <sub>3</sub> O⁺] (M)	[OH⁻] (M)	рН	рОН	Sample Solution
10 <sup>1</sup>	10 <sup>-15</sup>	-1	15	-
10 <sup>0</sup> or 1	10 <sup>-14</sup>	0	14	1 M HCI acidic
$10^{-1}$	10 <sup>-13</sup>	1	13	gastric juice
10 <sup>-2</sup>	10 <sup>-12</sup>	2	12	lime juice
10 <sup>-3</sup>	10 <sup>-11</sup>	3	11	_ stomach acid
10 <sup>-4</sup>	10 <sup>-10</sup>	4	10	→ wine → orange juice
10 <sup>-5</sup>	10 <sup>-9</sup>	5	9	coffee
10 <sup>-6</sup>	10 <sup>-8</sup>	6	8	◄ rain water
10 <sup>-7</sup>	10 <sup>-7</sup>	7	7	
10 <sup>-8</sup>	10 <sup>-6</sup>	8	6	blood ocean water
10 <sup>-9</sup>	10 <sup>-5</sup>	9	5	baking soda
10 <sup>-10</sup>	10 <sup>-4</sup>	10	4	-
10 <sup>-11</sup>	10 <sup>-3</sup>	11	3	
10 <sup>-12</sup>	10 <sup>-2</sup>	12	2	_ ← household ammonia, NH <sub>3</sub>
10 <sup>-13</sup>	10 <sup>-1</sup>	13	1	- bleach
$10^{-14}$	10 <sup>0</sup> or 1	14	0	1 M NaOH basic
10 <sup>-15</sup>	10 <sup>1</sup>	15	-1	-

**Figure 3.31** The pH and pOH scales represent concentrations of  $[H_3O^+]$  and  $OH^-$ , respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

### Example 3.13

Calculation of pH from [H<sub>3</sub>O<sup>+</sup>]

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of  $1.2 \times 10^{-3} M$ ?

Solution

$$pH = -\log[H_3 O^+]$$
$$= -\log(1.2 \times 10^{-3})$$
$$= -(-2.92) = 2.92$$

(The use of logarithms is explained in Appendix B (https://legacy.cnx.org/content/m51209/latest/) . Recall that, as we have done here, when taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

#### **Check Your Learning**

Water exposed to air contains carbonic acid, H<sub>2</sub>CO<sub>3</sub>, due to the reaction between carbon dioxide and water:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO<sub>2</sub> of 2.0  $\times$  10<sup>-6</sup> *M*, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer:

5.70

#### Example 3.14

#### Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$pH = -log[H_3O^+] = 7.3$$
  
 $log[H_3O^+] = -7.3$   
 $[H_3O^+] = 10^{-7.3}$  or  $[H_3O^+] = antilog of -7.3$ 

$$[H_3O^+] = 5 \times 10^{-8} M$$

(On a calculator take the antilog, or the "inverse" log, of -7.3, or calculate  $10^{-7.3}$ .)

#### **Check Your Learning**

Calculate the hydronium ion concentration of a solution with a pH of -1.07.

Answer:

12 M

#### **Environmental Science**

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved  $CO_2$  which forms carbonic acid:

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq)$$
$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, NO, and NO<sub>2</sub> being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2 O(l) + SO_3(g) \longrightarrow H_2 SO_4(aq)$$

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 3.32). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this website (http://openstax.org/l/16EPA) hosted by the US Environmental Protection Agency.



(a)



(b)

Figure 3.32 (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

#### Example 3.15

### Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

#### Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding  $[OH^-] = 0.0125 M$ :

$$pOH = -log[OH^{-}] = -log 0.0125$$
  
= -(-1.903) = 1.903

The pH can be found from the pOH:

$$pH + pOH = 14.00$$
  
 $pH = 14.00 - pOH = 14.00 - 1.903 = 12.10$ 

**Check Your Learning** 

The hydronium ion concentration of vinegar is approximately  $4 \times 10^{-3}$  *M*. What are the corresponding values of pOH and pH?

Answer:

pOH = 11.6, pH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 3.33).



**Figure 3.33** (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of  $\pm$  0.002 pH units, and may cost in excess of \$1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy ( $\pm$  0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 3.34).



**Figure 3.34** (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-*M* solutions of progressively weaker acids: HCl (pH = l), CH<sub>3</sub>CO<sub>2</sub>H (pH = 3), and NH<sub>4</sub>Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-*M* solutions of the progressively stronger bases: KCl (pH = 7), aniline, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (pH = 9), NH<sub>3</sub> (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa)

# **Key Concepts and Summary**

The concentration of hydronium ion in a solution of an acid in water is greater than  $1.0 \times 10^{-7}$  M at 25 °C.

The concentration of hydroxide ion in a solution of a base in water is greater than  $1.0 \times 10^{-7} M$  at 25 °C. The concentration of  $H_3O^+$  in a solution can be expressed as the pH of the solution; pH =  $-\log H_3O^+$ . The

concentration of  $OH^-$  can be expressed as the pOH of the solution:  $pOH = -log[OH^-]$ . In pure water, pH = 7.00 and pOH = 7.00

# **Key Equations**

- $pH = -log[H_3O^+]$
- pOH = -log[OH<sup>-</sup>]
- $[H_3O^+] = 10^{-pH}$
- [OH<sup>-</sup>] = 10<sup>-pOH</sup>
- $pH + pOH = pK_W = 14.00 \text{ at } 25 \text{ °C}$

# **Chemistry End of Chapter Exercises**

Exercise 3.70

Explain why a sample of pure water at 40 °C is neutral even though  $[H_3O^+] = 1.7 \times 10^{-7} M$ .  $K_w$  is 2.9  $\times 10^{-14}$  at 40 °C.

# Solution

In a neutral solution  $[H_3O^+] = [OH^-]$ . At 40 °C,  $[H_3O^+] = [OH^-] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}$ .

Exercise 3.71

The ionization constant for water ( $K_w$ ) is 2.9  $\times 10^{-14}$  at 40 °C. Calculate [H<sub>3</sub>O<sup>+</sup>], [OH<sup>-</sup>], pH, and pOH for pure water at 40 °C.

Exercise 3.72

The ionization constant for water ( $K_w$ ) is 9.311  $\times 10^{-14}$  at 60 °C. Calculate [H<sub>3</sub>O<sup>+</sup>], [OH<sup>-</sup>], pH, and pOH for pure water at 60 °C.

# Solution

 $x = 3.051 \times 10^{-7} M = [H_3O^+] = [OH^-]$ pH = -log3.051 × 10<sup>-7</sup> = -(-6.5156) = 6.5156 pOH = pH = 6.5156

Exercise 3.73

Calculate the pH and the pOH of each of the following solutions at 25  $^{\circ}$ C for which the substances ionize completely:

(a) 0.200 M HCI

(b) 0.0143 *M* NaOH

(c) 3.0 M HNO3

(d) 0.0031 M Ca(OH)2

Exercise 3.74

Calculate the pH and the pOH of each of the following solutions at 25  $^{\circ}\text{C}$  for which the substances ionize completely:

(a) 0.000259 M HClO4

# (b) 0.21 M NaOH

# (c) 0.000071 M Ba(OH)2

(d) 2.5 M KOH

# Solution

(a) pH = 3.587; pOH = 10.413; (b) pH = 0.68; pOH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pH = -0.40; pOH = -014.4

# Exercise 3.75

What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

# Exercise 3.76

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

# Solution

 $[H_{3}O^{+}] = 3.0 \times 10^{-7} M; [OH^{-}] = 3.3 \times 10^{-8} M$ 

# Exercise 3.77

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 3.31 for useful information.

# Exercise 3.78

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 3.31 for useful information.

# Solution

 $[H_{3}O^{+}] = 1 \times 10^{-2} M; [OH^{-}] = 1 \times 10^{-12} M$ 

# Exercise 3.79

The hydronium ion concentration in a sample of rainwater is found to be  $1.7 \times 10^{-6}$  M at 25 °C. What is the concentration of hydroxide ions in the rainwater?

# Exercise 3.80

The hydroxide ion concentration in household ammonia is  $3.2 \times 10^{-3}$  M at 25 °C. What is the concentration of hydronium ions in the solution?

Solution

 $[OH^{-}] = 3.1 \times 10^{-12} M$ 

# 3.8 Carbon

By the end of this section, you will be able to:

- · Explain why carbon is important for life
- Describe the role of functional groups in biological molecules

Cells are made of many complex molecules called macromolecules, such as proteins, nucleic acids (RNA and DNA), carbohydrates, and lipids. The macromolecules are a subset of organic molecules (any carboncontaining liquid, solid, or gas) that are especially important for life. The fundamental component for all of these macromolecules is carbon. The carbon atom has unique properties that allow it to form covalent bonds to as many as four different atoms, making this versatile element ideal to serve as the basic structural component, or "backbone," of the macromolecules.

Individual carbon atoms have an incomplete outermost electron shell. With an atomic number of 6 (six electrons and six protons), the first two electrons fill the inner shell, leaving four in the second shell. Therefore, carbon atoms can form up to four covalent bonds with other atoms to satisfy the octet rule. The methane molecule provides an example: it has the chemical formula CH<sub>4</sub>. Each of its four hydrogen atoms forms a single covalent bond with the carbon atom by sharing a pair of electrons. This results in a filled outermost shell.

# Hydrocarbons

**Hydrocarbons** are organic molecules consisting entirely of carbon and hydrogen, such as methane (CH<sub>4</sub>) described above. We often use hydrocarbons in our daily lives as fuels—like the propane in a gas grill or the butane in a lighter. The many covalent bonds between the atoms in hydrocarbons store a great amount of energy, which is released when these molecules are burned (oxidized). Methane, an excellent fuel, is the simplest hydrocarbon molecule, with a central carbon atom bonded to four different hydrogen atoms, as illustrated in **Figure 3.35**. The geometry of the methane molecule, where the atoms reside in three dimensions, is determined by the shape of its electron orbitals. The carbons and the four hydrogen atoms form a shape known as a tetrahedron, with four triangular faces; for this reason, methane is described as having tetrahedral geometry.



Figure 3.35 Methane has a tetrahedral geometry, with each of the four hydrogen atoms spaced 109.5° apart.

As the backbone of the large molecules of living things, hydrocarbons may exist as linear carbon chains, carbon rings, or combinations of both. Furthermore, individual carbon-to-carbon bonds may be single, double, or triple covalent bonds, and each type of bond affects the geometry of the molecule in a specific way. This three-dimensional shape or conformation of the large molecules of life (macromolecules) is critical to how they function.

# Hydrocarbon Chains

Hydrocarbon chains are formed by successive bonds between carbon atoms and may be branched or unbranched. Furthermore, the overall geometry of the molecule is altered by the different geometries of single, double, and triple covalent bonds, illustrated in **Figure 3.36**. The hydrocarbons ethane, ethene, and ethyne serve as examples of how different carbon-to-carbon bonds affect the geometry of the molecule. The names of all three molecules start with the prefix "eth-," which is the prefix for two carbon hydrocarbons. The suffixes "-ane," "-ene," and "-yne" refer to the presence of single, double, or triple carbon-carbon bonds, respectively. Thus, propane, propene, and propyne follow the same pattern with three carbon molecules, butane, butene, and butyne for four carbon molecules, and so on. Double and triple bonds change the geometry of the molecule: single bonds allow rotation along the axis of the bond, whereas double bonds lead to a planar configuration and triple bonds to a linear one. These geometries have a significant impact on the shape a particular molecule can assume.



**Figure 3.36** When carbon forms single bonds with other atoms, the shape is tetrahedral. When two carbon atoms form a double bond, the shape is planar, or flat. Single bonds, like those found in ethane, are able to rotate. Double bonds, like those found in ethene cannot rotate, so the atoms on either side are locked in place.

#### Hydrocarbon Rings

So far, the hydrocarbons we have discussed have been **aliphatic hydrocarbons**, which consist of linear chains of carbon atoms. Another type of hydrocarbon, **aromatic hydrocarbons**, consists of closed rings of carbon atoms. Ring structures are found in hydrocarbons, sometimes with the presence of double bonds, which can be seen by comparing the structure of cyclohexane to benzene in Figure 3.37. Examples of biological molecules that incorporate the benzene ring include some amino acids and cholesterol and its derivatives, including the hormones estrogen and testosterone. The benzene ring is also found in the herbicide 2,4-D. Benzene is a natural component of crude oil and has been classified as a carcinogen. Some hydrocarbons have both aliphatic and aromatic portions; beta-carotene is an example of such a hydrocarbon.



Figure 3.37 Carbon can form five-and six membered rings. Single or double bonds may connect the carbons in the ring, and nitrogen may be substituted for carbon.

### Isomers

The three-dimensional placement of atoms and chemical bonds within organic molecules is central to understanding their chemistry. Molecules that share the same chemical formula but differ in the placement (structure) of their atoms and/or chemical bonds are known as **isomers**. **Structural isomers** (like butane and isobutene shown in **Figure 3.38 a**) differ in the placement of their covalent bonds: both molecules have four carbons and ten hydrogens ( $C_4H_{10}$ ), but the different arrangement of the atoms within the molecules leads to differences in their chemical properties. For example, due to their different chemical properties, butane is suited for use as a fuel for cigarette lighters and torches, whereas isobutene is suited for use as a refrigerant and a propellant in spray cans.

**Geometric isomers**, on the other hand, have similar placements of their covalent bonds but differ in how these bonds are made to the surrounding atoms, especially in carbon-to-carbon double bonds. In the simple molecule butene ( $C_4H_8$ ), the two methyl groups ( $CH_3$ ) can be on either side of the double covalent bond central to the molecule, as illustrated in Figure 3.38 b. When the carbons are bound on the same side of the double bond, this is the *cis* configuration; if they are on opposite sides of the double bond, it is a *trans* configuration. In the *trans* configuration, the carbons form a more or less linear structure, whereas the carbons in the *cis* configuration make a bend (change in direction) of the carbon backbone.



**Figure 3.38** Molecules that have the same number and type of atoms arranged differently are called isomers. (a) Structural isomers have a different covalent arrangement of atoms. (b) Geometric isomers have a different arrangement of atoms around a double bond. (c) Enantiomers are mirror images of each other.

Which of the following statements is false?

- a. Molecules with the formulas CH<sub>3</sub>CH<sub>2</sub>COOH and C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> could be structural isomers.
- b. Molecules must have a double bond to be *cis-trans* isomers.
- c. To be enantiomers, a molecule must have at least three different atoms or groups connected to a central carbon.
- d. To be enantiomers, a molecule must have at least four different atoms or groups connected to a central carbon.

In triglycerides (fats and oils), long carbon chains known as fatty acids may contain double bonds, which can be in either the *cis* or *trans* configuration, illustrated in **Figure 3.39**. Fats with at least one double bond between carbon atoms are unsaturated fats. When some of these bonds are in the *cis* configuration, the resulting bend in the carbon backbone of the chain means that triglyceride molecules cannot pack tightly, so they remain liquid (oil) at room temperature. On the other hand, triglycerides with *trans* double bonds (popularly called trans fats),

have relatively linear fatty acids that are able to pack tightly together at room temperature and form solid fats. In the human diet, trans fats are linked to an increased risk of cardiovascular disease, so many food manufacturers have reduced or eliminated their use in recent years. In contrast to unsaturated fats, triglycerides without double bonds between carbon atoms are called saturated fats, meaning that they contain all the hydrogen atoms available. Saturated fats are a solid at room temperature and usually of animal origin.



Figure 3.39 These space-filling models show a *cis* (oleic acid) and a *trans* (eliadic acid) fatty acid. Notice the bend in the molecule cause by the *cis* configuration.

# Enantiomers

**Enantiomers** are molecules that share the same chemical structure and chemical bonds but differ in the threedimensional placement of atoms so that they are mirror images. As shown in **Figure 3.40**, an amino acid alanine example, the two structures are non-superimposable. In nature, only the L-forms of amino acids are used to make proteins. Some D forms of amino acids are seen in the cell walls of bacteria, but never in their proteins. Similarly, the D-form of glucose is the main product of photosynthesis and the L-form of the molecule is rarely seen in nature.



Figure 3.40 D-alanine and L-alanine are examples of enantiomers or mirror images. Only the L-forms of amino acids are used to make proteins.

# **Functional Groups**

**Functional groups** are groups of atoms that occur within molecules and confer specific chemical properties to those molecules. They are found along the "carbon backbone" of macromolecules. This carbon backbone is formed by chains and/or rings of carbon atoms with the occasional substitution of an element such as nitrogen or oxygen. Molecules with other elements in their carbon backbone are **substituted hydrocarbons**.

The functional groups in a macromolecule are usually attached to the carbon backbone at one or several different places along its chain and/or ring structure. Each of the four types of macromolecules—proteins, lipids, carbohydrates, and nucleic acids—has its own characteristic set of functional groups that contributes greatly to

its differing chemical properties and its function in living organisms.

A functional group can participate in specific chemical reactions. Some of the important functional groups in biological molecules are shown in **Figure 3.41**; they include: hydroxyl, methyl, carbonyl, carboxyl, amino, phosphate, and sulfhydryl. These groups play an important role in the formation of molecules like DNA, proteins, carbohydrates, and lipids. Functional groups are usually classified as hydrophobic or hydrophilic depending on their charge or polarity characteristics. An example of a hydrophobic group is the non-polar methane molecule. Among the hydrophilic functional groups is the carboxyl group found in amino acids, some amino acid side chains, and the fatty acids that form triglycerides and phospholipids. This carboxyl group ionizes to release hydrogen ions ( $H^+$ ) from the COOH group resulting in the negatively charged COO<sup>-</sup> group; this contributes to the hydrophilic nature of whatever molecule it is found on. Other functional groups, such as the carbonyl group, have a partially negatively charged oxygen atom that may form hydrogen bonds with water molecules, again making the molecule more hydrophilic.

Functional Group	Structure	Properties
Hydroxyl	о—н	Polar
Methyl	R —— CH <sub>3</sub>	Nonpolar
Carbonyl	0	Polar
Carboxyl	R OH	Charged, ionizes to release H <sup>+</sup> . Since carboxyl groups can release H <sup>+</sup> ions into solution, they are considered acidic.
Amino	RN H	Charged, accepts H <sup>+</sup> to form NH <sub>3</sub> <sup>+</sup> . Since amino groups can remove H <sup>+</sup> from solution, they are considered basic.
Phosphate		Charged, ionizes to release $H^+$ . Since phosphate groups can release $H^+$ ions into solution, they are considered acidic.
Sulfhydryl	R—S	Polar

Figure 3.41 The functional groups shown here are found in many different biological molecules.

Hydrogen bonds between functional groups (within the same molecule or between different molecules) are important to the function of many macromolecules and help them to fold properly into and maintain the appropriate shape for functioning. Hydrogen bonds are also involved in various recognition processes, such as DNA complementary base pairing and the binding of an enzyme to its substrate, as illustrated in Figure 3.42.



Figure 3.42 Hydrogen bonds connect two strands of DNA together to create the double-helix structure.

# **Section Summary**

The unique properties of carbon make it a central part of biological molecules. Carbon binds to oxygen, hydrogen, and nitrogen covalently to form the many molecules important for cellular function. Carbon has four electrons in its outermost shell and can form four bonds. Carbon and hydrogen can form hydrocarbon chains or rings. Functional groups are groups of atoms that confer specific properties to hydrocarbon (or substituted hydrocarbon) chains or rings that define their overall chemical characteristics and function.

# **Art Connections**

Exercise 3.81

Figure 3.38 Which of the following statements is false?

- a. Molecules with the formulas CH<sub>3</sub>CH<sub>2</sub>COOH and C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> could be structural isomers.
- b. Molecules must have a double bond to be *cis-trans* isomers.
- c. To be enantiomers, a molecule must have at least three different atoms or groups connected to a central carbon.
- d. To be enantiomers, a molecule must have at least four different atoms or groups connected to a central carbon.

#### Solution

Figure 3.38 C

# **Review Questions**

#### Exercise 3.82

Each carbon molecule can bond with as many as\_\_\_\_\_ other atom(s) or molecule(s).

- a. one
- b. two
- c. six
- d. four

# Solution

D

# Exercise 3.83

Which of the following is not a functional group that can bond with carbon?

- a. sodium
- b. hydroxyl
- c. phosphate
- d. carbonyl

# Solution

А

# **Free Response**

# Exercise 3.84

What property of carbon makes it essential for organic life?

# Solution

Carbon is unique and found in all living things because it can form up to four covalent bonds between atoms or molecules. These can be nonpolar or polar covalent bonds, and they allow for the formation of long chains of carbon molecules that combine to form proteins and DNA.

# Exercise 3.85

Compare and contrast saturated and unsaturated triglycerides.

# Solution

Saturated triglycerides contain no double bonds between carbon atoms; they are usually solid at room temperature. Unsaturated triglycerides contain at least one double bond between carbon atoms and are usually liquid at room temperature.

# 3.9 | Hydrocarbons

By the end of this section, you will be able to:

- · Explain the importance of hydrocarbons and the reason for their diversity
- Name saturated and unsaturated hydrocarbons, and molecules derived from them
- · Describe the reactions characteristic of saturated and unsaturated hydrocarbons
- · Identify structural and geometric isomers of hydrocarbons

The largest database<sup>[4]</sup> of organic compounds lists about 10 million substances, which include compounds originating from living organisms and those synthesized by chemists. The number of potential organic compounds has been estimated<sup>[5]</sup> at 10<sup>60</sup>—an astronomically high number. The existence of so many organic molecules is a consequence of the ability of carbon atoms to form up to four strong bonds to other carbon atoms, resulting in chains and rings of many different sizes, shapes, and complexities.

<sup>4.</sup> This is the Beilstein database, now available through the Reaxys site (www.elsevier.com/online-tools/reaxys).

<sup>5.</sup> Peplow, Mark. "Organic Synthesis: The Robo-Chemist," Nature 512 (2014): 20-2.

The simplest **organic compounds** contain only the elements carbon and hydrogen, and are called hydrocarbons. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

# Alkanes

**Alkanes**, or **saturated hydrocarbons**, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has  $sp^3$  hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane are illustrated in **Figure 3.43**. Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line. Because of the  $sp^3$  hybridization, the bond angles in carbon chains are close to 109.5°, giving such chains in an alkane a zigzag shape.

The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed. Condensed structural formulas for ethane and pentane are shown at the bottom of **Figure 3.43**, and several additional examples are provided in the exercises at the end of this chapter.



Figure 3.43 Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

A common method used by organic chemists to simplify the drawings of larger molecules is to use a **skeletal structure** (also called a line-angle structure). In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or bend in a line. Hydrogen atoms are not drawn if they are attached to a carbon. Other atoms besides carbon and hydrogen are represented by their elemental symbols. Figure 3.44 shows three different ways to draw the same structure.



Figure 3.44 The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

# Example 3.16

# **Drawing Skeletal Structures**

Draw the skeletal structures for these two molecules:



# Solution

Each carbon atom is converted into the end of a line or the place where lines intersect. All hydrogen atoms attached to the carbon atoms are left out of the structure (although we still need to recognize they are there):



# **Check Your Learning**

Draw the skeletal structures for these two molecules:



# Example 3.17

# **Interpreting Skeletal Structures**

Identify the chemical formula of the molecule represented here:



### Solution

There are eight places where lines intersect or end, meaning that there are eight carbon atoms in the molecule. Since we know that carbon atoms tend to make four bonds, each carbon atom will have the number of hydrogen atoms that are required for four bonds. This compound contains 16 hydrogen atoms for a molecular formula of  $C_8H_{16}$ .

Location of the hydrogen atoms:



# **Check Your Learning**

Identify the chemical formula of the molecule represented here:





All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of  $C_nH_{2n+2}$ . The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 3.4) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

# **Properties of Some Alkanes**<sup>[6]</sup>

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP <sup>[7]</sup>	Number of Structural Isomers
methane	CH <sub>4</sub>	-182.5	-161.5	gas	1
ethane	C <sub>2</sub> H <sub>6</sub>	-183.3	-88.6	gas	1
propane	C <sub>3</sub> H <sub>8</sub>	-187.7	-42.1	gas	1
butane	C <sub>4</sub> H <sub>10</sub>	-138.3	-0.5	gas	2
pentane	C5H12	-129.7	36.1	liquid	3
hexane	C <sub>6</sub> H <sub>14</sub>	-95.3	68.7	liquid	5
heptane	C7H16	-90.6	98.4	liquid	9
octane	C8H18	-56.8	125.7	liquid	18
nonane	C9H20	-53.6	150.8	liquid	35

### Table 3.4

<sup>6.</sup> Physical properties for C<sub>4</sub>H<sub>10</sub> and heavier molecules are those of the normal isomer, n-butane, n-pentane, etc.

<sup>7.</sup> STP indicates a temperature of 0  $^\circ\text{C}$  and a pressure of 1 atm.

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP	Number of Structural Isomers
decane	C <sub>10</sub> H <sub>22</sub>	-29.7	174.0	liquid	75
tetradecane	C <sub>14</sub> H <sub>30</sub>	5.9	253.5	solid	1858
octadecane	C <sub>18</sub> H <sub>38</sub>	28.2	316.1	solid	60,523

# **Properties of Some Alkanes**

### Table 3.4

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C<sub>4</sub>H<sub>10</sub>: They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:



The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2–methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 3.45 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.



Figure 3.45 These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

# The Basics of Organic Nomenclature: Naming Alkanes

The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

- 1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in Table 3.4.
- 2. Add prefixes to the name of the longest chain to indicate the positions and names of **substituents**. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.



When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a

substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

### Example 3.18

#### Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



Solution



The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

### **Check Your Learning**

Name the following molecule:



Answer:

3,3-dibromo-2-iodopentane

We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an **alkyl group** is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:



The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

# Example 3.19

# **Naming Substituted Alkanes**

Name the molecule whose structure is shown here:



### Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth*-and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

### **Check Your Learning**

Name the following molecule:



### Answer:

4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different "environments" in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in **Figure 3.43**. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent (**Figure 3.43**) and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2–methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:



Each of the six equivalent hydrogen atoms of the first type in propane and each of the nine equivalent hydrogen atoms of that type in 2-methylpropane (all shown in black) are bonded to a carbon atom that is bonded to only one other carbon atom. The two purple hydrogen atoms in propane are of a second type. They differ from the six hydrogen atoms of the first type in that they are bonded to a carbon atom bonded to two other carbon atoms. The green hydrogen atom in 2-methylpropane differs from the other nine hydrogen atoms in that molecule and from the purple hydrogen atoms in propane. The green hydrogen atom in 2-methylpropane is bonded to a carbon atom bonded to three other carbon atoms. Two different alkyl groups can be formed from each of these molecules, depending on which hydrogen atom is removed. The names and structures of these and several other alkyl groups are listed in Figure 3.46.

Alkyl Group	Structure
methyl	CH3-
ethyl	CH <sub>3</sub> CH <sub>2</sub> —
<i>n</i> -propyl	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —
isopropyl	 CH₃CHCH₃
<i>n</i> -butyl	$CH_3CH_2CH_2CH_2$ —
sec-butyl	 CH₃CH₂CHCH₃
isobutyl	CH <sub>3</sub> CHCH <sub>2</sub>   CH <sub>3</sub>
<i>tert</i> -butyl	 СН <sub>3</sub> ССН <sub>3</sub>   СН <sub>3</sub>

Figure 3.46 This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C-H

or C–C single bonds. Combustion is one such reaction:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH<sub>4</sub>, is the principal component of natural gas. Butane, C<sub>4</sub>H<sub>10</sub>, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (see Figure 3.47). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.



Figure 3.47 In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a **substitution reaction**, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:



The C–Cl portion of the chloroethane molecule is an example of a **functional group**, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic

molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.



Want more practice naming alkanes? Watch this brief video tutorial (http://openstax.org/l/16alkanes) to review the nomenclature process.

# Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called **alkenes**. Carbon atoms linked by a double bond are bound together by two bonds, one  $\sigma$  bond and one  $\pi$  bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene,  $C_2H_4$ , is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 3.48); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.



Figure 3.48 Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

### **Recycling Plastics**

Polymers (from Greek words poly meaning "many" and mer meaning "parts") are large molecules made up

of repeating units, referred to as monomers. Polymers can be natural (starch is a polymer of sugar residues and proteins are polymers of amino acids) or synthetic [like polyethylene, polyvinyl chloride (PVC), and polystyrene]. The variety of structures of polymers translates into a broad range of properties and uses that make them integral parts of our everyday lives. Adding functional groups to the structure of a polymer can result in significantly different properties (see the discussion about Kevlar later in this chapter).

An example of a polymerization reaction is shown in **Figure 3.49**. The monomer ethylene ( $C_2H_4$ ) is a gas at room temperature, but when polymerized, using a transition metal catalyst, it is transformed into a solid material made up of long chains of  $-CH_2$ - units called polyethylene. Polyethylene is a commodity plastic used primarily for packaging (bags and films).



Figure 3.49 The reaction for the polymerization of ethylene to polyethylene is shown.

Polyethylene is a member of one subset of synthetic polymers classified as plastics. Plastics are synthetic organic solids that can be molded; they are typically organic polymers with high molecular masses. Most of the monomers that go into common plastics (ethylene, propylene, vinyl chloride, styrene, and ethylene terephthalate) are derived from petrochemicals and are not very biodegradable, making them candidate materials for recycling. Recycling plastics helps minimize the need for using more of the petrochemical supplies and also minimizes the environmental damage caused by throwing away these nonbiodegradable materials.

Plastic recycling is the process of recovering waste, scrap, or used plastics, and reprocessing the material into useful products. For example, polyethylene terephthalate (soft drink bottles) can be melted down and used for plastic furniture, in carpets, or for other applications. Other plastics, like polyethylene (bags) and polypropylene (cups, plastic food containers), can be recycled or reprocessed to be used again. Many areas of the country have recycling programs that focus on one or more of the commodity plastics that have been assigned a recycling code (see Figure 3.50). These operations have been in effect since the 1970s and have made the production of some plastics among the most efficient industrial operations today.

PETE polyethylene terephthalate (PETE)	Soda bottles and oven-ready food trays
HDPE high-density polyethylene (HDPE)	Bottles for milk and dishwashing liquids
polyvinyl chloride (PVC)	Food trays, plastic wrap, bottles for mineral water and shampoo
LDPE low density polyethylene (LDPE)	Shopping bags and garbage bags
PP polypropylene (PP)	Margarine tubs, microwaveable food trays
PS polystyrene (PS)	Yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, packaging for electronics and toys
OTHER any other plastics (OTHER)	Plastics that do not fall into any of the above categories One example is melamine resin (plastic plates, plastic cups)

Figure 3.50 Each type of recyclable plastic is imprinted with a code for easy identification.

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



### **Isomers of Alkenes**

Molecules of 1-butene and 2-butene are structural isomers; the arrangement of the atoms in these two molecules differs. As an example of arrangement differences, the first carbon atom in 1-butene is bonded to two hydrogen atoms; the first carbon atom in 2-butene is bonded to three hydrogen atoms.

The compound 2-butene and some other alkenes also form a second type of isomer called a geometric isomer. In a set of geometric isomers, the same types of atoms are attached to each other in the same order, but the geometries of the two molecules differ. Geometric isomers of alkenes differ in the orientation of the groups on either side of a C = C bond.

Carbon atoms are free to rotate around a single bond but not around a double bond; a double bond is rigid. This makes it possible to have two isomers of 2-butene, one with both methyl groups on the same side of the double bond and one with the methyl groups on opposite sides. When structures of butene are drawn with 120° bond angles around the  $sp^2$ -hybridized carbon atoms participating in the double bond, the isomers are apparent. The

2-butene isomer in which the two methyl groups are on the same side is called a *cis*-isomer; the one in which the two methyl groups are on opposite sides is called a *trans*-isomer (Figure 3.51). The different geometries produce different physical properties, such as boiling point, that may make separation of the isomers possible:



Figure 3.51 These molecular models show the structural and geometric isomers of butene.

Alkenes are much more reactive than alkanes because the C = C moiety is a reactive functional group. A  $\pi$  bond, being a weaker bond, is disrupted much more easily than a  $\sigma$  bond. Thus, alkenes undergo a characteristic reaction in which the  $\pi$  bond is broken and replaced by two  $\sigma$  bonds. This reaction is called an **addition reaction**. The hybridization of the carbon atoms in the double bond in an alkene changes from  $sp^2$  to  $sp^3$  during an addition reaction. For example, halogens add to the double bond in an alkene instead of replacing hydrogen, as occurs in an alkane:



### Example 3.20

# **Alkene Reactivity and Naming**

Provide the IUPAC names for the reactant and product of the halogenation reaction shown here:



### Solution

The reactant is a five-carbon chain that contains a carbon-carbon double bond, so the base name will be

pentene. We begin counting at the end of the chain closest to the double bond—in this case, from the left—the double bond spans carbons 2 and 3, so the name becomes 2-pentene. Since there are two carbon-containing groups attached to the two carbon atoms in the double bond—and they are on the same side of the double bond—this molecule is the *cis*-isomer, making the name of the starting alkene *cis*-2-pentene. The product of the halogenation reaction will have two chlorine atoms attached to the carbon atoms that were a part of the carbon-carbon double bond:



This molecule is now a substituted alkane and will be named as such. The base of the name will be pentane. We will count from the end that numbers the carbon atoms where the chlorine atoms are attached as 2 and 3, making the name of the product 2,3-dichloropentane.

### **Check Your Learning**

Provide names for the reactant and product of the reaction shown:



Answer:

reactant: cis-3-hexene product: 3,4-dichlorohexane

# Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one  $\sigma$  bond and two  $\pi$  bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne,  $C_2H_2$ , commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:



# ethyne (acetylene)

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example,  $CH_3CH_2C \equiv CH$  is called 1-butyne.

# Example 3.21

### **Structure of Alkynes**

Describe the geometry and hybridization of the carbon atoms in the following molecule:



### Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with  $sp^3$  hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as sp hybrids.

### **Check Your Learning**

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:



carbon 1: *sp*, 180°; carbon 2: *sp*, 180°; carbon 3: *sp*<sup>2</sup>, 120°; carbon 4: *sp*<sup>2</sup>, 120°; carbon 5: *sp*<sup>3</sup>, 109.5°

Chemically, the alkynes are similar to the alkenes. Since the  $C \equiv C$  functional group has two  $\pi$  bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions. The reaction of acetylene with bromine is a typical example:



Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

# **Aromatic Hydrocarbons**

Benzene,  $C_6H_6$ , is the simplest member of a large family of hydrocarbons, called **aromatic hydrocarbons**. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene,  $C_6H_6$ , are:



Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of  $sp^2$ -hybridized carbon atoms with the unhybridized p orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the  $sp^2$  hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of  $\sigma$  bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized p orbitals to yield the  $\pi$  bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a C = C double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure 3.52.



Figure 3.52 This condensed formula shows the unique bonding structure of benzene.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:



Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

### Example 3.22

# Structure of Aromatic Hydrocarbons

One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



# Solution

Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:



### **Check Your Learning**

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer:



# **Key Concepts and Summary**

Strong, stable bonds between carbon atoms produce complex molecules containing chains, branches, and rings. The chemistry of these compounds is called organic chemistry. Hydrocarbons are organic compounds composed of only carbon and hydrogen. The alkanes are saturated hydrocarbons—that is, hydrocarbons that contain only single bonds. Alkenes contain one or more carbon-carbon double bonds. Alkynes contain one or more carbon-carbon triple bonds. Aromatic hydrocarbons contain ring structures with delocalized  $\pi$  electron systems.

# **Chemistry End of Chapter Exercises**

### Exercise 3.86

Write the chemical formula and Lewis structure of the following, each of which contains five carbon atoms:

(a) an alkane

(b) an alkene

(c) an alkyne

### Solution

There are several sets of answers; one is: (a)  $C_5H_{12}$ 



#### , (b) C<sub>5</sub>H<sub>10</sub>



(c) C<sub>5</sub>H<sub>8</sub>



# Exercise 3.87

What is the difference between the hybridization of carbon atoms' valence orbitals in saturated and unsaturated hydrocarbons?

### Exercise 3.88

On a microscopic level, how does the reaction of bromine with a saturated hydrocarbon differ from its reaction with an unsaturated hydrocarbon? How are they similar?

### Solution

Both reactions result in bromine being incorporated into the structure of the product. The difference is the way in which that incorporation takes place. In the saturated hydrocarbon, an existing C–H bond is broken, and a bond between the C and the Br can then be formed. In the unsaturated hydrocarbon, the only bond broken in the hydrocarbon is the  $\pi$  bond whose electrons can be used to form a bond to one of the bromine atoms in Br<sub>2</sub> (the electrons from the Br–Br bond form the other C–Br bond on the other carbon that was part of the  $\pi$  bond in the starting unsaturated hydrocarbon).

### Exercise 3.89

On a microscopic level, how does the reaction of bromine with an alkene differ from its reaction with an alkyne? How are they similar?

### Exercise 3.90

Explain why unbranched alkenes can form geometric isomers while unbranched alkanes cannot. Does this explanation involve the macroscopic domain or the microscopic domain?

### Solution

Unbranched alkanes have free rotation about the C–C bonds, yielding all orientations of the substituents about these bonds equivalent, interchangeable by rotation. In the unbranched alkenes, the inability to rotate about the C = C bond results in fixed (unchanging) substituent orientations, thus permitting different isomers. Since these concepts pertain to phenomena at the molecular level, this explanation involves the microscopic domain.

Exercise 3.91

Explain why these two molecules are not isomers:





# Exercise 3.92

Explain why these two molecules are not isomers:



### Solution

They are the same compound because each is a saturated hydrocarbon containing an unbranched chain of six carbon atoms.

### Exercise 3.93

How does the carbon-atom hybridization change when polyethylene is prepared from ethylene?

#### Exercise 3.94

Write the Lewis structure and molecular formula for each of the following hydrocarbons:

- (a) hexane
- (b) 3-methylpentane
- (c) cis-3-hexene
- (d) 4-methyl-1-pentene
- (e) 3-hexyne
- (f) 4-methyl-2-pentyne

### Solution

(a) C<sub>6</sub>H<sub>14</sub>



, (b) C<sub>6</sub>H<sub>14</sub>



, (c) C<sub>6</sub>H<sub>12</sub>



, (d) C<sub>6</sub>H<sub>12</sub>



, (e) C<sub>6</sub>H<sub>10</sub>



, (f) C<sub>6</sub>H<sub>10</sub>



# Exercise 3.95

Write the chemical formula, condensed formula, and Lewis structure for each of the following hydrocarbons:

- (a) heptane
- (b) 3-methylhexane
- (c) trans-3-heptene

(d) 4-methyl-1-hexene

(e) 2-heptyne

(f) 3,4-dimethyl-1-pentyne

Exercise 3.96

Give the complete IUPAC name for each of the following compounds:

(a) CH<sub>3</sub>CH<sub>2</sub>CBr<sub>2</sub>CH<sub>3</sub>

(b) (CH<sub>3</sub>)<sub>3</sub>CCl

(C)



(d)  $CH_3CH_2C \equiv CHCH_3CH_2C \equiv CH$ 

(e)

(f)



(g)  $(CH_3)_2 CHCH_2 CH = CH_2$ 

# Solution

(a) 2,2-dibromobutane; (b) 2-chloro-2-methylpropane; (c) 2-methylbutane; (d) 1-butyne; (e) 4-fluoro-4-methyl-1-octyne; (f) *trans*-1-chloropropene; (g) 5-methyl-1-pentene

Exercise 3.97

Give the complete IUPAC name for each of the following compounds:

(a) (CH<sub>3</sub>)<sub>2</sub>CHF

(b) CH<sub>3</sub>CHCICHCICH<sub>3</sub>

(C)



(d)  $CH_3CH_2CH = CHCH_3$ 

(e)

$$CH_3CH_2CH_2CHBrCH_2CH_3$$
  
|  
 $CH_2CH=CH_2$ 

(f)  $(CH_3)_3 CCH_2 C \equiv CH$ 

Exercise 3.98

Butane is used as a fuel in disposable lighters. Write the Lewis structure for each isomer of butane. **Solution** 



*n*-butane



2-methylpropane

Exercise 3.99

Write Lewis structures and name the five structural isomers of hexane.

Exercise 3.100

Write Lewis structures for the *cis*-*trans* isomers of  $CH_3CH = CHCI$ .

Solution



Exercise 3.101

Write structures for the three isomers of the aromatic hydrocarbon xylene, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>.

Exercise 3.102

Isooctane is the common name of the isomer of  $C_8H_{18}$  used as the standard of 100 for the gasoline octane rating:



(a) What is the IUPAC name for the compound?

(b) Name the other isomers that contain a five-carbon chain with three methyl substituents.

### Solution

(a) 2,2,4-trimethylpentane; (b) 2,2,3-trimethylpentane, 2,3,4-trimethylpentane, and 2,3,3-trimethylpentane:



Exercise 3.103

Write Lewis structures and IUPAC names for the alkyne isomers of C<sub>4</sub>H<sub>6</sub>.

Exercise 3.104

Write Lewis structures and IUPAC names for all isomers of C<sub>4</sub>H<sub>9</sub>Cl.

# Solution



# Exercise 3.105

Name and write the structures of all isomers of the propyl and butyl alkyl groups.

#### Exercise 3.106

Write the structures for all the isomers of the -C<sub>5</sub>H<sub>11</sub> alkyl group.

### Solution

In the following, the carbon backbone and the appropriate number of hydrogen atoms are shown in condensed form:

$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3}$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{3}$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{3}-CH_{2}-CH_{3}-CH_{2}-CH_{3}-CH_{2}-CH_{3}-CH_{2}-CH_{3}-CH_{3}-CH_{2}-CH_{3}-CH_{3}-CH_{2}-CH_{3}-CH_{3}-CH_{2}-CH_{3}-CH_{3}-CH_{2}-CH_{3}-CH_{3}-CH_{2}-CH_{3}-CH_{3}-CH_{2}-CH_{3}-CH_$$

### Exercise 3.107

Write Lewis structures and describe the molecular geometry at each carbon atom in the following compounds:

- (a) cis-3-hexene
- (b) cis-1-chloro-2-bromoethene
- (c) 2-pentyne
- (d) trans-6-ethyl-7-methyl-2-octene

Exercise 3.108

Benzene is one of the compounds used as an octane enhancer in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene:

 $3C_2H_2 \longrightarrow C_6H_6$ 

Draw Lewis structures for these compounds, with resonance structures as appropriate, and determine the hybridization of the carbon atoms in each.

# Solution



In acetylene, the bonding uses *sp* hybrids on carbon atoms and *s* orbitals on hydrogen atoms. In benzene, the carbon atoms are  $sp^2$  hybridized.

#### Exercise 3.109

Teflon is prepared by the polymerization of tetrafluoroethylene. Write the equation that describes the polymerization using Lewis symbols.

#### Exercise 3.110

Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 1 mol of 1-butyne reacts with 2 mol of iodine.

(b) Pentane is burned in air.

#### Solution

(a)  $CH \equiv CCH_2CH_3 + 2I_2 \longrightarrow CHI_2CI_2CH_2CH_3$ 



(b)  $CH_3CH_2CH_2CH_2CH_3 + 8O_2 \longrightarrow 5CO_2 + 6H_2O$ 



Exercise 3.111

Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 2-butene reacts with chlorine.

(b) benzene burns in air.

Exercise 3.112

What mass of 2-bromopropane could be prepared from 25.5 g of propene? Assume a 100% yield of product.

#### Solution 65.2 g

Exercise 3.113

Acetylene is a very weak acid; however, it will react with moist silver(I) oxide and form water and a compound composed of silver and carbon. Addition of a solution of HCl to a 0.2352-g sample of the compound of silver and carbon produced acetylene and 0.2822 g of AgCl.

(a) What is the empirical formula of the compound of silver and carbon?

(b) The production of acetylene on addition of HCl to the compound of silver and carbon suggests that the carbon is present as the acetylide ion,  $C_2^{2-}$ . Write the formula of the compound showing the acetylide ion.

Exercise 3.114

Ethylene can be produced by the pyrolysis of ethane:  $C_2H_6 \longrightarrow C_2H_4 + H_2$ 

How many kilograms of ethylene is produced by the pyrolysis of 1.000  $\times$  10<sup>3</sup> kg of ethane, assuming a 100.0% yield?

Solution

 $9.328 \times 10^{2} \text{ kg}$ 

# 3.10 | Alcohols and Ethers

By the end of this section, you will be able to:

- · Describe the structure and properties of alcohols
- Describe the structure and properties of ethers
- · Name and draw structures for alcohols and ethers

In this section, we will learn about alcohols and ethers.

# Alcohols

Incorporation of an oxygen atom into carbon- and hydrogen-containing molecules leads to new functional groups and new families of compounds. When the oxygen atom is attached by single bonds, the molecule is either an alcohol or ether.

**Alcohols** are derivatives of hydrocarbons in which an –OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (–OH) functional groups, they do not behave like bases such as NaOH and KOH. NaOH and KOH are ionic compounds that contain OH<sup>-</sup> ions. Alcohols are covalent molecules; the –OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

Ethanol, CH<sub>3</sub>CH<sub>2</sub>OH, also called ethyl alcohol, is a particularly important alcohol for human use. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:



Large quantities of ethanol are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:



Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):



# 1,2-ethanediol



1,2,3-propanetriol

### Naming Alcohols

The name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.<sup>[8]</sup>

### Example 3.23

### Naming Alcohols

Consider the following example. How should it be named?



## Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

## **Check Your Learning**

Name the following molecule:



Answer: 2-methyl-2-pentanol

# Ethers

**Ethers** are compounds that contain the functional group –O–. Ethers do not have a designated suffix like the other types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named "methoxy." The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by "ether." The common name for the compound shown in **Example 3.24** is ethylmethyl ether:

<sup>8.</sup> The IUPAC adopted new nomenclature guidelines in 2013 that require this number to be placed as an "infix" rather than a prefix. For example, the new name for 2-propanol would be propan-2-ol. Widespread adoption of this new nomenclature will take some time, and students are encouraged to be familiar with both the old and new naming protocols.



# Example 3.24

# Naming Ethers

Provide the IUPAC and common name for the ether shown here:



# Solution

IUPAC: The molecule is made up of an ethoxy group attached to an ethane chain, so the IUPAC name would be ethoxyethane.

Common: The groups attached to the oxygen atom are both ethyl groups, so the common name would be diethyl ether.

# **Check Your Learning**

Provide the IUPAC and common name for the ether shown:



Answer:

IUPAC: 2-methoxypropane; common: isopropylmethyl ether

Ethers can be obtained from alcohols by the elimination of a molecule of water from two molecules of the alcohol. For example, when ethanol is treated with a limited amount of sulfuric acid and heated to 140 °C, diethyl ether and water are formed:



In the general formula for ethers, R-O-R, the hydrocarbon groups (R) may be the same or different. Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, C<sub>4</sub>H<sub>9</sub>OCH<sub>3</sub> (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.



Want more practice naming ethers? This brief video review (http://openstax.org/l/16ethers) summarizes the nomenclature for ethers.

### Carbohydrates and Diabetes

Carbohydrates are large biomolecules made up of carbon, hydrogen, and oxygen. The dietary forms of carbohydrates are foods rich in these types of molecules, like pastas, bread, and candy. The name "carbohydrate" comes from the formula of the molecules, which can be described by the general formula  $C_m(H_2O)_n$ , which shows that they are in a sense "carbon and water" or "hydrates of carbon." In many cases, *m* and *n* have the same value, but they can be different. The smaller carbohydrates are generally referred to as "sugars," the biochemical term for this group of molecules is "saccharide" from the Greek word for sugar (Figure 3.53). Depending on the number of sugar units joined together, they may be classified as monosaccharides (one sugar unit), disaccharides (two sugar units), oligosaccharides (a few sugars), or polysaccharides (the polymeric version of sugars—polymers were described in the feature box earlier in this chapter on recycling plastics). The scientific names of sugars can be recognized by the suffix -ose at the end of the name (for instance, fruit sugar is a monosaccharide called "fructose" and milk sugar is a disaccharide called lactose composed of two monosaccharides, glucose and galactose, connected together). Sugars contain some of the functional groups we have discussed: Note the alcohol groups present in the structures and how monosaccharide units are linked to form a disaccharide by formation of an ether.



**Figure 3.53** The illustrations show the molecular structures of fructose, a five-carbon monosaccharide, and of lactose, a disaccharide composed of two isomeric, six-carbon sugars.

Organisms use carbohydrates for a variety of functions. Carbohydrates can store energy, such as the polysaccharides glycogen in animals or starch in plants. They also provide structural support, such as the polysaccharide cellulose in plants and the modified polysaccharide chitin in fungi and animals. The sugars
ribose and deoxyribose are components of the backbones of RNA and DNA, respectively. Other sugars play key roles in the function of the immune system, in cell-cell recognition, and in many other biological roles.

Diabetes is a group of metabolic diseases in which a person has a high sugar concentration in their blood (Figure 3.54). Diabetes may be caused by insufficient insulin production by the pancreas or by the body's cells not responding properly to the insulin that is produced. In a healthy person, insulin is produced when it is needed and functions to transport glucose from the blood into the cells where it can be used for energy. The long-term complications of diabetes can include loss of eyesight, heart disease, and kidney failure.

In 2013, it was estimated that approximately 3.3% of the world's population (~380 million people) suffered from diabetes, resulting in over a million deaths annually. Prevention involves eating a healthy diet, getting plenty of exercise, and maintaining a normal body weight. Treatment involves all of these lifestyle practices and may require injections of insulin.



**Figure 3.54** Diabetes is a disease characterized by high concentrations of glucose in the blood. Treating diabetes involves making lifestyle changes, monitoring blood-sugar levels, and sometimes insulin injections. (credit: "Blausen Medical Communications"/Wikimedia Commons)

# **Key Concepts and Summary**

Many organic compounds that are not hydrocarbons can be thought of as derivatives of hydrocarbons. A hydrocarbon derivative can be formed by replacing one or more hydrogen atoms of a hydrocarbon by a functional group, which contains at least one atom of an element other than carbon or hydrogen. The properties of hydrocarbon derivatives are determined largely by the functional group. The –OH group is the functional group of an alcohol. The –R–O–R– group is the functional group of an ether.

# **Chemistry End of Chapter Exercises**

Exercise 3.115

Why do the compounds hexane, hexanol, and hexene have such similar names?

Exercise 3.116

Write condensed formulas and provide IUPAC names for the following compounds:

- (a) ethyl alcohol (in beverages)
- (b) methyl alcohol (used as a solvent, for example, in shellac)
- (c) ethylene glycol (antifreeze)
- (d) isopropyl alcohol (used in rubbing alcohol)
- (e) glycerine

# Solution

(a) ethyl alcohol, ethanol: CH<sub>3</sub>CH<sub>2</sub>OH; (b) methyl alcohol, methanol: CH<sub>3</sub>OH; (c) ethylene glycol, ethanediol: HOCH<sub>2</sub>CH<sub>2</sub>OH; (d) isopropyl alcohol, 2-propanol: CH<sub>3</sub>CH(OH)CH<sub>3</sub>; (e) glycerine, I,2,3-trihydroxypropane: HOCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH

Exercise 3.117

Give the complete IUPAC name for each of the following compounds:

(a)



(b)



(C)



#### Exercise 3.118

Give the complete IUPAC name and the common name for each of the following compounds:

(a)





#### Solution

(a) 1-ethoxybutane, butyl ethyl ether; (b) 1-ethoxypropane, ethyl propyl ether; (c) 1-methoxypropane, methyl propyl ether

## Exercise 3.119

Write the condensed structures of both isomers with the formula  $C_2H_6O$ . Label the functional group of each isomer.

## Exercise 3.120

Write the condensed structures of all isomers with the formula  $C_2H_6O_2$ . Label the functional group (or groups) of each isomer.

# Solution

HOCH<sub>2</sub>CH<sub>2</sub>OH, two alcohol groups; CH<sub>3</sub>OCH<sub>2</sub>OH, ether and alcohol groups

## Exercise 3.121

Draw the condensed formulas for each of the following compounds:

(a) dipropyl ether

(b) 2,2-dimethyl-3-hexanol

## (c) 2-ethoxybutane

# Exercise 3.122

MTBE, Methyl *tert*-butyl ether, CH<sub>3</sub>OC(CH<sub>3</sub>)<sub>3</sub>, is used as an oxygen source in oxygenated gasolines. MTBE is manufactured by reacting 2-methylpropene with methanol.

(a) Using Lewis structures, write the chemical equation representing the reaction.

(b) What volume of methanol, density 0.7915 g/mL, is required to produce exactly 1000 kg of MTBE, assuming a 100% yield?

## Solution

(a)



;

(b)  $4.593 \times 10^2$  L

## Exercise 3.123

Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

- (a) propanol is converted to dipropyl ether
- (b) propene is treated with water in dilute acid.

## Exercise 3.124

Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 2-butene is treated with water in dilute acid

(b) ethanol is dehydrated to yield ethene

## Solution

(a)  $CH_3CH = CHCH_3 + H_2O \longrightarrow CH_3CH_2CH(OH)CH_3$ 



(b) 
$$CH_3CH_2OH \longrightarrow CH_2 = CH_2 + H_2O$$



# 3.11 Aldehydes, Ketones, Carboxylic Acids, and **Esters**

By the end of this section, you will be able to:

Describe the structure and properties of aldehydes, ketones, carboxylic acids and esters

Another class of organic molecules contains a carbon atom connected to an oxygen atom by a double bond, commonly called a carbonyl group. The trigonal planar carbon in the carbonyl group can attach to two other substituents leading to several subfamilies (aldehydes, ketones, carboxylic acids and esters) described in this section.

# Aldehydes and Ketones

Both aldehydes and ketones contain a carbonyl group, a functional group with a carbon-oxygen double bond. The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for alkanes and alcohols, and include the class-identifying suffixes -al and -one, respectively:



In an aldehyde, the carbonyl group is bonded to at least one hydrogen atom. In a ketone, the carbonyl group is bonded to two carbon atoms:

Functional group Functional group of an aldehyde



of a ketone



As text, an aldehyde group is represented as -CHO; a ketone is represented as -C(O)- or -CO-.

In both aldehydes and ketones, the geometry around the carbon atom in the carbonyl group is trigonal planar; the carbon atom exhibits  $sp^2$  hybridization. Two of the  $sp^2$  orbitals on the carbon atom in the carbonyl group are used to form  $\sigma$  bonds to the other carbon or hydrogen atoms in a molecule. The remaining  $sp^2$  hybrid orbital forms a  $\sigma$  bond to the oxygen atom. The unhybridized *p* orbital on the carbon atom in the carbonyl group overlaps a *p* orbital on the oxygen atom to form the  $\pi$  bond in the double bond.

Like the C = O bond in carbon dioxide, the C = O bond of a carbonyl group is polar (recall that oxygen is significantly more electronegative than carbon, and the shared electrons are pulled toward the oxygen atom and away from the carbon atom). Many of the reactions of aldehydes and ketones start with the reaction between a Lewis base and the carbon atom at the positive end of the polar C = O bond to yield an unstable intermediate that subsequently undergoes one or more structural rearrangements to form the final product (Figure 3.55).



Figure 3.55 The carbonyl group is polar, and the geometry of the bonds around the central carbon is trigonal planar.

The importance of molecular structure in the reactivity of organic compounds is illustrated by the reactions that produce aldehydes and ketones. We can prepare a carbonyl group by oxidation of an alcohol—for organic molecules, oxidation of a carbon atom is said to occur when a carbon-hydrogen bond is replaced by a carbon-oxygen bond. The reverse reaction—replacing a carbon-oxygen bond by a carbon-hydrogen bond—is a reduction of that carbon atom. Recall that oxygen is generally assigned a -2 oxidation number unless it is elemental or attached to a fluorine. Hydrogen is generally assigned an oxidation number of +1 unless it is attached to a metal. Since carbon does not have a specific rule, its oxidation number is determined algebraically by factoring the atoms it is attached to and the overall charge of the molecule or ion. In general, a carbon atom attached to a noxygen atom will have a more positive oxidation number and a carbon atom attached to a hydrogen atom will have a more positive oxidation number and a carbon atom attached to a hydrogen atom will have a more positive oxidation number and a carbon atom attached to a hydrogen to oxidation number. This should fit nicely with your understanding of the polarity of C–O and C–H bonds. The other reagents and possible products of these reactions are beyond the scope of this chapter, so we will focus only on the changes to the carbon atoms:



# Example 3.25

#### **Oxidation and Reduction in Organic Chemistry**

Methane represents the completely reduced form of an organic molecule that contains one carbon atom. Sequentially replacing each of the carbon-hydrogen bonds with a carbon-oxygen bond would lead to an alcohol, then an aldehyde, then a carboxylic acid (discussed later), and, finally, carbon dioxide:

 $CH_4 \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow HCO_2H \longrightarrow CO_2$ 

What are the oxidation numbers for the carbon atoms in the molecules shown here?

#### Solution

In this example, we can calculate the oxidation number (review the chapter on oxidation-reduction reactions if necessary) for the carbon atom in each case (note how this would become difficult for larger molecules with additional carbon atoms and hydrogen atoms, which is why organic chemists use the definition dealing with replacing C–H bonds with C–O bonds described). For CH<sub>4</sub>, the carbon atom carries a –4 oxidation number (the hydrogen atoms are assigned oxidation numbers of +1 and the carbon atom balances that by having an oxidation number of –4). For the alcohol (in this case, methanol), the carbon atom has an oxidation number of –2 (the oxygen atom is assigned –2, the four hydrogen atoms each are assigned +1, and the carbon atom balances the sum by having an oxidation number of –2; note that compared to the carbon atom in CH<sub>4</sub>, this carbon atom has lost two electrons so it was oxidized); for the aldehyde, the carbon atom's oxidation number is 0 (–2 for the oxygen atom and +1 for each hydrogen atom already balances to 0, so the oxidation number for the carbon atom is 0); for the carboxylic acid, the carbon atom's oxidation number is +2 (two oxygen atoms each at –2 and two hydrogen atoms at +1); and for carbon dioxide, the carbon atom's oxidation number is +4 (here, the carbon atom needs to balance the –4 sum from the two oxygen atoms).

#### **Check Your Learning**

Indicate whether the marked carbon atoms in the three molecules here are oxidized or reduced relative to the marked carbon atom in ethanol:



There is no need to calculate oxidation states in this case; instead, just compare the types of atoms bonded to the marked carbon atoms:



## Answer:

(a) reduced (bond to oxygen atom replaced by bond to hydrogen atom); (b) oxidized (one bond to hydrogen atom replaced by one bond to oxygen atom); (c) oxidized (2 bonds to hydrogen atoms have been replaced by bonds to an oxygen atom)

Aldehydes are commonly prepared by the oxidation of alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



Alcohols that have their –OH groups in the middle of the chain are necessary to synthesize a ketone, which requires the carbonyl group to be bonded to two other carbon atoms:



An alcohol with its –OH group bonded to a carbon atom that is bonded to no or one other carbon atom will form an aldehyde. An alcohol with its –OH group attached to two other carbon atoms will form a ketone. If three carbons are attached to the carbon bonded to the –OH, the molecule will not have a C–H bond to be replaced, so it will not be susceptible to oxidation.

Formaldehyde, an aldehyde with the formula HCHO, is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Dimethyl ketone, CH<sub>3</sub>COCH<sub>3</sub>, commonly called acetone, is the simplest ketone. It is made commercially by fermenting corn or molasses, or by oxidation of 2-propanol. Acetone is a colorless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

# **Carboxylic Acids and Esters**

The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odor of ripe

bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived (see Figure 3.56).



Figure 3.56 Esters are responsible for the odors associated with various plants and their fruits.

Both **carboxylic acids** and **esters** contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):



The functional groups for an acid and for an ester are shown in red in these formulas.

The hydrogen atom in the functional group of a carboxylic acid will react with a base to form an ionic salt:



Carboxylic acids are weak acids (see the chapter on acids and bases), meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, CH<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, is formed when acetic acid reacts with ethanol:



The simplest carboxylic acid is formic acid, HCO<sub>2</sub>H, known since 1670. Its name comes from the Latin word *formicus*, which means "ant"; it was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings, and is responsible for a characteristic odor of ants that can be sometimes detected in their nests.

Acetic acid, CH<sub>3</sub>CO<sub>2</sub>H, constitutes 3–6% vinegar. Cider vinegar is produced by allowing apple juice to ferment without oxygen present. Yeast cells present in the juice carry out the fermentation reactions. The fermentation reactions change the sugar present in the juice to ethanol, then to acetic acid. Pure acetic acid has a penetrating odor and produces painful burns. It is an excellent solvent for many organic and some inorganic compounds, and it is essential in the production of cellulose acetate, a component of many synthetic fibers such as rayon.

The distinctive and attractive odors and flavors of many flowers, perfumes, and ripe fruits are due to the presence of one or more esters (Figure 3.57). Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine,  $C_3H_5(OH)_3$ , with large carboxylic acids, such as palmitic acid,  $CH_3(CH_2)_{14}CO_2H$ , stearic acid,  $CH_3(CH_2)_{16}CO_2H$ , and oleic acid,  $CH_3(CH_2)_7CH = CH(CH_2)_7CO_2H$ . Oleic acid is an unsaturated acid; it contains a C = C double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.



Figure 3.57 Over 350 different volatile molecules (many members of the ester family) have been identified in strawberries. (credit: Rebecca Siegel)

# **Key Concepts and Summary**

Functional groups related to the carbonyl group include the –CHO group of an aldehyde, the –CO– group of a ketone, the –CO<sub>2</sub>H group of a carboxylic acid, and the –CO<sub>2</sub>R group of an ester. The carbonyl group, a carbonoxygen double bond, is the key structure in these classes of organic molecules: Aldehydes contain at least one hydrogen atom attached to the carbonyl carbon atom, ketones contain two carbon groups attached to the carbonyl carbon atom, carboxylic acids contain a hydroxyl group attached to the carbonyl carbon atom, and esters contain an oxygen atom attached to another carbon group connected to the carbonyl carbon atom. All of these compounds contain oxidized carbon atoms relative to the carbon atom of an alcohol group.

# **Chemistry End of Chapter Exercises**

## Exercise 3.125

Order the following molecules from least to most oxidized, based on the marked carbon atom:



## Exercise 3.126

Predict the products of oxidizing the molecules shown in this problem. In each case, identify the product that will result from the minimal increase in oxidation state for the highlighted carbon atom:



(b)



(C)



# Solution

(a)



; (b)



; (C)



Exercise 3.127

Predict the products of reducing the following molecules. In each case, identify the product that will result from the minimal decrease in oxidation state for the highlighted carbon atom:

(a)

(b)



(C)

# Exercise 3.128

Explain why it is not possible to prepare a ketone that contains only two carbon atoms.

# Solution

A ketone contains a group bonded to two additional carbon atoms; thus, a minimum of three carbon atoms are needed.

# Exercise 3.129

How does hybridization of the substituted carbon atom change when an alcohol is converted into an aldehyde? An aldehyde to a carboxylic acid?

Exercise 3.130

Fatty acids are carboxylic acids that have long hydrocarbon chains attached to a carboxylate group. How does a saturated fatty acid differ from an unsaturated fatty acid? How are they similar?

## Solution

Since they are both carboxylic acids, they each contain the –COOH functional group and its characteristics. The difference is the hydrocarbon chain in a saturated fatty acid contains no double or triple bonds, whereas the hydrocarbon chain in an unsaturated fatty acid contains one or more multiple bonds.

## Exercise 3.131

Write a condensed structural formula, such as CH<sub>3</sub>CH<sub>3</sub>, and describe the molecular geometry at each carbon atom.

- (a) propene
- (b) 1-butanol
- (c) ethyl propyl ether
- (d) cis-4-bromo-2-heptene
- (e) 2,2,3-trimethylhexane
- (f) formaldehyde

## Exercise 3.132

Write a condensed structural formula, such as CH<sub>3</sub>CH<sub>3</sub>, and describe the molecular geometry at each carbon atom.

- (a) 2-propanol
- (b) acetone
- (c) dimethyl ether
- (d) acetic acid
- (e) 3-methyl-1-hexene

# Solution

(a)  $CH_3CH(OH)CH_3$ : all carbons are tetrahedral; (b)  $CH_3COCH_3$ : the end carbons are tetrahedral and the central carbon is trigonal planar; (c)  $CH_3OCH_3$ : all are tetrahedral; (d)  $CH_3COOH$ : the methyl carbon is tetrahedral and the acid carbon is trigonal planar; (e)  $CH_3CH_2CH_2CH(CH_3)CHCH_2$ : all are tetrahedral except the right-most two carbons, which are trigonal planar

## Exercise 3.133

The foul odor of rancid butter is caused by butyric acid, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H.

(a) Draw the Lewis structure and determine the oxidation number and hybridization for each carbon atom in the molecule.

(b) The esters formed from butyric acid are pleasant-smelling compounds found in fruits and used in perfumes. Draw the Lewis structure for the ester formed from the reaction of butyric acid with 2-propanol.

Exercise 3.134

Write the two-resonance structures for the acetate ion.

## Solution



Exercise 3.135

Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures:

(a) ethanol reacts with propionic acid

(b) benzoic acid, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H, is added to a solution of sodium hydroxide

#### Exercise 3.136

Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 1-butanol reacts with acetic acid

(b) propionic acid is poured onto solid calcium carbonate

#### Solution

(a)  $CH_3CH_2CH_2CH_2OH + CH_3C(O)OH \longrightarrow CH_3C(O)OCH_2CH_2CH_2CH_3 + H_2O$ :



(b)  $2CH_3CH_2COOH + CaCO_3 \longrightarrow (CH_3CH_2COO)_2Ca + CO_2 + H_2O$ :



Exercise 3.137

Yields in organic reactions are sometimes low. What is the percent yield of a process that produces 13.0 g of ethyl acetate from 10.0 g of CH<sub>3</sub>CO<sub>2</sub>H?

#### Exercise 3.138

Alcohols A, B, and C all have the composition  $C_{4}H_{10}O$ . Molecules of alcohol A contain a branched carbon chain and can be oxidized to an aldehyde; molecules of alcohol B contain a linear carbon chain and can be oxidized to a ketone; and molecules of alcohol C can be oxidized to neither an aldehyde nor a ketone. Write the Lewis structures of these molecules.

#### Solution



# 3.12 | Amines and Amides

By the end of this section, you will be able to:

- · Describe the structure and properties of an amine
- · Describe the structure and properties of an amide

**Amines** are molecules that contain carbon-nitrogen bonds. The nitrogen atom in an amine has a lone pair of electrons and three bonds to other atoms, either carbon or hydrogen. Various nomenclatures are used to derive names for amines, but all involve the class-identifying suffix *—ine* as illustrated here for a few simple examples:



methyl amine

dimethyl amine

trimethyl amine

In some amines, the nitrogen atom replaces a carbon atom in an aromatic hydrocarbon. Pyridine (Figure 3.58) is one such heterocyclic amine. A heterocyclic compound contains atoms of two or more different elements in its ring structure.



Figure 3.58 The illustration shows one of the resonance structures of pyridine.

DNA in Forensics and Paternity

The genetic material for all living things is a polymer of four different molecules, which are themselves a combination of three subunits. The genetic information, the code for developing an organism, is contained in the specific sequence of the four molecules, similar to the way the letters of the alphabet can be sequenced to form words that convey information. The information in a DNA sequence is used to form two other types of polymers, one of which are proteins. The proteins interact to form a specific type of organism with individual characteristics.

A genetic molecule is called DNA, which stands for deoxyribonucleic acid. The four molecules that make up DNA are called nucleotides. Each nucleotide consists of a single- or double-ringed molecule containing nitrogen, carbon, oxygen, and hydrogen called a nitrogenous base. Each base is bonded to a five-carbon sugar called deoxyribose. The sugar is in turn bonded to a phosphate group  $(-PO_4^{3-})$  When new DNA

is made, a polymerization reaction occurs that binds the phosphate group of one nucleotide to the sugar group of a second nucleotide. The nitrogenous bases of each nucleotide stick out from this sugar-phosphate backbone. DNA is actually formed from two such polymers coiled around each other and held together by hydrogen bonds between the nitrogenous bases. Thus, the two backbones are on the outside of the coiled pair of strands, and the bases are on the inside. The shape of the two strands wound around each other is called a double helix (see Figure 3.59).

It probably makes sense that the sequence of nucleotides in the DNA of a cat differs from those of a dog. But it is also true that the sequences of the DNA in the cells of two individual pugs differ. Likewise, the sequences of DNA in you and a sibling differ (unless your sibling is an identical twin), as do those between you and an unrelated individual. However, the DNA sequences of two related individuals are more similar than the sequences of two unrelated individuals, and these similarities in sequence can be observed in various ways. This is the principle behind DNA fingerprinting, which is a method used to determine whether two DNA samples came from related (or the same) individuals or unrelated individuals.



**Figure 3.59** DNA is an organic molecule and the genetic material for all living organisms. (a) DNA is a double helix consisting of two single DNA strands hydrogen bonded together at each nitrogenous base. (b) This detail shows the hydrogen bonding (dotted lines) between nitrogenous bases on each DNA strand and the way in which each nucleotide is joined to the next, forming a backbone of sugars and phosphate groups along each strand. (c) This detail shows the structure of one of the four nucleotides that makes up the DNA polymer. Each nucleotide consists of a nitrogenous base (a double-ring molecule, in this case), a five-carbon sugar (deoxyribose), and a phosphate group.

Using similarities in sequences, technicians can determine whether a man is the father of a child (the identity of the mother is rarely in doubt, except in the case of an adopted child and a potential birth mother). Likewise, forensic geneticists can determine whether a crime scene sample of human tissue, such as blood or skin cells, contains DNA that matches exactly the DNA of a suspect.



Watch this video animation (http://openstax.org/l/16dnapackaging) of how DNA is packaged for a visual lesson in its structure.

Like ammonia, amines are weak bases due to the lone pair of electrons on their nitrogen atoms:



The basicity of an amine's nitrogen atom plays an important role in much of the compound's chemistry. Amine functional groups are found in a wide variety of compounds, including natural and synthetic dyes, polymers, vitamins, and medications such as penicillin and codeine. They are also found in many molecules essential to life, such as amino acids, hormones, neurotransmitters, and DNA.

# Addictive Alkaloids

Since ancient times, plants have been used for medicinal purposes. One class of substances, called *alkaloids*, found in many of these plants has been isolated and found to contain cyclic molecules with an amine functional group. These amines are bases. They can react with  $H_3O^+$  in a dilute acid to form an ammonium salt, and this property is used to extract them from the plant:

$$R_3 N + H_3 O^+ + Cl^- \longrightarrow [R_3 NH^+]Cl^- + H_2 O$$

The name alkaloid means "like an alkali." Thus, an alkaloid reacts with acid. The free compound can be recovered after extraction by reaction with a base:

$$\left[ R_{3}NH^{+}\right]CI^{-} + OH^{-} \longrightarrow R_{3}N + H_{2}O + CI^{-}$$

The structures of many naturally occurring alkaloids have profound physiological and psychotropic effects in humans. Examples of these drugs include nicotine, morphine, codeine, and heroin. The plant produces these substances, collectively called secondary plant compounds, as chemical defenses against the numerous pests that attempt to feed on the plant:



In these diagrams, as is common in representing structures of large organic compounds, carbon atoms in the rings and the hydrogen atoms bonded to them have been omitted for clarity. The solid wedges indicate bonds that extend out of the page. The dashed wedges indicate bonds that extend into the page. Notice that small changes to a part of the molecule change the properties of morphine, codeine, and heroin. Morphine, a strong narcotic used to relieve pain, contains two hydroxyl functional groups, located at the bottom of the molecule in this structural formula. Changing one of these hydroxyl groups to a methyl ether group forms codeine, a less potent drug used as a local anesthetic. If both hydroxyl groups are converted to esters of acetic acid, the powerfully addictive drug heroin results (Figure 3.60).



Figure 3.60 Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

**Amides** are molecules that contain nitrogen atoms connected to the carbon atom of a carbonyl group. Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:



Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation. A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine (note the similarity to formation of an ester from a carboxylic acid and an alcohol discussed in the previous section):



The reaction between amines and carboxylic acids to form amides is biologically important. It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

#### Proteins and Enzymes

Proteins are large biological molecules made up of long chains of smaller molecules called amino acids. Organisms rely on proteins for a variety of functions—proteins transport molecules across cell membranes, replicate DNA, and catalyze metabolic reactions, to name only a few of their functions. The properties of proteins are functions of the combination of amino acids that compose them and can vary greatly. Interactions between amino acid sequences in the chains of proteins result in the folding of the chain into specific, three-dimensional structures that determine the protein's activity.

Amino acids are organic molecules that contain an amine functional group (–NH<sub>2</sub>), a carboxylic acid functional group (–COOH), and a side chain (that is specific to each individual amino acid). Most living things build proteins from the same 20 different amino acids. Amino acids connect by the formation of a peptide bond, which is a covalent bond formed between two amino acids when the carboxylic acid group of one amino acid reacts with the amine group of the other amino acid. The formation of the bond results in the production of a molecule of water (in general, reactions that result in the production of water when two other molecules combine are referred to as condensation reactions). The resulting bond—between the carbonyl group carbon atom and the amine nitrogen atom is called a peptide link or peptide bond. Since each of the original amino acids has an unreacted group (one has an unreacted amine and the other an unreacted carboxylic acid), more peptide bonds can form to other amino acids, extending the structure. (Figure 3.61) A chain of connected amino acids is called a polypeptide. Proteins contain at least one long polypeptide chain.



Polypeptide chain

Figure 3.61 This condensation reaction forms a dipeptide from two amino acids and leads to the formation of water.

Enzymes are large biological molecules, mostly composed of proteins, which are responsible for the thousands of metabolic processes that occur in living organisms. Enzymes are highly specific catalysts; they speed up the rates of certain reactions. Enzymes function by lowering the activation energy of the reaction they are catalyzing, which can dramatically increase the rate of the reaction. Most reactions catalyzed by enzymes have rates that are millions of times faster than the noncatalyzed version. Like all catalysts, enzymes are not consumed during the reactions that they catalyze. Enzymes do differ from other catalysts in how specific they are for their substrates (the molecules that an enzyme will convert into a different product). Each enzyme is only capable of speeding up one or a few very specific reactions or types of reactions. Since the function of enzymes is so specific, the lack or malfunctioning of an enzyme can lead to serious health consequences. One disease that is the result of an enzyme malfunction is phenylketonuria. In this disease, the enzyme that catalyzes the first step in the degradation of the amino acid phenylalanine is not functional (Figure 3.62). Untreated, this can lead to an accumulation of phenylalanine, which can lead to intellectual disabilities.



**Figure 3.62** A computer rendering shows the three-dimensional structure of the enzyme phenylalanine hydroxylase. In the disease phenylketonuria, a defect in the shape of phenylalanine hydroxylase causes it to lose its function in breaking down phenylalanine.

#### Kevlar

Kevlar (Figure 3.63) is a synthetic polymer made from two monomers 1,4-phenylene-diamine and terephthaloyl chloride (Kevlar is a registered trademark of DuPont). Kevlar's first commercial use was as a replacement for steel in racing tires. Kevlar is typically spun into ropes or fibers. The material has a high tensile strength-to-weight ratio (it is about 5 times stronger than an equal weight of steel), making it useful for many applications from bicycle tires to sails to body armor.



Figure 3.63 This illustration shows the formula for polymeric Kevlar.

The material owes much of its strength to hydrogen bonds between polymer chains (refer back to the chapter on intermolecular interactions). These bonds form between the carbonyl group oxygen atom (which has a partial negative charge due to oxygen's electronegativity) on one monomer and the partially positively charged hydrogen atom in the N–H bond of an adjacent monomer in the polymer structure (see dashed line in **Figure 3.64**). There is additional strength derived from the interaction between the unhybridized *p* orbitals in the six-membered rings, called aromatic stacking.



Figure 3.64 The diagram shows the polymer structure of Kevlar, with hydrogen bonds between polymer chains represented by dotted lines.

Kevlar may be best known as a component of body armor, combat helmets, and face masks. Since the 1980s, the US military has used Kevlar as a component of the PASGT (personal armor system for ground troops) helmet and vest. Kevlar is also used to protect armored fighting vehicles and aircraft carriers. Civilian applications include protective gear for emergency service personnel such as body armor for police officers and heat-resistant clothing for fire fighters. Kevlar based clothing is considerably lighter and thinner than equivalent gear made from other materials (Figure 3.65).



**Figure 3.65** (a) These soldiers are sorting through pieces of a Kevlar helmet that helped absorb a grenade blast. Kevlar is also used to make (b) canoes and (c) marine mooring lines. (credit a: modification of work by "Cla68"/Wikimedia Commons; credit b: modification of work by "OakleyOriginals"/Flickr; credit c: modification of work by Casey H. Kyhl)

In addition to its better-known uses, Kevlar is also often used in cryogenics for its very low thermal conductivity (along with its high strength). Kevlar maintains its high strength when cooled to the temperature of liquid nitrogen (-196 °C).

The table here summarizes the structures discussed in this chapter:

Compound Name	Structure of Compound and Functional Group (red)	Example		
		Formula	Name	
alkene	c=c	C <sub>2</sub> H <sub>4</sub>	ethene	
alkyne	c≡c	C₂H₂ ↔	ethyne	
alcohol	R-::-н	сн <sub>3</sub> сн <sub>2</sub> он	ethanol	
ether	R-0-R'	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	diethyl ether	
aldehyde	:о: Ш R—С—Н	сн <sub>3</sub> сно	ethanal	
ketone	:0:    R—C—R'	сн <sub>3</sub> сосн <sub>2</sub> сн <sub>3</sub>	methyl ethyl ketone	
carboxylic acid	:0: Пн R. — С. — Ю. — Н	сн <sub>з</sub> соон	acetic acid	
ester	:0:    R—C—O,—R'	сн <sub>3</sub> со <sub>2</sub> сн <sub>2</sub> сн <sub>3</sub>	ethyl acetate	
amine	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	ethylamine	
amide	:0:    R—C—N—R'   H	CH <sub>3</sub> CONH <sub>2</sub>	acetamide	

# **Key Concepts and Summary**

The addition of nitrogen into an organic framework leads to two families of molecules. Compounds containing a nitrogen atom bonded in a hydrocarbon framework are classified as amines. Compounds that have a nitrogen atom bonded to one side of a carbonyl group are classified as amides. Amines are a basic functional group. Amines and carboxylic acids can combine in a condensation reaction to form amides.

# **Chemistry End of Chapter Exercises**

# Exercise 3.139

Write the Lewis structures of both isomers with the formula  $C_2H_7N$ .

# Exercise 3.140

What is the molecular structure about the nitrogen atom in trimethyl amine and in the trimethyl ammonium ion,  $(CH_3)_3NH^+$ ? What is the hybridization of the nitrogen atom in trimethyl amine and in the trimethyl ammonium ion?

# Solution

Trimethyl amine: trigonal pyramidal,  $sp^3$ ; trimethyl ammonium ion: tetrahedral,  $sp^3$ 

## Exercise 3.141

Write the two resonance structures for the pyridinium ion, C<sub>5</sub>H<sub>5</sub>NH<sup>+</sup>.

## Exercise 3.142

Draw Lewis structures for pyridine and its conjugate acid, the pyridinium ion, C<sub>5</sub>H<sub>5</sub>NH<sup>+</sup>. What are the geometries and hybridizations about the nitrogen atoms in pyridine and in the pyridinium ion?

# Solution





# pyridine, trigonal planar, sp<sup>2</sup>

# pyridinium ion, trigonal planar, sp<sup>2</sup>

Exercise 3.143

Write the Lewis structures of all isomers with the formula C<sub>3</sub>H<sub>7</sub>ON that contain an amide linkage.

#### Exercise 3.144

Write two complete balanced equations for the following reaction, one using condensed formulas and one using Lewis structures.

Methyl amine is added to a solution of HCl.

# Solution

 $CH_3NH_2 + H_3O^+ \longrightarrow CH_3NH_3^+ + H_2O$ 

Exercise 3.145

Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

Ethylammonium chloride is added to a solution of sodium hydroxide.

Exercise 3.146

Identify any carbon atoms that change hybridization and the change in hybridization during the reactions in **Exercise 3.111**.

# Solution

 $\begin{array}{rcl} \mathsf{CH}_3\underline{\mathsf{C}}\mathsf{H} = \underline{\mathsf{C}}\mathsf{H}\mathsf{CH}_3(\mathsf{s}p^2) + \mathsf{CI} &\longrightarrow & \mathsf{CH}_3\underline{\mathsf{C}}\mathsf{H}(\mathsf{CI})\mathsf{H}(\mathsf{CI})\mathsf{CH}_3(\mathsf{s}p^3);\\ 2\underline{\mathsf{C}}_6\mathsf{H}_6(\mathsf{s}p^2) + 15\mathsf{O}_2 &\longrightarrow & 12\underline{\mathsf{C}}\mathsf{O}_2(\mathsf{s}p) + 6\mathsf{H}_2\mathsf{O} \end{array}$ 

# Exercise 3.147

Identify any carbon atoms that change hybridization and the change in hybridization during the reactions in **Exercise 3.124**.

# Exercise 3.148

Identify any carbon atoms that change hybridization and the change in hybridization during the reactions in **Exercise 3.136**.

# Solution

the carbon in  $CO_3^{2^-}$ , initially at  $sp^2$ , changes hybridization to sp in  $CO_2$ 

# 3.13 | Intermolecular Forces

By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- · Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move

independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. **Figure 3.66** illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.



Increasing IMF

**Figure 3.66** 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.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H<sub>2</sub>O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H<sub>2</sub>O. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure 3.67.



**Figure 3.67** Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong

relative to their KE. Consequently, they form liquids. Butane, C<sub>4</sub>H<sub>10</sub>, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 3.68.



Figure 3.68 Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.



Access this **interactive simulation (http://openstax.org/l/16phetvisual)** on states of matter, phase transitions, and intermolecular forces. This simulation is useful for visualizing concepts introduced throughout this chapter.

# **Forces between Molecules**

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 3.69 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.



Figure 3.69 Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

# **Dispersion Forces**

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 3.70.



Figure 3.70 Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules.  $F_2$  and  $Cl_2$  are gases at room temperature (reflecting weaker attractive forces);  $Br_2$  is a liquid, and  $I_2$  is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 3.5.

Halogen	Molar Mass	Atomic Radius	Melting Point	<b>Boiling Point</b>
fluorine, $F_2$	38 g/mol	72 pm	53 K	85 K
chlorine, Cl <sub>2</sub>	71 g/mol	99 pm	172 K	238 K
bromine, $Br_2$	160 g/mol	114 pm	266 K	332 K
iodine, I2	254 g/mol	133 pm	387 K	457 K
astatine, At <sub>2</sub>	420 g/mol	150 pm	575 K	610 K

# Melting and Boiling Points of the Halogens

Table 3.5

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 3.26

# London Forces and Their Effects

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH<sub>4</sub>, SiH<sub>4</sub>, GeH<sub>4</sub>, and SnH<sub>4</sub>. 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<sub>4</sub>, SiH<sub>4</sub>, GeH<sub>4</sub>, and SnH<sub>4</sub> are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH<sub>4</sub> is expected to have the lowest boiling point and SnH<sub>4</sub> the highest boiling point. The ordering from lowest to highest boiling point is expected to be CH<sub>4</sub> < SiH<sub>4</sub> < GeH<sub>4</sub> < SnH<sub>4</sub>.

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



# **Check Your Learning**

Order the following hydrocarbons from lowest to highest boiling point: C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>.

Answer:

 $C_2H_6 < C_3H_8 < C_4H_{10}$ . All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore  $C_2H_6 < C_3H_8 < C_4H_{10}$ .

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 3.71) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula,

C<sub>5</sub>H<sub>12</sub>, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.



Figure 3.71 The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

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.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 3.72, 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 "nonsticky." 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.



Setae

Spatulae

**Figure 3.72** 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)



Watch this video (http://openstax.org/l/16kellaraut) to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

# **Dipole-Dipole Attractions**

Recall from the chapter 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 end of one HCl molecule and the negative end of another. This attractive force is called a **dipole**. **dipole**. **dipole**. **dipole**. **dipole**. 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 3.73.



Figure 3.73 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.

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 KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to
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form a liquid, whereas the relatively weaker dispersion forces between nonpolar F<sub>2</sub> molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCI (188 K) compared to F<sub>2</sub> (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCI molecules, compared to the attractions between nonpolar F<sub>2</sub> molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

#### Example 3.27

#### **Dipole-Dipole Forces and Their Effects**

Predict which will have the higher boiling point: N2 or CO. Explain your reasoning.

#### Solution

CO and N<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> molecules, so CO is expected to have the higher boiling point.

#### **Check Your Learning**

Predict which will have the higher boiling point: ICl or Br<sub>2</sub>. Explain your reasoning.

Answer:

ICI. ICI and Br<sub>2</sub> have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICI is polar and thus also exhibits dipole-dipole attractions; Br<sub>2</sub> is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICI will have the higher boiling point.

## **Hydrogen Bonding**

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H<sub>2</sub>O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). 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. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include HF···HF, H<sub>2</sub>O···HOH, and H<sub>3</sub>N···HNH<sub>2</sub>, in which the hydrogen bonds are denoted by dots. Figure 3.74 illustrates hydrogen bonding between water molecules.



Figure 3.74 Water 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, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, and SbH<sub>3</sub>), group 16 hydrides (H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te), and group 17 hydrides (HF, HCI, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 3.75. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.



Figure 3.75 For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH<sub>3</sub> to boil at about -120 °C, H<sub>2</sub>O to boil at about -80 °C, and HF to boil at about -110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in **Figure 3.76**. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.



**Figure 3.76** In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

#### Example 3.28

#### Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH<sub>3</sub>OCH<sub>3</sub>), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), and propane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>). 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 VSEPR-predicted shapes of CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, and CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> is nonpolar, it may exhibit *only* dispersion forces. Because CH<sub>3</sub>OCH<sub>3</sub> is polar, it will also experience dipole-dipole attractions. Finally, CH<sub>3</sub>CH<sub>2</sub>OH has an –OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> < CH<sub>3</sub>OCH<sub>3</sub> < CH<sub>3</sub>OCH<sub>3</sub> < CH<sub>3</sub>CH<sub>2</sub>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.

#### **Check Your Learning**

Ethane (CH<sub>3</sub>CH<sub>3</sub>) has a melting point of -183 °C and a boiling point of -89 °C. Predict the melting and boiling points for methylamine (CH<sub>3</sub>NH<sub>2</sub>). Explain your reasoning.

#### Answer:

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane.  $CH_3CH_3$  and  $CH_3NH_2$  are similar in size and mass, but methylamine possesses an -NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of -93 °C and a boiling

point of -6 °C.

#### Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 3.77.



Figure 3.77 Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure **Figure 3.78**.



**Figure 3.78** The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

## Key Concepts and Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. 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. 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.

## **Chemistry End of Chapter Exercises**

#### Exercise 3.149

In terms of their bulk properties, how do liquids and solids differ? How are they similar?

#### Solution

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

#### Exercise 3.150

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids

#### different from solids?

#### Exercise 3.151

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

#### Solution

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

#### Exercise 3.152

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

#### Exercise 3.153

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

#### Solution

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

#### Exercise 3.154

Open the **PhET States of Matter Simulation (http://openstax.org/l/16phetvisual)** to answer the following questions:

(a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?

(b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.

(c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

#### Exercise 3.155

Define the following and give an example of each:

- (a) dispersion force
- (b) dipole-dipole attraction
- (c) hydrogen bond

#### Solution

(a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICI molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: HF····HF).

#### Exercise 3.156

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

#### Exercise 3.157

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

#### Solution

The London forces typically increase as the number of electrons increase.

#### Exercise 3.158

Neon and HF have approximately the same molecular masses.

(a) Explain why the boiling points of Neon and HF differ.

(b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

#### Exercise 3.159

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

(a) HCl, H<sub>2</sub>O, SiH<sub>4</sub>

(b) F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>

(c) CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>

(d) O<sub>2</sub>, NO, N<sub>2</sub>

#### Solution

(a) SiH<sub>4</sub> < HCl < H<sub>2</sub>O; (b) F<sub>2</sub> < Cl<sub>2</sub> < Br<sub>2</sub>; (c) CH<sub>4</sub> < C<sub>2</sub>H<sub>6</sub> < C<sub>3</sub>H<sub>8</sub>; (d) N<sub>2</sub> < O<sub>2</sub> < NO

#### Exercise 3.160

The molecular mass of butanol, C4H<sub>9</sub>OH, is 74.14; that of ethylene glycol, CH<sub>2</sub>(OH)CH<sub>2</sub>OH, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

#### Exercise 3.161

On the basis of intermolecular attractions, explain the differences in the boiling points of n-butane (-1 °C) and chloroethane (12 °C), which have similar molar masses.

#### Solution

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.

#### Exercise 3.162

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

#### Exercise 3.163

The melting point of H<sub>2</sub>O(s) is 0 °C. Would you expect the melting point of H<sub>2</sub>S(s) to be -85 °C, 0 °C, or 185 °C? Explain your answer.

#### Solution

-85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.

#### Exercise 3.164

Silane (SiH<sub>4</sub>), phosphine (PH<sub>3</sub>), and hydrogen sulfide (H<sub>2</sub>S) melt at -185 °C, -133 °C, and -85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

#### Exercise 3.165

Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

#### Solution

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

#### Exercise 3.166

Under certain conditions, molecules of acetic acid, CH<sub>3</sub>COOH, form "dimers," pairs of acetic acid molecules held together by strong intermolecular attractions:



Draw a dimer of acetic acid, showing how two CH<sub>3</sub>COOH molecules are held together, and stating the type of IMF that is responsible.

#### Exercise 3.167

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



#### Solution

H-bonding is the principle IMF holding the protein strands together. The H-bonding is between the N - H and C = O.

#### Exercise 3.168

The density of liquid NH<sub>3</sub> is 0.64 g/mL; the density of gaseous NH<sub>3</sub> at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

#### Exercise 3.169

Identify the intermolecular forces present in the following solids:

- (a) CH<sub>3</sub>CH<sub>2</sub>OH
- (b) CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>
- (c) CH<sub>3</sub>CH<sub>2</sub>Cl
- Solution

(a) hydrogen bonding, dipole-dipole attraction, and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

## **KEY TERMS**

acid molecule that donates hydrogen ions and increases the concentration of hydrogen ions in a solution

- acid ionization reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid
- **acidic** describes a solution in which  $[H_3O^+] > [OH^-]$
- **addition reaction** reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.
- adhesion attraction between water molecules and other molecules
- alcohol organic compound with a hydroxyl group (-OH) bonded to a carbon atom
- **aldehyde** organic compound containing a carbonyl group bonded to two hydrogen atoms or a hydrogen atom and a carbon substituent
- aliphatic hydrocarbon hydrocarbon consisting of a linear chain of carbon atoms

**alkane** molecule consisting of only carbon and hydrogen atoms connected by single ( $\sigma$ ) bonds

alkene molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

alkyl group substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

alkyne molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

amide organic molecule that features a nitrogen atom connected to the carbon atom in a carbonyl group

amine organic molecule in which a nitrogen atom is bonded to one or more alkyl group

amphiprotic species that may either gain or lose a proton in a reaction

**amphoteric** species that can act as either an acid or a base

aromatic hydrocarbon hydrocarbon consisting of closed rings of carbon atoms

- **aromatic hydrocarbon** cyclic molecule consisting of carbon and hydrogen with delocalized alternating carboncarbon single and double bonds, resulting in enhanced stability
- **autoionization** reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions
- **base** molecule that donates hydroxide ions or otherwise binds excess hydrogen ions and decreases the concentration of hydrogen ions in a solution
- **base ionization** reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

**basic** describes a solution in which  $[H_3O^+] < [OH^-]$ 

bond length distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

Brønsted-Lowry acid proton donor

Brønsted-Lowry base proton acceptor

buffer substance that prevents a change in pH by absorbing or releasing hydrogen or hydroxide ions

calorie amount of heat required to change the temperature of one gram of water by one degree Celsius

**capillary action** occurs because water molecules are attracted to charges on the inner surfaces of narrow tubular structures such as glass tubes, drawing the water molecules to the sides of the tubes

carbonyl group carbon atom double bonded to an oxygen atom

- carboxylic acid organic compound containing a carbonyl group with an attached hydroxyl group
- **cohesion** intermolecular forces between water molecules caused by the polar nature of water; responsible for surface tension
- conjugate acid substance formed when a base gains a proton
- conjugate base substance formed when an acid loses a proton
- **covalent bond** attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms
- covalent bond bond formed when electrons are shared between atoms
- covalent compound (also, molecular compound) composed of molecules formed by atoms of two or more different elements
- dipole-dipole attraction intermolecular attraction between two permanent dipoles
- **dispersion force** (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together
- **dissociation** release of an ion from a molecule such that the original molecule now consists of an ion and the charged remains of the original, such as when water dissociates into H<sup>+</sup> and OH<sup>-</sup>
- double bond covalent bond in which two pairs of electrons are shared between two atoms
- electronegativity tendency of an atom to attract electrons in a bond to itself
- empirical formula formula showing the composition of a compound given as the simplest whole-number ratio of atoms
- **enantiomers** molecules that share overall structure and bonding patterns, but differ in how the atoms are three dimensionally placed such that they are mirror images of each other
- ester organic compound containing a carbonyl group with an attached oxygen atom that is bonded to a carbon substituent
- ether organic compound with an oxygen atom that is bonded to two carbon atoms
- evaporation separation of individual molecules from the surface of a body of water, leaves of a plant, or the skin of an organism
- free radical molecule that contains an odd number of electrons
- functional group group of atoms that provides or imparts a specific function to a carbon skeleton
- functional group part of an organic molecule that imparts a specific chemical reactivity to the molecule
- geometric isomer isomer with similar bonding patterns differing in the placement of atoms alongside a double covalent bond
- heat of vaporization of water high amount of energy required for liquid water to turn into water vapor
- hydrocarbon molecule that consists only of carbon and hydrogen
- **hydrogen bonding** occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

hydrophilic describes ions or polar molecules that interact well with other polar molecules such as water

- **hydrophobic** describes uncharged non-polar molecules that do not interact well with polar molecules such as water
- hypervalent molecule molecule containing at least one main group element that has more than eight electrons in its valence shell
- induced dipole temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule
- **instantaneous dipole** temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force noncovalent attractive force between atoms, molecules, and/or ions

- ion-product constant for water ( $K_{W}$ ) equilibrium constant for the autoionization of water
- ionic bond electrostatic forces of attraction between the oppositely charged ions of an ionic compound
- **ionic compound** composed of cations and anions combined in ratios, yielding an electrically neutral substance
- isomers compounds with the same chemical formula but different structures
- isomers molecules that differ from one another even though they share the same chemical formula

ketone organic compound containing a carbonyl group with two carbon substituents attached to it

- Lewis structure diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion
- Lewis symbol symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion
- **litmus paper** (also, pH paper) filter paper that has been treated with a natural water-soluble dye that changes its color as the pH of the environment changes so it can be used as a pH indicator
- lone pair two (a pair of) valence electrons that are not used to form a covalent bond
- molecular compound (also, covalent compound) composed of molecules formed by atoms of two or more different elements
- **molecular formula** formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.
- monatomic ion ion composed of a single atom
- **neutral** describes a solution in which  $[H_3O^+] = [OH^-]$
- **octet rule** guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

organic compound natural or synthetic compound that contains carbon

organic molecule any molecule containing carbon (except carbon dioxide)

- oxyanion polyatomic anion composed of a central atom bonded to oxygen atoms
- **pH** logarithmic measure of the concentration of hydronium ions in a solution

pH paper see litmus paper

pH scale scale ranging from zero to 14 that is inversely proportional to the concentration of hydrogen ions in a

solution

**pOH** logarithmic measure of the concentration of hydroxide ions in a solution

- **polar covalent bond** covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end
- polarizability measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)
- polyatomic ion ion composed of more than one atom
- pure covalent bond (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities
- saturated hydrocarbon molecule containing carbon and hydrogen that has only single bonds between carbon atoms
- single bond bond in which a single pair of electrons is shared between two atoms
- **skeletal structure** shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)
- solvent substance capable of dissolving another substance
- spatial isomers compounds in which the relative orientations of the atoms in space differ
- specific heat capacity the amount of heat one gram of a substance must absorb or lose to change its temperature by one degree Celsius
- **sphere of hydration** when a polar water molecule surrounds charged or polar molecules thus keeping them dissolved and in solution
- structural formula shows the atoms in a molecule and how they are connected
- structural isomer one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently
- structural isomers molecules that share a chemical formula but differ in the placement of their chemical bonds
- substituent branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain
- substituted hydrocarbon hydrocarbon chain or ring containing an atom of another element in place of one of the backbone carbons
- substitution reaction reaction in which one atom replaces another in a molecule
- surface tension tension at the surface of a body of liquid that prevents the molecules from separating; created by the attractive cohesive forces between the molecules of the liquid
- triple bond bond in which three pairs of electrons are shared between two atoms
- van der Waals force attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

# 4 | BIOLOGICAL MACROMOLECULES: LARGE MOLECULES OF LIFE



Figure 4.1 Foods such as bread, fruit, and cheese are rich sources of biological macromolecules. (credit: modification of work by Bengt Nyman)

## **Chapter Outline**

- 4.1: Synthesis of Biological Macromolecules
- 4.2: Carbohydrates
- 4.3: Lipids
- 4.4: Proteins
- 4.5: Nucleic Acids

## Introduction

Food provides the body with the nutrients it needs to survive. Many of these critical nutrients are biological macromolecules, or large molecules, necessary for life. These macromolecules (polymers) are built from different combinations of smaller organic molecules (monomers). What specific types of biological macromolecules do living things require? How are these molecules formed? What functions do they serve? In

this chapter, these questions will be explored.

# 4.1 | Synthesis of Biological Macromolecules

By the end of this section, you will be able to:

- · Understand the synthesis of macromolecules
- · Explain dehydration (or condensation) and hydrolysis reactions

As you've learned, **biological macromolecules** are large molecules, necessary for life, that are built from smaller organic molecules. There are four major classes of biological macromolecules (carbohydrates, lipids, proteins, and nucleic acids); each is an important cell component and performs a wide array of functions. Combined, these molecules make up the majority of a cell's dry mass (recall that water makes up the majority of its complete mass). Biological macromolecules are organic, meaning they contain carbon. In addition, they may contain hydrogen, oxygen, nitrogen, and additional minor elements.

## **Dehydration Synthesis**

Most macromolecules are made from single subunits, or building blocks, called **monomers**. The monomers combine with each other using covalent bonds to form larger molecules known as **polymers**. In doing so, monomers release water molecules as byproducts. This type of reaction is known as **dehydration synthesis**, which means "to put together while losing water."



Figure 4.2 In the dehydration synthesis reaction depicted above, two molecules of glucose are linked together to form the disaccharide maltose. In the process, a water molecule is formed.

In a dehydration synthesis reaction (Figure 4.2), the hydrogen of one monomer combines with the hydroxyl group of another monomer, releasing a molecule of water. At the same time, the monomers share electrons and form covalent bonds. As additional monomers join, this chain of repeating monomers forms a polymer. Different types of monomers can combine in many configurations, giving rise to a diverse group of macromolecules. Even one kind of monomer can combine in a variety of ways to form several different polymers: for example, glucose monomers are the constituents of starch, glycogen, and cellulose.

## **Hydrolysis**

Polymers are broken down into monomers in a process known as hydrolysis, which means "to split water," a reaction in which a water molecule is used during the breakdown (Figure 4.3). During these reactions, the polymer is broken into two components: one part gains a hydrogen atom (H+) and the other gains a hydroxyl molecule (OH–) from a split water molecule.



Figure 4.3 In the hydrolysis reaction shown here, the disaccharide maltose is broken down to form two glucose monomers with the addition of a water molecule. Note that this reaction is the reverse of the synthesis reaction shown in Figure 4.2.

Dehydration and **hydrolysis reactions** are catalyzed, or "sped up," by specific enzymes; dehydration reactions involve the formation of new bonds, requiring energy, while hydrolysis reactions break bonds and release energy. These reactions are similar for most macromolecules, but each monomer and polymer reaction is specific for its class. For example, in our bodies, food is hydrolyzed, or broken down, into smaller molecules by catalytic enzymes in the digestive system. This allows for easy absorption of nutrients by cells in the intestine. Each macromolecule is broken down by a specific enzyme. For instance, carbohydrates are broken down by amylase, sucrase, lactase, or maltase. Proteins are broken down by the enzymes pepsin and peptidase, and by hydrochloric acid. Lipids are broken down by lipases. Breakdown of these macromolecules provides energy for cellular activities.





Visit this site (http://openstaxcollege.org/l/hydrolysis) to see visual representations of dehydration synthesis and hydrolysis.

# 4.2 | Carbohydrates

By the end of this section, you will be able to:

- · Discuss the role of carbohydrates in cells and in the extracellular materials of animals and plants
- · Explain the classifications of carbohydrates
- · List common monosaccharides, disaccharides, and polysaccharides

Most people are familiar with carbohydrates, one type of macromolecule, especially when it comes to what we eat. To lose weight, some individuals adhere to "low-carb" diets. Athletes, in contrast, often "carb-load" before important competitions to ensure that they have enough energy to compete at a high level. Carbohydrates are, in fact, an essential part of our diet; grains, fruits, and vegetables are all natural sources of carbohydrates. Carbohydrates provide energy to the body, particularly through glucose, a simple sugar that is a component of **starch** and an ingredient in many staple foods. Carbohydrates also have other important functions in humans, animals, and plants.

### **Molecular Structures**

**Carbohydrates** can be represented by the stoichiometric formula  $(CH_2O)_n$ , where n is the number of carbons in the molecule. In other words, the ratio of carbon to hydrogen to oxygen is 1:2:1 in carbohydrate molecules. This formula also explains the origin of the term "carbohydrate": the components are carbon ("carbo") and the components of water (hence, "hydrate"). Carbohydrates are classified into three subtypes: monosaccharides, disaccharides, and polysaccharides.

#### Monosaccharides

**Monosaccharides** (mono- = "one"; sacchar- = "sweet") are simple sugars, the most common of which is glucose. In monosaccharides, the number of carbons usually ranges from three to seven. Most monosaccharide names end with the suffix -ose. If the sugar has an aldehyde group (the functional group with the structure R-CHO), it is known as an aldose, and if it has a ketone group (the functional group with the structure RC(=O)R'), it is known as a ketose. Depending on the number of carbons in the sugar, they also may be known as trioses (three carbons), pentoses (five carbons), and or hexoses (six carbons). See Figure 4.4 for an illustration of the monosaccharides.



**Figure 4.4** Monosaccharides are classified based on the position of their carbonyl group and the number of carbons in the backbone. Aldoses have a carbonyl group (indicated in green) at the end of the carbon chain, and ketoses have a carbonyl group in the middle of the carbon chain. Trioses, pentoses, and hexoses have three, five, and six carbon backbones, respectively.

The chemical formula for glucose is  $C_6H_{12}O_6$ . In humans, glucose is an important source of energy. During cellular respiration, energy is released from glucose, and that energy is used to help make adenosine triphosphate (ATP). Plants synthesize glucose using carbon dioxide and water, and glucose in turn is used for energy requirements for the plant. Excess glucose is often stored as starch that is catabolized (the breakdown of larger molecules by cells) by humans and other animals that feed on plants.

Galactose (part of lactose, or milk sugar) and fructose (found in sucrose, in fruit) are other common monosaccharides. Although glucose, galactose, and fructose all have the same chemical formula (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), they differ structurally and chemically (and are known as isomers) because of the different arrangement of functional groups around the asymmetric carbon; all of these monosaccharides have more than one asymmetric

#### carbon (Figure 4.5).



Figure 4.5 Glucose, galactose, and fructose are all hexoses. They are structural isomers, meaning they have the same chemical formula ( $C_6H_{12}O_6$ ) but a different arrangement of atoms.

What kind of sugars are these, aldose or ketose?

Glucose, galactose, and fructose are isomeric monosaccharides (hexoses), meaning they have the same chemical formula but have slightly different structures. Glucose and galactose are aldoses, and fructose is a ketose.

Monosaccharides can exist as a linear chain or as ring-shaped molecules; in aqueous solutions they are usually found in ring forms (Figure 4.6). Glucose in a ring form can have two different arrangements of the hydroxyl group (OH) around the anomeric carbon (carbon 1 that becomes asymmetric in the process of ring formation). If the hydroxyl group is below carbon number 1 in the sugar, it is said to be in the alpha ( $\alpha$ ) position, and if it is above the plane, it is said to be in the beta ( $\beta$ ) position.



**Figure 4.6** Five and six carbon monosaccharides exist in equilibrium between linear and ring forms. When the ring forms, the side chain it closes on is locked into an  $\alpha$  or  $\beta$  position. Fructose and ribose also form rings, although they form five-membered rings as opposed to the six-membered ring of glucose.

#### Disaccharides

**Disaccharides** (di- = "two") form when two monosaccharides undergo a dehydration reaction (also known as a condensation reaction or dehydration synthesis). During this process, the hydroxyl group of one monosaccharide combines with the hydrogen of another monosaccharide, releasing a molecule of water and forming a covalent bond. A covalent bond formed between a carbohydrate molecule and another molecule (in this case, between two monosaccharides) is known as a **glycosidic bond (Figure 4.7)**. Glycosidic bonds (also called glycosidic linkages) can be of the alpha or the beta type.



**Figure 4.7** Sucrose is formed when a monomer of glucose and a monomer of fructose are joined in a dehydration reaction to form a glycosidic bond. In the process, a water molecule is lost. By convention, the carbon atoms in a monosaccharide are numbered from the terminal carbon closest to the carbonyl group. In sucrose, a glycosidic linkage is formed between carbon 1 in glucose and carbon 2 in fructose.

Common disaccharides include lactose, maltose, and sucrose (Figure 4.8). Lactose is a disaccharide consisting of the monomers glucose and galactose. It is found naturally in milk. Maltose, or malt sugar, is a disaccharide formed by a dehydration reaction between two glucose molecules. The most common disaccharide is sucrose, or table sugar, which is composed of the monomers glucose and fructose.



Figure 4.8 Common disaccharides include maltose (grain sugar), lactose (milk sugar), and sucrose (table sugar).

#### Polysaccharides

A long chain of monosaccharides linked by glycosidic bonds is known as a **polysaccharide** (poly- = "many"). The chain may be branched or unbranched, and it may contain different types of monosaccharides. The molecular weight may be 100,000 daltons or more depending on the number of monomers joined. Starch, glycogen, cellulose, and chitin are primary examples of polysaccharides.

Starch is the stored form of sugars in plants and is made up of a mixture of amylose and amylopectin (both polymers of glucose). Plants are able to synthesize glucose, and the excess glucose, beyond the plant's immediate energy needs, is stored as starch in different plant parts, including roots and seeds. The starch in the seeds provides food for the embryo as it germinates and can also act as a source of food for humans and animals. The starch that is consumed by humans is broken down by enzymes, such as salivary amylases, into smaller molecules, such as maltose and glucose. The cells can then absorb the glucose.

Starch is made up of glucose monomers that are joined by  $\alpha$  1-4 or  $\alpha$  1-6 glycosidic bonds. The numbers 1-4 and 1-6 refer to the carbon number of the two residues that have joined to form the bond. As illustrated in **Figure 4.9**, amylose is starch formed by unbranched chains of glucose monomers (only  $\alpha$  1-4 linkages), whereas amylopectin is a branched polysaccharide ( $\alpha$  1-6 linkages at the branch points).



**Figure 4.9** Amylose and amylopectin are two different forms of starch. Amylose is composed of unbranched chains of glucose monomers connected by  $\alpha$  1,4 glycosidic linkages. Amylopectin is composed of branched chains of glucose monomers connected by  $\alpha$  1,4 and  $\alpha$  1,6 glycosidic linkages. Because of the way the subunits are joined, the glucose chains have a helical structure. Glycogen (not shown) is similar in structure to amylopectin but more highly branched.

**Glycogen** is the storage form of glucose in humans and other vertebrates and is made up of monomers of glucose. Glycogen is the animal equivalent of starch and is a highly branched molecule usually stored in liver and muscle cells. Whenever blood glucose levels decrease, glycogen is broken down to release glucose in a process known as glycogenolysis.

**Cellulose** is the most abundant natural biopolymer. The cell wall of plants is mostly made of cellulose; this provides structural support to the cell. Wood and paper are mostly cellulosic in nature. Cellulose is made up of glucose monomers that are linked by  $\beta$  1-4 glycosidic bonds (Figure 4.10).



**Figure 4.10** In cellulose, glucose monomers are linked in unbranched chains by  $\beta$  1-4 glycosidic linkages. Because of the way the glucose subunits are joined, every glucose monomer is flipped relative to the next one resulting in a linear, fibrous structure.

As shown in **Figure 4.10**, every other glucose monomer in cellulose is flipped over, and the monomers are packed tightly as extended long chains. This gives cellulose its rigidity and high tensile strength—which is so important to plant cells. While the  $\beta$  1-4 linkage cannot be broken down by human digestive enzymes, herbivores such as cows, koalas, and buffalos are able, with the help of the specialized flora in their stomach, to digest plant material that is rich in cellulose and use it as a food source. In these animals, certain species of bacteria and protists reside in the rumen (part of the digestive system of herbivores) and secrete the enzyme cellulase. The appendix of grazing animals also contains bacteria that digest cellulose, giving it an important role in the digestive systems of ruminants. Cellulases can break down cellulose into glucose monomers that can be used as an energy source by the animal. Termites are also able to break down cellulose because of the presence of other organisms in their bodies that secrete cellulases.

Carbohydrates serve various functions in different animals. Arthropods (insects, crustaceans, and others) have an outer skeleton, called the exoskeleton, which protects their internal body parts (as seen in the bee in **Figure 4.11**). This exoskeleton is made of the biological macromolecule chitin, which is a polysaccharide-containing nitrogen. It is made of repeating units of N-acetyl- $\beta$ -d-glucosamine, a modified sugar. Chitin is also a major component of fungal cell walls; fungi are neither animals nor plants and form a kingdom of their own in the domain Eukarya.



Figure 4.11 Insects have a hard outer exoskeleton made of chitin, a type of polysaccharide. (credit: Louise Docker)



## **Registered Dietitian**

Obesity is a worldwide health concern, and many diseases such as diabetes and heart disease are becoming more prevalent because of obesity. This is one of the reasons why registered dietitians are increasingly sought after for advice. Registered dietitians help plan nutrition programs for individuals in various settings. They often work with patients in health care facilities, designing nutrition plans to treat and prevent diseases. For example, dietitians may teach a patient with diabetes how to manage blood sugar levels by eating the correct types and amounts of carbohydrates. Dietitians may also work in nursing homes, schools, and private practices.

To become a registered dietitian, one needs to earn at least a bachelor's degree in dietetics, nutrition, food technology, or a related field. In addition, registered dietitians must complete a supervised internship program and pass a national exam. Those who pursue careers in dietetics take courses in nutrition, chemistry, biochemistry, biology, microbiology, and human physiology. Dietitians must become experts in the chemistry and physiology (biological functions) of food (proteins, carbohydrates, and fats).

## **Benefits of Carbohydrates**

Are carbohydrates good for you? People who wish to lose weight are often told that carbohydrates are bad for them and should be avoided. Some diets completely forbid carbohydrate consumption, claiming that a low-carbohydrate diet helps people to lose weight faster. However, carbohydrates have been an important part of the human diet for thousands of years; artifacts from ancient civilizations show the presence of wheat, rice, and corn in our ancestors' storage areas.

Carbohydrates should be supplemented with proteins, vitamins, and fats to be parts of a well-balanced diet. Calorie-wise, a gram of carbohydrate provides 4.3 Kcal. For comparison, fats provide 9 Kcal/g, a less desirable ratio. Carbohydrates contain soluble and insoluble elements; the insoluble part is known as fiber, which is mostly cellulose. Fiber has many uses; it promotes regular bowel movement by adding bulk, and it regulates the rate of consumption of blood glucose. Fiber also helps to remove excess cholesterol from the body: fiber binds to the cholesterol in the small intestine, then attaches to the cholesterol and prevents the cholesterol particles from entering the bloodstream, and then cholesterol exits the body via the feces. Fiber-rich diets also have a protective role in reducing the occurrence of colon cancer. In addition, a meal containing whole grains and vegetables gives a feeling of fullness. As an immediate source of energy, glucose is broken down during the process of cellular respiration, which produces ATP, the energy currency of the cell. Without the consumption of carbohydrates, the availability of "instant energy" would be reduced. Eliminating carbohydrates from the diet is not the best way to lose weight. A low-calorie diet that is rich in whole grains, fruits, vegetables, and lean meat, together with plenty of exercise and plent





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For an additional perspective on carbohydrates, explore "Biomolecules: the Carbohydrates" through this interactive animation (http://openstaxcollege.org/l/carbohydrates).

## 4.3 | Lipids

By the end of this section, you will be able to:

- · Describe the four major types of lipids
- Explain the role of fats in storing energy
- · Differentiate between saturated and unsaturated fatty acids
- · Describe phospholipids and their role in cells
- · Define the basic structure of a steroid and some functions of steroids
- Explain the how cholesterol helps to maintain the fluid nature of the plasma membrane

**Lipids** include a diverse group of compounds that are largely nonpolar in nature. This is because they are hydrocarbons that include mostly nonpolar carbon–carbon or carbon–hydrogen bonds. Non-polar molecules are hydrophobic ("water fearing"), or insoluble in water. Lipids perform many different functions in a cell. Cells store energy for long-term use in the form of fats. Lipids also provide insulation from the environment for plants and animals (**Figure 4.12**). For example, they help keep aquatic birds and mammals dry when forming a protective layer over fur or feathers because of their water-repellant hydrophobic nature. Lipids are also the building blocks of many hormones and are an important constituent of all cellular membranes. Lipids include fats, oils, waxes, phospholipids, and steroids.



Figure 4.12 Hydrophobic lipids in the fur of aquatic mammals, such as this river otter, protect them from the elements. (credit: Ken Bosma)

## Fats and Oils

A fat molecule consists of two main components—glycerol and fatty acids. Glycerol is an organic compound (alcohol) with three carbons, five hydrogens, and three hydroxyl (OH) groups. Fatty acids have a long chain of hydrocarbons to which a carboxyl group is attached, hence the name "fatty acid." The number of carbons in the fatty acid may range from 4 to 36; most common are those containing 12–18 carbons. In a fat molecule, the fatty acids are attached to each of the three carbons of the glycerol molecule with an ester bond through an oxygen atom (Figure 4.13).





Fatty Acid



Figure 4.13 Triacylglycerol is formed by the joining of three fatty acids to a glycerol backbone in a dehydration reaction. Three molecules of water are released in the process.

During this ester bond formation, three water molecules are released. The three fatty acids in the triacylglycerol may be similar or dissimilar. Fats are also called **triacylglycerols** or **triglycerides** because of their chemical structure. Some fatty acids have common names that specify their origin. For example, palmitic acid, a **saturated fatty acid**, is derived from the palm tree. Arachidic acid is derived from *Arachis hypogea*, the scientific name for groundnuts or peanuts.

Fatty acids may be saturated or unsaturated. In a fatty acid chain, if there are only single bonds between neighboring carbons in the hydrocarbon chain, the fatty acid is said to be saturated. Saturated fatty acids are saturated with hydrogen; in other words, the number of hydrogen atoms attached to the carbon skeleton is maximized. Stearic acid is an example of a saturated fatty acid (Figure 4.14)



Figure 4.14 Stearic acid is a common saturated fatty acid.

When the hydrocarbon chain contains a double bond, the fatty acid is said to be **unsaturated**. Oleic acid is an example of an unsaturated fatty acid (Figure 4.15).



Figure 4.15 Oleic acid is a common unsaturated fatty acid.

Most unsaturated fats are liquid at room temperature and are called oils. If there is one double bond in the molecule, then it is known as a monounsaturated fat (e.g., olive oil), and if there is more than one double bond, then it is known as a polyunsaturated fat (e.g., canola oil).

When a fatty acid has no double bonds, it is known as a saturated fatty acid because no more hydrogen may be added to the carbon atoms of the chain. A fat may contain similar or different fatty acids attached to glycerol. Long straight fatty acids with single bonds tend to get packed tightly and are solid at room temperature. Animal fats with stearic acid and palmitic acid (common in meat) and the fat with butyric acid (common in butter) are examples of saturated fats. Mammals store fats in specialized cells called adipocytes, where globules of fat occupy most of the cell's volume. In plants, fat or oil is stored in many seeds and is used as a source of energy during seedling development. Unsaturated fats or oils are usually of plant origin and contain *cis* unsaturated fatty acids. *Cis* and *trans* indicate the configuration of the molecule around the double bond. If hydrogens are present in the same plane, it is referred to as a cis fat; if the hydrogen atoms are on two different planes, it is referred to as a **trans fat**. The *cis* double bond causes a bend or a "kink" that prevents the fatty acids from packing tightly, keeping them liquid at room temperature (Figure 4.16). Olive oil, corn oil, canola oil, and cod liver oil are examples of unsaturated fats. Unsaturated fats help to lower blood cholesterol levels whereas saturated fats contribute to plaque formation in the arteries.

#### Saturated fatty acid

Stearic acid



#### Unsaturated fatty acids

Cis oleic acid



**Figure 4.16** Saturated fatty acids have hydrocarbon chains connected by single bonds only. Unsaturated fatty acids have one or more double bonds. Each double bond may be in a *cis* or *trans* configuration. In the *cis* configuration, both hydrogens are on the same side of the hydrocarbon chain. In the *trans* configuration, the hydrogens are on opposite sides. A *cis* double bond causes a kink in the chain.

#### **Trans Fats**

In the food industry, oils are artificially hydrogenated to make them semi-solid and of a consistency desirable for many processed food products. Simply speaking, hydrogen gas is bubbled through oils to solidify them. During this hydrogenation process, double bonds of the *cis*- conformation in the hydrocarbon chain may be converted to double bonds in the trans- conformation.

Margarine, some types of peanut butter, and shortening are examples of artificially hydrogenated trans fats. Recent studies have shown that an increase in trans fats in the human diet may lead to an increase in levels of low-density lipoproteins (LDL), or "bad" cholesterol, which in turn may lead to plaque deposition in the arteries, resulting in heart disease. Many fast food restaurants have recently banned the use of trans fats, and food labels are required to display the trans fat content.

#### **Omega Fatty Acids**

Essential fatty acids are fatty acids required but not synthesized by the human body. Consequently, they have to be supplemented through ingestion via the diet. **Omega**-3 fatty acids (like that shown in **Figure 4.17**) fall into this category and are one of only two known for humans (the other being omega-6 fatty acid). These are polyunsaturated fatty acids and are called omega-3 because the third carbon from the end of the hydrocarbon chain is connected to its neighboring carbon by a double bond.



Figure 4.17 Alpha-linolenic acid is an example of an omega-3 fatty acid. It has three *cis* double bonds and, as a result, a curved shape. For clarity, the carbons are not shown. Each singly bonded carbon has two hydrogens associated with it, also not shown.

The farthest carbon away from the carboxyl group is numbered as the omega ( $\omega$ ) carbon, and if the double bond is between the third and fourth carbon from that end, it is known as an omega-3 fatty acid. Nutritionally important because the body does not make them, omega-3 fatty acids include alpha-linoleic acid (ALA), eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA), all of which are polyunsaturated. Salmon, trout, and tuna are good sources of omega-3 fatty acids. Research indicates that omega-3 fatty acids reduce the risk of sudden death from heart attacks, reduce triglycerides in the blood, lower blood pressure, and prevent thrombosis by inhibiting blood clotting. They also reduce inflammation, and may help reduce the risk of some cancers in animals.

Like carbohydrates, fats have received a lot of bad publicity. It is true that eating an excess of fried foods and other "fatty" foods leads to weight gain. However, fats do have important functions. Many vitamins are fat soluble, and fats serve as a long-term storage form of fatty acids: a source of energy. They also provide insulation for the body. Therefore, "healthy" fats in moderate amounts should be consumed on a regular basis.

### Waxes

**Wax** covers the feathers of some aquatic birds and the leaf surfaces of some plants. Because of the hydrophobic nature of waxes, they prevent water from sticking on the surface (Figure 4.18). Waxes are made up of long fatty acid chains esterified to long-chain alcohols.



Figure 4.18 Waxy coverings on some leaves are made of lipids. (credit: Roger Griffith)

## **Phospholipids**

**Phospholipids** are major constituents of the plasma membrane, the outermost layer of animal cells. Like fats, they are composed of fatty acid chains attached to a glycerol or sphingosine backbone. Instead of three fatty acids attached as in triglycerides, however, there are two fatty acids forming diacylglycerol, and the third carbon

of the glycerol backbone is occupied by a modified phosphate group (Figure 4.19). A phosphate group alone attached to a diaglycerol does not qualify as a phospholipid; it is phosphatidate (diacylglycerol 3-phosphate), the precursor of phospholipids. The phosphate group is modified by an alcohol. Phosphatidylcholine and phosphatidylserine are two important phospholipids that are found in plasma membranes.



**Figure 4.19** A phospholipid is a molecule with two fatty acids and a modified phosphate group attached to a glycerol backbone. The phosphate may be modified by the addition of charged or polar chemical groups. Two chemical groups that may modify the phosphate, choline and serine, are shown here. Both choline and serine attach to the phosphate group at the position labeled R via the hydroxyl group indicated in green.

A phospholipid is an amphipathic molecule, meaning it has a hydrophobic and a hydrophilic part. The fatty acid chains are hydrophobic and cannot interact with water, whereas the phosphate-containing group is hydrophilic and interacts with water (Figure 4.20).



'Hydrophilic head group

**Figure 4.20** The phospholipid bilayer is the major component of all cellular membranes. The hydrophilic head groups of the phospholipids face the aqueous solution. The hydrophobic tails are sequestered in the middle of the bilayer.

The head is the hydrophilic part, and the tail contains the hydrophobic fatty acids. In a membrane, a bilayer of phospholipids forms the matrix of the structure, the fatty acid tails of phospholipids face inside, away from water, whereas the phosphate group faces the outside, aqueous side (Figure 4.20).

Phospholipids are responsible for the dynamic nature of the plasma membrane. If a drop of phospholipids is placed in water, it spontaneously forms a structure known as a micelle, where the hydrophilic phosphate heads face the outside and the fatty acids face the interior of this structure.

## **Steroids**

Unlike the phospholipids and fats discussed earlier, **steroids** have a fused ring structure. Although they do not resemble the other lipids, they are grouped with them because they are also hydrophobic and insoluble in water. All steroids have four linked carbon rings and several of them, like cholesterol, have a short tail (**Figure 4.21**). Many steroids also have the –OH functional group, which puts them in the alcohol classification (sterols).



Cholesterol



#### Cortisol



Cholesterol is the most common steroid. Cholesterol is mainly synthesized in the liver and is the precursor to many steroid hormones such as testosterone and estradiol, which are secreted by the gonads and endocrine glands. It is also the precursor to Vitamin D. Cholesterol is also the precursor of bile salts, which help in the emulsification of fats and their subsequent absorption by cells. Although cholesterol is often spoken of in negative terms by lay people, it is necessary for proper functioning of the body. It is a component of the plasma membrane of animal cells and is found within the phospholipid bilayer. Being the outermost structure in animal cells, the plasma membrane is responsible for the transport of materials and cellular recognition and it is involved in cell-to-cell communication.





For an additional perspective on lipids, explore the interactive animation "Biomolecules: The Lipids" (http://openstaxcollege.org/l/lipids)

## 4.4 | Proteins

By the end of this section, you will be able to:

- Describe the functions proteins perform in the cell and in tissues
- · Discuss the relationship between amino acids and proteins
- Explain the four levels of protein organization
- · Describe the ways in which protein shape and function are linked

**Proteins** are one of the most abundant organic molecules in living systems and have the most diverse range of functions of all macromolecules. Proteins may be structural, regulatory, contractile, or protective; they may serve in transport, storage, or membranes; or they may be toxins or enzymes. Each cell in a living system may contain thousands of proteins, each with a unique function. Their structures, like their functions, vary greatly. They are all, however, polymers of amino acids, arranged in a linear sequence.

## **Types and Functions of Proteins**

**Enzymes**, which are produced by living cells, are catalysts in biochemical reactions (like digestion) and are usually complex or conjugated proteins. Each enzyme is specific for the substrate (a reactant that binds to an enzyme) it acts on. The enzyme may help in breakdown, rearrangement, or synthesis reactions. Enzymes that break down their substrates are called catabolic enzymes, enzymes that build more complex molecules from their substrates are called anabolic enzymes, and enzymes that affect the rate of reaction are called catalytic enzymes. It should be noted that all enzymes increase the rate of reaction and, therefore, are considered to be organic catalysts. An example of an enzyme is salivary amylase, which hydrolyzes its substrate amylose, a component of starch.

**Hormones** are chemical-signaling molecules, usually small proteins or steroids, secreted by endocrine cells that act to control or regulate specific physiological processes, including growth, development, metabolism, and reproduction. For example, insulin is a protein hormone that helps to regulate the blood glucose level. The primary types and functions of proteins are listed in Table 4.1.

Туре	Examples	Functions
Digestive Enzymes	Amylase, lipase, pepsin, trypsin	Help in digestion of food by catabolizing nutrients into monomeric units
Transport	Hemoglobin, albumin	Carry substances in the blood or lymph throughout the body
Structural	Actin, tubulin, keratin	Construct different structures, like the cytoskeleton
Hormones	Insulin, thyroxine	Coordinate the activity of different body systems
Defense	Immunoglobulins	Protect the body from foreign pathogens
Contractile	Actin, myosin	Effect muscle contraction
Storage	Legume storage proteins, egg white (albumin)	Provide nourishment in early development of the embryo and the seedling

#### **Protein Types and Functions**

#### Table 4.1

Proteins have different shapes and molecular weights; some proteins are globular in shape whereas others are fibrous in nature. For example, hemoglobin is a globular protein, but collagen, found in our skin, is a fibrous protein. Protein shape is critical to its function, and this shape is maintained by many different types of chemical bonds. Changes in temperature, pH, and exposure to chemicals may lead to permanent changes in the shape of the protein, leading to loss of function, known as **denaturation**. All proteins are made up of different

arrangements of the same 20 types of amino acids.

## **Amino Acids**

**Amino acids** are the monomers that make up proteins. Each amino acid has the same fundamental structure, which consists of a central carbon atom, also known as the alpha ( $\alpha$ ) carbon, bonded to an amino group (NH<sub>2</sub>), a carboxyl group (COOH), and to a hydrogen atom. Every amino acid also has another atom or group of atoms bonded to the central atom known as the R group (Figure 4.22).



Figure 4.22 Amino acids have a central asymmetric carbon to which an amino group, a carboxyl group, a hydrogen atom, and a side chain (R group) are attached.

The name "amino acid" is derived from the fact that they contain both amino group and carboxyl-acid-group in their basic structure. As mentioned, there are 20 amino acids present in proteins. Nine of these are considered essential amino acids in humans because the human body cannot produce them and they are obtained from the diet. For each amino acid, the R group (or side chain) is different (Figure 4.23).

# visual CONNECTION



**Figure 4.23** There are 20 common amino acids commonly found in proteins, each with a different R group (variant group) that determines its chemical nature.

Which categories of amino acid would you expect to find on the surface of a soluble protein, and which would you expect to find in the interior? What distribution of amino acids would you expect to find in a protein embedded in a lipid bilayer?

The chemical nature of the side chain determines the nature of the amino acid (that is, whether it is acidic, basic, polar, or nonpolar). For example, the amino acid glycine has a hydrogen atom as the R group. Amino acids such as valine, methionine, and alanine are nonpolar or hydrophobic in nature, while amino acids such as serine, threonine, and cysteine are polar and have hydrophilic side chains. The side chains of lysine and arginine are positively charged, and therefore these amino acids are also known as basic amino acids. Proline has an R group that is linked to the amino group, forming a ring-like structure. Proline is an exception to the standard structure of an animo acid since its amino group is not separate from the side chain (Figure 4.23).

Amino acids are represented by a single upper case letter or a three-letter abbreviation. For example, valine is known by the letter V or the three-letter symbol val. Just as some fatty acids are essential to a diet, some amino acids are necessary as well. They are known as essential amino acids, and in humans they include isoleucine, leucine, and cysteine. Essential amino acids refer to those necessary for construction of proteins in the body, although not produced by the body; which amino acids are essential varies from organism to organism.

The sequence and the number of amino acids ultimately determine the protein's shape, size, and function. Each amino acid is attached to another amino acid by a covalent bond, known as a **peptide bond**, which is formed by a dehydration reaction. The carboxyl group of one amino acid and the amino group of the incoming amino acid combine, releasing a molecule of water. The resulting bond is the peptide bond (Figure 4.24).



Figure 4.24 Peptide bond formation is a dehydration synthesis reaction. The carboxyl group of one amino acid is linked to the amino group of the incoming amino acid. In the process, a molecule of water is released.

The products formed by such linkages are called peptides. As more amino acids join to this growing chain, the resulting chain is known as a polypeptide. Each polypeptide has a free amino group at one end. This end is called the N terminal, or the amino terminal, and the other end has a free carboxyl group, also known as the C or carboxyl terminal. While the terms polypeptide and protein are sometimes used interchangeably, a polypeptide is technically a polymer of amino acids, whereas the term protein is used for a polypeptide or polypeptides that have combined together, often have bound non-peptide prosthetic groups, have a distinct shape, and have a unique function. After protein synthesis (translation), most proteins are modified. These are known as posttranslational modifications. They may undergo cleavage, phosphorylation, or may require the addition of other chemical groups. Only after these modific completely functional.





Click through the steps of protein synthesis in this interactive tutorial (http://openstaxcollege.org/l/ protein synth).

# tion CONNECTION

## The Evolutionary Significance of Cytochrome c

Cytochrome c is an important component of the electron transport chain, a part of cellular respiration, and it is normally found in the cellular organelle, the mitochondrion. This protein has a heme prosthetic group, and the central ion of the heme gets alternately reduced and oxidized during electron transfer. Because this essential protein's role in producing cellular energy is crucial, it has changed very little over millions of years. Protein sequencing has shown that there is a considerable amount of cytochrome c amino acid sequence homology among different species; in other words, evolutionary kinship can be assessed by measuring the similarities or differences among various species' DNA or protein sequences.

Scientists have determined that human cytochrome c contains 104 amino acids. For each cytochrome c molecule from different organisms that has been sequenced to date, 37 of these amino acids appear in the same position in all samples of cytochrome c. This indicates that there may have been a common ancestor. On comparing the human and chimpanzee protein sequences, no sequence difference was found. When human and rhesus monkey sequences were compared, the single difference found was in one amino acid. In another comparison, human to yeast sequencing shows a difference in the 44th position.
## **Protein Structure**

As discussed earlier, the shape of a protein is critical to its function. For example, an enzyme can bind to a specific substrate at a site known as the active site. If this active site is altered because of local changes or changes in overall protein structure, the enzyme may be unable to bind to the substrate. To understand how the protein gets its final shape or conformation, we need to understand the four levels of protein structure: primary, secondary, tertiary, and quaternary.

#### **Primary Structure**

The unique sequence of amino acids in a polypeptide chain is its **primary structure**. For example, the pancreatic hormone insulin has two polypeptide chains, A and B, and they are linked together by disulfide bonds. The N terminal amino acid of the A chain is glycine, whereas the C terminal amino acid is asparagine (Figure 4.25). The sequences of amino acids in the A and B chains are unique to insulin.



**Figure 4.25** Bovine serum insulin is a protein hormone made of two peptide chains, A (21 amino acids long) and B (30 amino acids long). In each chain, primary structure is indicated by three-letter abbreviations that represent the names of the amino acids in the order they are present. The amino acid cysteine (cys) has a sulfhydryl (SH) group as a side chain. Two sulfhydryl groups can react in the presence of oxygen to form a disulfide (S-S) bond. Two disulfide bonds connect the A and B chains together, and a third helps the A chain fold into the correct shape. Note that all disulfide bonds are the same length, but are drawn different sizes for clarity.

The unique sequence for every protein is ultimately determined by the gene encoding the protein. A change in nucleotide sequence of the gene's coding region may lead to a different amino acid being added to the growing polypeptide chain, causing a change in protein structure and function. In sickle cell anemia, the hemoglobin  $\beta$  chain (a small portion of which is shown in Figure 4.26) has a single amino acid substitution, causing a change in protein structure and function acid is substituted by valine in the  $\beta$  chain. What is most remarkable to consider is that a hemoglobin molecule is made up of two alpha chains and two beta chains that each consist of about 150 amino acids. The molecule, therefore, has about 600 amino acids. The structural difference between a normal hemoglobin molecule and a sickle cell molecule—which dramatically decreases life expectancy—is a single amino acid of the 600. What is even more remarkable is that those 600 amino acids are encoded by three nucleotides each, and the mutation is caused by a single base change (point mutation), 1 in 1800 bases.



Figure 4.26 The beta chain of hemoglobin is 147 residues in length, yet a single amino acid substitution leads to sickle cell anemia. In normal hemoglobin, the amino acid at position seven is glutamate. In sickle cell hemoglobin, this glutamate is replaced by a valine.

Because of this change of one amino acid in the chain, hemoglobin molecules form long fibers that distort the biconcave, or disc-shaped, red blood cells and assume a crescent or "sickle" shape, which clogs arteries (Figure 4.27). This can lead to myriad serious health problems such as breathlessness, dizziness, headaches, and abdominal pain for those affected by this disease.



Figure 4.27 In this blood smear, visualized at 535x magnification using bright field microscopy, sickle cells are crescent shaped, while normal cells are disc-shaped. (credit: modification of work by Ed Uthman; scale-bar data from Matt Russell)

#### Secondary Structure

The local folding of the polypeptide in some regions gives rise to the **secondary structure** of the protein. The most common are the  $\alpha$ -helix and  $\beta$ -pleated sheet structures (Figure 4.28). Both structures are the  $\alpha$ -helix structure—the helix held in shape by hydrogen bonds. The hydrogen bonds form between the oxygen atom in the carbonyl group in one amino acid and another amino acid that is four amino acids farther along the chain.



**Figure 4.28** The  $\alpha$ -helix and  $\beta$ -pleated sheet are secondary structures of proteins that form because of hydrogen bonding between carbonyl and amino groups in the peptide backbone. Certain amino acids have a propensity to form an  $\alpha$ -helix, while others have a propensity to form a  $\beta$ -pleated sheet.

Every helical turn in an alpha helix has 3.6 amino acid residues. The R groups (the variant groups) of the polypeptide protrude out from the  $\alpha$ -helix chain. In the  $\beta$ -pleated sheet, the "pleats" are formed by hydrogen bonding between atoms on the backbone of the polypeptide chain. The R groups are attached to the carbons and extend above and below the folds of the pleat. The pleated segments align parallel or antiparallel to each other, and hydrogen bonds form between the partially positive nitrogen atom in the amino group and the partially negative oxygen atom in the carbonyl group of the peptide backbone. The  $\alpha$ -helix and  $\beta$ -pleated sheet structures are found in most globular and fibrous proteins and they play an important structural role.

#### **Tertiary Structure**

The unique three-dimensional structure of a polypeptide is its **tertiary structure** (Figure 4.29). This structure is in part due to chemical interactions at work on the polypeptide chain. Primarily, the interactions among R groups creates the complex three-dimensional tertiary structure of a protein. The nature of the R groups found in the amino acids involved can counteract the formation of the hydrogen bonds described for standard secondary structures. For example, R groups with like charges are repelled by each other and those with unlike charges are attracted to each other (ionic bonds). When protein folding takes place, the hydrophobic R groups of nonpolar amino acids lay in the interior of the protein, whereas the hydrophilic R groups lay on the outside. The former types of interactions are also known as hydrophobic interactions. Interaction between cysteine side chains forms disulfide linkages in the presence of oxygen, the only covalent bond forming during protein folding.



**Figure 4.29** The tertiary structure of proteins is determined by a variety of chemical interactions. These include hydrophobic interactions, ionic bonding, hydrogen bonding and disulfide linkages.

All of these interactions, weak and strong, determine the final three-dimensional shape of the protein. When a protein loses its three-dimensional shape, it may no longer be functional.

#### **Quaternary Structure**

In nature, some proteins are formed from several polypeptides, also known as subunits, and the interaction of these subunits forms the **quaternary structure**. Weak interactions between the subunits help to stabilize the overall structure. For example, insulin (a globular protein) has a combination of hydrogen bonds and disulfide bonds that cause it to be mostly clumped into a ball shape. Insulin starts out as a single polypeptide and loses some internal sequences in the presence of post-translational modification after the formation of the disulfide linkages that hold the remaining chains together. Silk (a fibrous protein), however, has a  $\beta$ -pleated sheet structure that is the result of hydrogen bonding between different chains.

The four levels of protein structure (primary, secondary, tertiary, and quaternary) are illustrated in Figure 4.30.



Figure 4.30 The four levels of protein structure can be observed in these illustrations. (credit: modification of work by National Human Genome Research Institute)

## **Denaturation and Protein Folding**

Each protein has its own unique sequence and shape that are held together by chemical interactions. If the protein is subject to changes in temperature, pH, or exposure to chemicals, the protein structure may change, losing its shape without losing its primary sequence in what is known as denaturation. Denaturation is often reversible because the primary structure of the polypeptide is conserved in the process if the denaturing agent is removed, allowing the protein to resume its function. Sometimes denaturation is irreversible, leading to loss of function. One example of irreversible protein denaturation is when an egg is fried. The albumin protein in the liquid egg white is denatured when placed in a hot pan. Not all proteins are denatured at high temperatures; for instance, bacteria that survive in hot springs have proteins that function at temperatures close to boiling. The stomach is also very acidic, has a low pH, and denatures proteins as part of the digestion process; however, the digestive enzymes of the stomach retain their activity under these conditions.

Protein folding is critical to its function. It was originally thought that the proteins themselves were responsible for the folding process. Only recently was it found that often they receive assistance in the folding process from protein helpers known as **chaperones** (or chaperonins) that associate with the target protein during the folding process. They act by preventing aggregation of polypeptides that make up the complete protein structure, and

they disassociate from the protein once t





For an additional perspective on proteins, view this animation (http://openstaxcollege.org/l/proteins) called "Biomolecules: The Proteins."

ded.

## 4.5 | Nucleic Acids

By the end of this section, you will be able to:

- · Describe the structure of nucleic acids and define the two types of nucleic acids
- Explain the structure and role of DNA
- Explain the structure and roles of RNA

**Nucleic acids** are the most important macromolecules for the continuity of life. They carry the genetic blueprint of a cell and carry instructions for the functioning of the cell.

## **DNA and RNA**

The two main types of nucleic acids are **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. DNA is the genetic material found in all living organisms, ranging from single-celled bacteria to multicellular mammals. It is found in the nucleus of eukaryotes and in the organelles, chloroplasts, and mitochondria. In prokaryotes, the DNA is not enclosed in a membranous envelope.

The entire genetic content of a cell is known as its genome, and the study of genomes is genomics. In eukaryotic cells but not in prokaryotes, DNA forms a complex with histone proteins to form chromatin, the substance of eukaryotic chromosomes. A chromosome may contain tens of thousands of genes. Many genes contain the information to make protein products; other genes code for RNA products. DNA controls all of the cellular activities by turning the genes "on" or "off."

The other type of nucleic acid, RNA, is mostly involved in protein synthesis. The DNA molecules never leave the nucleus but instead use an intermediary to communicate with the rest of the cell. This intermediary is the **messenger RNA (mRNA)**. Other types of RNA—like rRNA, tRNA, and microRNA—are involved in protein synthesis and its regulation.

DNA and RNA are made up of monomers known as **nucleotides**. The nucleotides combine with each other to form a **polynucleotide**, DNA or RNA. Each nucleotide is made up of three components: a nitrogenous base, a pentose (five-carbon) sugar, and a phosphate group (Figure 4.31). Each nitrogenous base in a nucleotide is attached to a sugar molecule, which is attached to one or more phosphate groups.



**Figure 4.31** A nucleotide is made up of three components: a nitrogenous base, a pentose sugar, and one or more phosphate groups. Carbon residues in the pentose are numbered 1' through 5' (the prime distinguishes these residues from those in the base, which are numbered without using a prime notation). The base is attached to the 1' position of the ribose, and the phosphate is attached to the 5' position. When a polynucleotide is formed, the 5' phosphate of the incoming nucleotide attaches to the 3' hydroxyl group at the end of the growing chain. Two types of pentose are found in nucleotides, deoxyribose (found in DNA) and ribose (found in RNA). Deoxyribose is similar in structure to ribose, but it has an H instead of an OH at the 2' position. Bases can be divided into two categories: purines and pyrimidines. Purines have a double ring structure, and pyrimidines have a single ring.

The nitrogenous bases, important components of nucleotides, are organic molecules and are so named because they contain carbon and nitrogen. They are bases because they contain an amino group that has the potential of binding an extra hydrogen, and thus, decreases the hydrogen ion concentration in its environment, making it more basic. Each nucleotide in DNA contains one of four possible nitrogenous bases: adenine (A), guanine (G) cytosine (C), and thymine (T).

Adenine and guanine are classified as **purines**. The primary structure of a purine is two carbon-nitrogen rings. Cytosine, thymine, and uracil are classified as **pyrimidines** which have a single carbon-nitrogen ring as their primary structure (**Figure 4.31**). Each of these basic carbon-nitrogen rings has different functional groups attached to it. In molecular biology shorthand, the nitrogenous bases are simply known by their symbols A, T, G, C, and U. DNA contains A, T, G, and C whereas RNA contains A, U, G, and C.

The pentose sugar in DNA is deoxyribose, and in RNA, the sugar is ribose (**Figure 4.31**). The difference between the sugars is the presence of the hydroxyl group on the second carbon of the ribose and hydrogen on the second carbon of the deoxyribose. The carbon atoms of the sugar molecule are numbered as 1', 2', 3', 4', and 5' (1' is read as "one prime"). The phosphate residue is attached to the hydroxyl group of the 5' carbon of one sugar and the hydroxyl group of the 3' carbon of the sugar of the next nucleotide, which forms a 5'-3'

**phosphodiester** linkage. The phosphodiester linkage is not formed by simple dehydration reaction like the other linkages connecting monomers in macromolecules: its formation involves the removal of two phosphate groups. A polynucleotide may have thousands of such phosphodiester linkages.

#### **DNA Double-Helix Structure**

DNA has a double-helix structure (Figure 4.32). The sugar and phosphate lie on the outside of the helix, forming the backbone of the DNA. The nitrogenous bases are stacked in the interior, like the steps of a staircase, in pairs; the pairs are bound to each other by hydrogen bonds. Every base pair in the double helivx is separated from the next base pair by 0.34 nm. The two strands of the helix run in opposite directions, meaning that the 5' carbon end of one strand will face the 3' carbon end of its matching strand. (This is referred to as antiparallel orientation and is important to DNA replication and in many nucleic acid interactions.)



**Figure 4.32** Native DNA is an antiparallel double helix. The phosphate backbone (indicated by the curvy lines) is on the outside, and the bases are on the inside. Each base from one strand interacts via hydrogen bonding with a base from the opposing strand. (credit: Jerome Walker/Dennis Myts)

Only certain types of base pairing are allowed. For example, a certain purine can only pair with a certain pyrimidine. This means A can pair with T, and G can pair with C, as shown in **Figure 4.33**. This is known as the base complementary rule. In other words, the DNA strands are complementary to each other. If the sequence of one strand is AATTGGCC, the complementary strand would have the sequence TTAACCGG. During DNA replication, each strand is copied, resulting in a daughter DNA double helix containing one parental DNA strand and a newly synthesized strand.



**Figure 4.33** In a double stranded DNA molecule, the two strands run antiparallel to one another so that one strand runs 5' to 3' and the other 3' to 5'. The phosphate backbone is located on the outside, and the bases are in the middle. Adenine forms hydrogen bonds (or base pairs) with thymine, and guanine base pairs with cytosine.

A mutation occurs, and cytosine is replaced with adenine. What impact do you think this will have on the DNA structure?

### **RNA**

Ribonucleic acid, or RNA, is mainly involved in the process of protein synthesis under the direction of DNA. RNA is usually single-stranded and is made of ribonucleotides that are linked by phosphodiester bonds. A ribonucleotide in the RNA chain contains ribose (the pentose sugar), one of the four nitrogenous bases (A, U, G, and C), and the phosphate group.

There are four major types of RNA: messenger RNA (mRNA), ribosomal RNA (rRNA), transfer RNA (tRNA), and microRNA (miRNA). The first, mRNA, carries the message from DNA, which controls all of the cellular activities in a cell. If a cell requires a certain protein to be synthesized, the gene for this product is turned "on" and the messenger RNA is synthesized in the nucleus. The RNA base sequence is complementary to the coding sequence of the DNA from which it has been copied. However, in RNA, the base T is absent and U is present instead. If the DNA strand has a sequence AATTGCGC, the sequence of the complementary RNA is UUAACGCG. In the cytoplasm, the mRNA interacts with ribosomes and other cellular machinery (Figure 4.34).



**Figure 4.34** A ribosome has two parts: a large subunit and a small subunit. The mRNA sits in between the two subunits. A tRNA molecule recognizes a codon on the mRNA, binds to it by complementary base pairing, and adds the correct amino acid to the growing peptide chain.

The mRNA is read in sets of three bases known as codons. Each codon codes for a single amino acid. In this way, the mRNA is read and the protein product is made. Ribosomal RNA (rRNA) is a major constituent of

ribosomes on which the mRNA binds. The rRNA ensures the proper alignment of the mRNA and the ribosomes; the rRNA of the ribosome also has an enzymatic activity (peptidyl transferase) and catalyzes the formation of the peptide bonds between two aligned amino acids. **Transfer RNA (tRNA)** is one of the smallest of the four types of RNA, usually 70–90 nucleotides long. It carries the correct amino acid to the site of protein synthesis. It is the base pairing between the tRNA and mRNA that allows for the correct amino acid to be inserted in the polypeptide chain. microRNAs are the smallest RNA molecules and their role involves the regulation of gene expression by interfering with the expression of certain mRNA messages. **Table 4.2** summarizes features of DNA and RNA.

	DNA	RNA
Function	Carries genetic information	Involved in protein synthesis
Location	Remains in the nucleus	Leaves the nucleus
Structure	Double helix	Usually single-stranded
Sugar	Deoxyribose	Ribose
Pyrimidines	Cytosine, thymine	Cytosine, uracil
Purines	Adenine, guanine	Adenine, guanine

#### Features of DNA and RNA

Table 4.2

Even though the RNA is single stranded, most RNA types show extensive intramolecular base pairing between complementary sequences, creating a predictable three-dimensional structure essential for their function.

As you have learned, information flow in an organism takes place from DNA to RNA to protein. DNA dictates the structure of mRNA in a process known as **transcription**, and RNA dictates the structure of protein in a process known as **translation**. This is known as the Central Dogma of Life, which holds true for all organisms; however, exceptions to the rule occur in connection

LINK TA LEARNING



To learn more about DNA, explore the Howard Hughes Medical Institute BioInteractive animations (http://openstaxcollege.org/I/DNA) on the topic of DNA.

## **KEY TERMS**

- **alpha-helix structure (α-helix)** type of secondary structure of proteins formed by folding of the polypeptide into a helix shape with hydrogen bonds stabilizing the structure
- **amino acid** monomer of a protein; has a central carbon or alpha carbon to which an amino group, a carboxyl group, a hydrogen, and an R group or side chain is attached; the R group is different for all 20 amino acids
- **beta-pleated sheet (β-pleated)** secondary structure found in proteins in which "pleats" are formed by hydrogen bonding between atoms on the backbone of the polypeptide chain
- biological macromolecule large molecule necessary for life that is built from smaller organic molecules
- **carbohydrate** biological macromolecule in which the ratio of carbon to hydrogen and to oxygen is 1:2:1; carbohydrates serve as energy sources and structural support in cells and form the a cellular exoskeleton of arthropods
- cellulose polysaccharide that makes up the cell wall of plants; provides structural support to the cell
- chaperone (also, chaperonin) protein that helps nascent protein in the folding process
- chitin type of carbohydrate that forms the outer skeleton of all arthropods that include crustaceans and insects; it also forms the cell walls of fungi
- **dehydration synthesis** (also, condensation) reaction that links monomer molecules together, releasing a molecule of water for each bond formed
- denaturation loss of shape in a protein as a result of changes in temperature, pH, or exposure to chemicals
- deoxyribonucleic acid (DNA) double-helical molecule that carries the hereditary information of the cell
- disaccharide two sugar monomers that are linked together by a glycosidic bond
- enzyme catalyst in a biochemical reaction that is usually a complex or conjugated protein
- glycogen storage carbohydrate in animals
- **glycosidic bond** bond formed by a dehydration reaction between two monosaccharides with the elimination of a water molecule
- **hormone** chemical signaling molecule, usually protein or steroid, secreted by endocrine cells that act to control or regulate specific physiological processes
- hydrolysis reaction causes breakdown of larger molecules into smaller molecules with the utilization of water
- lipid macromolecule that is nonpolar and insoluble in water
- messenger RNA (mRNA) RNA that carries information from DNA to ribosomes during protein synthesis
- monomer smallest unit of larger molecules called polymers
- monosaccharide single unit or monomer of carbohydrates
- **nucleic acid** biological macromolecule that carries the genetic blueprint of a cell and carries instructions for the functioning of the cell
- **nucleotide** monomer of nucleic acids; contains a pentose sugar, one or more phosphate groups, and a nitrogenous base
- **omega fat** type of polyunsaturated fat that is required by the body; the numbering of the carbon omega starts from the methyl end or the end that is farthest from the carboxylic end
- peptide bond bond formed between two amino acids by a dehydration reaction

- **phosphodiester** linkage covalent chemical bond that holds together the polynucleotide chains with a phosphate group linking two pentose sugars of neighboring nucleotides
- **phospholipid** major constituent of the membranes; composed of two fatty acids and a phosphate-containing group attached to a glycerol backbone
- **polymer** chain of monomer residues that is linked by covalent bonds; polymerization is the process of polymer formation from monomers by condensation
- polynucleotide long chain of nucleotides
- **polypeptide** long chain of amino acids linked by peptide bonds
- polysaccharide long chain of monosaccharides; may be branched or unbranched
- primary structure linear sequence of amino acids in a protein
- protein biological macromolecule composed of one or more chains of amino acids
- purine type of nitrogenous base in DNA and RNA; adenine and guanine are purines
- pyrimidine type of nitrogenous base in DNA and RNA; cytosine, thymine, and uracil are pyrimidines
- quaternary structure association of discrete polypeptide subunits in a protein
- ribonucleic acid (RNA) single-stranded, often internally base paired, molecule that is involved in protein synthesis
- **ribosomal RNA (rRNA)** RNA that ensures the proper alignment of the mRNA and the ribosomes during protein synthesis and catalyzes the formation of the peptide linkage
- saturated fatty acid long-chain of hydrocarbon with single covalent bonds in the carbon chain; the number of hydrogen atoms attached to the carbon skeleton is maximized
- **secondary structure** regular structure formed by proteins by intramolecular hydrogen bonding between the oxygen atom of one amino acid residue and the hydrogen attached to the nitrogen atom of another amino acid residue
- starch storage carbohydrate in plants
- steroid type of lipid composed of four fused hydrocarbon rings forming a planar structure
- **tertiary structure** three-dimensional conformation of a protein, including interactions between secondary structural elements; formed from interactions between amino acid side chains
- **trans fat** fat formed artificially by hydrogenating oils, leading to a different arrangement of double bond(s) than those found in naturally occurring lipids
- transcription process through which messenger RNA forms on a template of DNA

transfer RNA (tRNA) RNA that carries activated amino acids to the site of protein synthesis on the ribosome

translation process through which RNA directs the formation of protein

triacylglycerol (also, triglyceride) fat molecule; consists of three fatty acids linked to a glycerol molecule

unsaturated fatty acid long-chain hydrocarbon that has one or more double bonds in the hydrocarbon chain

wax lipid made of a long-chain fatty acid that is esterified to a long-chain alcohol; serves as a protective coating on some feathers, aquatic mammal fur, and leaves

#### CHAPTER SUMMARY

#### 4.1 Synthesis of Biological Macromolecules

Proteins, carbohydrates, nucleic acids, and lipids are the four major classes of biological macromolecules—large molecules necessary for life that are built from smaller organic molecules. Macromolecules are made up of single units known as monomers that are joined by covalent bonds to form larger polymers. The polymer is more than the sum of its parts: it acquires new characteristics, and leads to an osmotic pressure that is much lower than that formed by its ingredients; this is an important advantage in the maintenance of cellular osmotic conditions. A monomer joins with another monomer with the release of a water molecule, leading to the formation of a covalent bond. These types of reactions are known as dehydration or condensation reactions. When polymers are broken down into smaller units (monomers), a molecule of water is used for each bond broken by these reactions; such reactions are known as hydrolysis reactions. Dehydration and hydrolysis reactions are similar for all macromolecules, but each monomer and polymer reaction is specific to its class. Dehydration reactions typically require an investment of energy for new bond formation, while hydrolysis reactions typically release energy by breaking bonds.

#### 4.2 Carbohydrates

Carbohydrates are a group of macromolecules that are a vital energy source for the cell and provide structural support to plant cells, fungi, and all of the arthropods that include lobsters, crabs, shrimp, insects, and spiders. Carbohydrates are classified as monosaccharides, disaccharides, and polysaccharides depending on the number of monomers in the molecule. Monosaccharides are linked by glycosidic bonds that are formed as a result of dehydration reactions, forming disaccharides and polysaccharides with the elimination of a water molecule for each bond formed. Glucose, galactose, and fructose are common monosaccharides, whereas common disaccharides include lactose, maltose, and sucrose. Starch and glycogen, examples of polysaccharides, are the storage forms of glucose in plants and animals, respectively. The long polysaccharide chains may be branched or unbranched. Cellulose is an example of an unbranched polysaccharide, whereas amylopectin, a constituent of starch, is a highly branched molecule. Storage of glucose, in the form of polymers like starch of glycogen, makes it slightly less accessible for metabolism; however, this prevents it from leaking out of the cell or creating a high osmotic pressure that could cause excessive water uptake by the cell.

#### 4.3 Lipids

Lipids are a class of macromolecules that are nonpolar and hydrophobic in nature. Major types include fats and oils, waxes, phospholipids, and steroids. Fats are a stored form of energy and are also known as triacylglycerols or triglycerides. Fats are made up of fatty acids and either glycerol or sphingosine. Fatty acids may be unsaturated or saturated, depending on the presence or absence of double bonds in the hydrocarbon chain. If only single bonds are present, they are known as saturated fatty acids. Unsaturated fatty acids may have one or more double bonds in the hydrocarbon chain. Phospholipids make up the matrix of membranes. They have a glycerol or sphingosine backbone to which two fatty acid chains and a phosphate-containing group are attached. Steroids are another class of lipids. Their basic structure has four fused carbon rings. Cholesterol is a type of steroid and is an important constituent of the plasma membrane, where it helps to maintain the fluid nature of the membrane. It is also the precursor of steroid hormones such as testosterone.

#### **4.4 Proteins**

Proteins are a class of macromolecules that perform a diverse range of functions for the cell. They help in metabolism by providing structural support and by acting as enzymes, carriers, or hormones. The building blocks of proteins (monomers) are amino acids. Each amino acid has a central carbon that is linked to an amino group, a carboxyl group, a hydrogen atom, and an R group or side chain. There are 20 commonly occurring amino acids, each of which differs in the R group. Each amino acid is linked to its neighbors by a peptide bond. A long chain of amino acids is known as a polypeptide.

Proteins are organized at four levels: primary, secondary, tertiary, and (optional) quaternary. The primary structure is the unique sequence of amino acids. The local folding of the polypeptide to form structures such as the  $\alpha$  helix and  $\beta$ -pleated sheet constitutes the secondary structure. The overall three-dimensional structure is the tertiary structure. When two or more polypeptides combine to form the complete protein structure, the configuration is known as the quaternary structure of a protein. Protein shape and function are intricately linked; any change in shape caused by changes in temperature or pH may lead to protein denaturation and a loss in

function.

#### 4.5 Nucleic Acids

Nucleic acids are molecules made up of nucleotides that direct cellular activities such as cell division and protein synthesis. Each nucleotide is made up of a pentose sugar, a nitrogenous base, and a phosphate group. There are two types of nucleic acids: DNA and RNA. DNA carries the genetic blueprint of the cell and is passed on from parents to offspring (in the form of chromosomes). It has a double-helical structure with the two strands running in opposite directions, connected by hydrogen bonds, and complementary to each other. RNA is single-stranded and is made of a pentose sugar (ribose), a nitrogenous base, and a phosphate group. RNA is involved in protein synthesis and its regulation. Messenger RNA (mRNA) is copied from the DNA, is exported from the nucleus to the cytoplasm, and contains information for the construction of proteins. Ribosomal RNA (rRNA) is a part of the ribosomes at the site of protein synthesis, whereas transfer RNA (tRNA) carries the amino acid to the site of protein synthesis.

## **ART CONNECTION QUESTIONS**

**1. Figure 4.5** What kind of sugars are these, aldose or ketose?

**2. Figure 4.23** Which categories of amino acid would you expect to find on the surface of a soluble protein, and which would you expect to find in the interior?

## **REVIEW QUESTIONS**

4. Dehydration synthesis leads to formation of

- a. monomers
- b. polymers
- c. water and polymers
- d. none of the above

**5.** During the breakdown of polymers, which of the following reactions takes place?

- a. hydrolysis
- b. dehydration
- c. condensation
- d. covalent bond

6. An example of a monosaccharide is \_\_\_\_\_

- a. fructose
- b. glucose
- c. galactose
- d. all of the above

7. Cellulose and starch are examples of:

- a. monosaccharides
- b. disaccharides
- c. lipids
- d. polysaccharides

**8.** Plant cell walls contain which of the following in abundance?

- a. starch
- b. cellulose
- c. glycogen
- d. lactose

**9.** Lactose is a disaccharide formed by the formation of a \_\_\_\_\_\_ bond between glucose and \_\_\_\_\_\_

What distribution of amino acids would you expect to find in a protein embedded in a lipid bilayer?

**3. Figure 4.33** A mutation occurs, and cytosine is replaced with adenine. What impact do you think this will have on the DNA structure?

- a. glycosidic; lactose
- b. glycosidic; galactose
- c. hydrogen; sucrose
- d. hydrogen; fructose

**10.** Saturated fats have all of the following characteristics except:

- a. they are solid at room temperature
- b. they have single bonds within the carbon chain
- c. they are usually obtained from animal sources
- d. they tend to dissolve in water easily
- 11. Phospholipids are important components of

  - a. the plasma membrane of animal cells
  - b. the ring structure of steroids
  - c. the waxy covering on leaves
  - d. the double bond in hydrocarbon chains
- 12. The monomers that make up proteins are called
  - a. nucleotides
  - b. disaccharides
  - c. amino acids
  - d. chaperones

**13.** The  $\alpha$  helix and the  $\beta$ -pleated sheet are part of which protein structure?

- a. primary
- b. secondary
- c. tertiary
- d. quaternary

**14.** A nucleotide of DNA may contain \_\_\_\_\_.

- a. ribose, uracil, and a phosphate group
- b. deoxyribose, uracil, and a phosphate group
- c. deoxyribose, thymine, and a phosphate group
- d. ribose, thymine, and a phosphate group

## **CRITICAL THINKING QUESTIONS**

**16.** Why are biological macromolecules considered organic?

**17.** What role do electrons play in dehydration synthesis and hydrolysis?

**18.** Describe the similarities and differences between glycogen and starch.

**19.** Why is it impossible for humans to digest food that contains cellulose?

**20.** Explain at least three functions that lipids serve in plants and/or animals.

21. Why have trans fats been banned from some

- 15. The building blocks of nucleic acids are
  - a. sugars
  - b. nitrogenous bases
  - c. peptides
  - d. nucleotides

restaurants? How are they created?

**22.** Explain what happens if even one amino acid is substituted for another in a polypeptide chain. Provide a specific example.

**23.** Describe the differences in the four protein structures.

**24.** What are the structural differences between RNA and DNA?

**25.** What are the four types of RNA and how do they function?

# **5 | CELL STRUCTURE**



**Figure 5.1** (a) Nasal sinus cells (viewed with a light microscope), (b) onion cells (viewed with a light microscope), and (c) *Vibrio tasmaniensis* bacterial cells (seen through a scanning electron microscope) are from very different organisms, yet all share certain characteristics of basic cell structure. (credit a: modification of work by Ed Uthman, MD; credit b: modification of work by Umberto Salvagnin; credit c: modification of work by Anthony D'Onofrio, William H. Fowle, Eric J. Stewart, and Kim Lewis of the Lewis Lab at Northeastern University; scale-bar data from Matt Russell)

## **Chapter Outline**

5.1: Studying Cells

5.2: Eukaryotic Cells

## Introduction

Close your eyes and picture a brick wall. What is the basic building block of that wall? A single brick, of course. Like a brick wall, your body is composed of basic building blocks, and the building blocks of your body are cells.

Your body has many kinds of cells, each specialized for a specific purpose. Just as a home is made from a variety of building materials, the human body is constructed from many cell types. For example, epithelial cells protect the surface of the body and cover the organs and body cavities within. Bone cells help to support and protect the body. Cells of the immune system fight invading bacteria. Additionally, blood and blood cells carry nutrients and oxygen throughout the body while removing carbon dioxide. Each of these cell types plays a vital role during the growth, development, and day-to-day maintenance of the body. In spite of their enormous variety, however, cells from all organisms—even ones as diverse as bacteria, onion, and human—share certain fundamental characteristics.

## 5.1 | Studying Cells

By the end of this section, you will be able to:

- · Describe the role of cells in organisms
- · Compare and contrast light microscopy and electron microscopy
- Summarize cell theory

A cell is the smallest unit of a living thing. A living thing, whether made of one cell (like bacteria) or many cells (like a human), is called an organism. Thus, cells are the basic building blocks of all organisms.

Several cells of one kind that interconnect with each other and perform a shared function form tissues, several tissues combine to form an organ (your stomach, heart, or brain), and several organs make up an organ system (such as the digestive system, circulatory system, or nervous system). Several systems that function together form an organism (like a human being). Here, we will examine the structure and function of cells.

There are many types of cells, all grouped into one of two broad categories: prokaryotic and eukaryotic. For example, both animal and plant cells are classified as eukaryotic cells, whereas bacterial cells are classified as prokaryotic. Before discussing the criteria for determining whether a cell is prokaryotic or eukaryotic, let's first examine how biologists study cells.

#### Microscopy

Cells vary in size. With few exceptions, individual cells cannot be seen with the naked eye, so scientists use microscopes (micro- = "small"; -scope = "to look at") to study them. A **microscope** is an instrument that magnifies an object. Most photographs of cells are taken with a microscope, and these images can also be called micrographs.

The optics of a microscope's lenses change the orientation of the image that the user sees. A specimen that is right-side up and facing right on the microscope slide will appear upside-down and facing left when viewed through a microscope, and vice versa. Similarly, if the slide is moved left while looking through the microscope, it will appear to move right, and if moved down, it will seem to move up. This occurs because microscopes use two sets of lenses to magnify the image. Because of the manner by which light travels through the lenses, this system of two lenses produces an inverted image (binocular, or dissecting microscopes, work in a similar manner, but include an additional magnification system that makes the final image appear to be upright).

#### Light Microscopes

To give you a sense of cell size, a typical human red blood cell is about eight millionths of a meter or eight micrometers (abbreviated as eight  $\mu$ m) in diameter; the head of a pin of is about two thousandths of a meter (two mm) in diameter. That means about 250 red blood cells could fit on the head of a pin.

Most student microscopes are classified as **light microscopes** (Figure 5.2a). Visible light passes and is bent through the lens system to enable the user to see the specimen. Light microscopes are advantageous for viewing living organisms, but since individual cells are generally transparent, their components are not distinguishable unless they are colored with special stains. Staining, however, usually kills the cells.

Light microscopes commonly used in the undergraduate college laboratory magnify up to approximately 400 times. Two parameters that are important in microscopy are magnification and resolving power. Magnification is the process of enlarging an object in appearance. Resolving power is the ability of a microscope to distinguish two adjacent structures as separate: the higher the resolution, the better the clarity and detail of the image. When oil immersion lenses are used for the study of small objects, magnification is usually increased to 1,000 times. In order to gain a better understanding of cellular structure and function, scientists typically use electron microscopes.



**Figure 5.2** (a) Most light microscopes used in a college biology lab can magnify cells up to approximately 400 times and have a resolution of about 200 nanometers. (b) Electron microscopes provide a much higher magnification, 100,000x, and a have a resolution of 50 picometers. (credit a: modification of work by "GcG"/Wikimedia Commons; credit b: modification of work by Evan Bench)

#### Electron Microscopes

In contrast to light microscopes, **electron microscopes** (Figure 5.2b) use a beam of electrons instead of a beam of light. Not only does this allow for higher magnification and, thus, more detail (Figure 5.3), it also

provides higher resolving power. The method used to prepare the specimen for viewing with an electron microscope kills the specimen. Electrons have short wavelengths (shorter than photons) that move best in a vacuum, so living cells cannot be viewed with an electron microscope.

In a scanning electron microscope, a beam of electrons moves back and forth across a cell's surface, creating details of cell surface characteristics. In a transmission electron microscope, the electron beam penetrates the cell and provides details of a cell's internal structures. As you might imagine, electron microscopes are significantly more bulky and expensive than light microscopes.



**Figure 5.3** (a) These *Salmonella* bacteria appear as tiny purple dots when viewed with a light microscope. (b) This scanning electron microscope micrograph shows *Salmonella* bacteria (in red) invading human cells (yellow). Even though subfigure (b) shows a different *Salmonella* specimen than subfigure (a), you can still observe the comparative increase in magnification and detail. (credit a: modification of work by CDC/Armed Forces Institute of Pathology, Charles N. Farmer, Rocky Mountain Laboratories; credit b: modification of work by NIAID, NIH; scale-bar data from Matt Russell)





For another perspective on cell size, try the HowBig interactive at this site (http://openstaxcollege.org/l/ cell\_sizes).

## **Cell Theory**

The microscopes we use today are far more complex than those used in the 1600s by Antony van Leeuwenhoek, a Dutch shopkeeper who had great skill in crafting lenses. Despite the limitations of his now-ancient lenses, van Leeuwenhoek observed the movements of protista (a type of single-celled organism) and sperm, which he collectively termed "animalcules."

In a 1665 publication called *Micrographia*, experimental scientist Robert Hooke coined the term "cell" for the boxlike structures he observed when viewing cork tissue through a lens. In the 1670s, van Leeuwenhoek discovered bacteria and protozoa. Later advances in lenses, microscope construction, and staining techniques enabled other scientists to see some components inside cells.

By the late 1830s, botanist Matthias Schleiden and zoologist Theodor Schwann were studying tissues and proposed the **unified cell theory**, which states that all living things are composed of one or more cells, the cell is the basic unit of life, and new cells arise from existing cells. Rudolf Virchow later made important contributions to this theory.

## ca eer connection

## Cytotechnologist

Have you ever heard of a medical test called a Pap smear (Figure 5.4)? In this test, a doctor takes a small sample of cells from the uterine cervix of a patient and sends it to a medical lab where a cytotechnologist stains the cells and examines them for any changes that could indicate cervical cancer or a microbial infection.

Cytotechnologists (cyto- = "cell") are professionals who study cells via microscopic examinations and other laboratory tests. They are trained to determine which cellular changes are within normal limits and which are abnormal. Their focus is not limited to cervical cells; they study cellular specimens that come from all organs. When they notice abnormalities, they consult a pathologist, who is a medical doctor who can make a clinical diagnosis.

Cytotechnologists play a vital role in saving people's lives. When abnormalities are discovered early, a patient's treatment can begin sooner, which usually increases the chances of a successful outcome.



**Figure 5.4** These uterine cervix cells, viewed through a light microscope, were obtained from a Pap smear. Normal cells are on the left. The cells on the right are infected with human papillomavirus (HPV). Notice that the infected cells are larger; also, two of these cells each have two nuclei instead of one, the normal number. (credit: modification of work by Ed Uthman, MD; scale-bar data from Matt Russell)

## 5.2 | Eukaryotic Cells

By the end of this section, you will be able to:

- · Describe the structure of eukaryotic cells
- Compare animal cells with plant cells
- State the role of the plasma membrane
- · Summarize the functions of the major cell organelles

Have you ever heard the phrase "form follows function?" It's a philosophy practiced in many industries. In architecture, this means that buildings should be constructed to support the activities that will be carried out inside them. For example, a skyscraper should be built with several elevator banks; a hospital should be built so that its emergency room is easily accessible.

Our natural world also utilizes the principle of form following function, especially in cell biology, and this will become clear as we explore eukaryotic cells (**Figure 5.5**). Unlike prokaryotic cells, **eukaryotic cells** have: 1) a membrane-bound nucleus; 2) numerous membrane-bound **organelles** such as the endoplasmic reticulum, Golgi apparatus, chloroplasts, mitochondria, and others; and 3) several, rod-shaped chromosomes. Because a eukaryotic cell's nucleus is surrounded by a membrane, it is often said to have a "true nucleus." The word

"organelle" means "little organ," and, as already mentioned, organelles have specialized cellular functions, just as the organs of your body have specialized functions.

At this point, it should be clear to you that eukaryotic cells have a more complex structure than prokaryotic cells. Organelles allow different functions to be compartmentalized in different areas of the cell. Before turning to organelles, let's first examine two important components of the cell: the plasma membrane and the cytoplasm.



**Figure 5.5** These figures show the major organelles and other cell components of (a) a typical animal cell and (b) a typical eukaryotic plant cell. The plant cell has a cell wall, chloroplasts, plastids, and a central vacuole—structures not found in animal cells. Plant cells do not have lysosomes or centrosomes.

If the nucleolus were not able to carry out its function, what other cellular organelles would be affected?

## The Plasma Membrane

Like prokaryotes, eukaryotic cells have a **plasma membrane** (Figure 5.6), a phospholipid bilayer with embedded proteins that separates the internal contents of the cell from its surrounding environment. A

phospholipid is a lipid molecule with two fatty acid chains and a phosphate-containing group. The plasma membrane controls the passage of organic molecules, ions, water, and oxygen into and out of the cell. Wastes (such as carbon dioxide and ammonia) also leave the cell by passing through the plasma membrane.



Figure 5.6 The eukaryotic plasma membrane is a phospholipid bilayer with proteins and cholesterol embedded in it.

The plasma membranes of cells that specialize in absorption are folded into fingerlike projections called microvilli (singular = microvillus); (**Figure 5.7**). Such cells are typically found lining the small intestine, the organ that absorbs nutrients from digested food. This is an excellent example of form following function. People with celiac disease have an immune response to gluten, which is a protein found in wheat, barley, and rye. The immune response damages microvilli, and thus, afflicted individuals cannot absorb nutrients. This leads to malnutrition, cramping, and diarrhea. Patients suffering from celiac disease must follow a gluten-free diet.



Figure 5.7 Microvilli, shown here as they appear on cells lining the small intestine, increase the surface area available for absorption. These microvilli are only found on the area of the plasma membrane that faces the cavity from which substances will be absorbed. (credit "micrograph": modification of work by Louisa Howard)

## The Cytoplasm

The **cytoplasm** is the entire region of a cell between the plasma membrane and the nuclear envelope (a structure to be discussed shortly). It is made up of organelles suspended in the gel-like **cytosol**, the cytoskeleton, and various chemicals (**Figure 5.5**). Even though the cytoplasm consists of 70 to 80 percent water, it has a semi-solid consistency, which comes from the proteins within it. However, proteins are not the only organic molecules found in the cytoplasm. Glucose and other simple sugars, polysaccharides, amino acids, nucleic acids, fatty acids, and derivatives of glycerol are found there, too. Ions of sodium, potassium, calcium, and many other elements are also dissolved in the cytoplasm. Many metabolic reactions, including protein synthesis, take place in the cytoplasm.

## The Nucleus

Typically, the nucleus is the most prominent organelle in a cell (Figure 5.5). The nucleus (plural = nuclei)

houses the cell's DNA and directs the synthesis of ribosomes and proteins. Let's look at it in more detail (Figure 5.8).



**Figure 5.8** The nucleus stores chromatin (DNA plus proteins) in a gel-like substance called the nucleoplasm. The nucleolus is a condensed region of chromatin where ribosome synthesis occurs. The boundary of the nucleus is called the nuclear envelope. It consists of two phospholipid bilayers: an outer membrane and an inner membrane. The nuclear membrane is continuous with the endoplasmic reticulum. Nuclear pores allow substances to enter and exit the nucleus.

#### The Nuclear Envelope

The **nuclear envelope** is a double-membrane structure that constitutes the outermost portion of the nucleus ( **Figure 5.8**). Both the inner and outer membranes of the nuclear envelope are phospholipid bilayers.

The nuclear envelope is punctuated with pores that control the passage of ions, molecules, and RNA between the nucleoplasm and cytoplasm. The **nucleoplasm** is the semi-solid fluid inside the nucleus, where we find the chromatin and the nucleolus.

#### **Chromatin and Chromosomes**

To understand chromatin, it is helpful to first consider chromosomes. **Chromosomes** are structures within the nucleus that are made up of DNA, the hereditary material. You may remember that in prokaryotes, DNA is organized into a single circular chromosome. In eukaryotes, chromosomes are linear structures. Every eukaryotic species has a specific number of chromosomes in the nuclei of its body's cells. For example, in humans, the chromosome number is 46, while in fruit flies, it is eight. Chromosomes are only visible and distinguishable from one another when the cell is getting ready to divide. When the cell is in the growth and maintenance phases of its life cycle, proteins are attached to chromosomes, and they resemble an unwound, jumbled bunch of threads. These unwound protein-chromosome complexes are called **chromatin** (Figure 5.9); chromatin describes the material that makes up the chromosomes both when condensed and decondensed.



**Figure 5.9** (a) This image shows various levels of the organization of chromatin (DNA and protein). (b) This image shows paired chromosomes. (credit b: modification of work by NIH; scale-bar data from Matt Russell)

#### The Nucleolus

We already know that the nucleus directs the synthesis of ribosomes, but how does it do this? Some chromosomes have sections of DNA that encode ribosomal RNA. A darkly staining area within the nucleus called the **nucleolus** (plural = nucleoli) aggregates the ribosomal RNA with associated proteins to assemble the ribosomal subunits that are then transported out through the pores in the nuclear envelope to the cytoplasm.

#### Ribosomes

**Ribosomes** are the cellular structures responsible for protein synthesis. When viewed through an electron microscope, ribosomes appear either as clusters (polyribosomes) or single, tiny dots that float freely in the cytoplasm. They may be attached to the cytoplasmic side of the plasma membrane or the cytoplasmic side of the endoplasmic reticulum and the outer membrane of the nuclear envelope (**Figure 5.5**). Electron microscopy has shown us that ribosomes, which are large complexes of protein and RNA, consist of two subunits, aptly called large and small (**Figure 5.10**). Ribosomes receive their "orders" for protein synthesis from the nucleus where the DNA is transcribed into messenger RNA (mRNA). The mRNA travels to the ribosomes, which translate the code provided by the sequence of the nitrogenous bases in the mRNA into a specific order of amino acids in a protein. Amino acids are the building blocks of proteins.



Figure 5.10 Ribosomes are made up of a large subunit (top) and a small subunit (bottom). During protein synthesis, ribosomes assemble amino acids into proteins.

Because proteins synthesis is an essential function of all cells (including enzymes, hormones, antibodies,

pigments, structural components, and surface receptors), ribosomes are found in practically every cell. Ribosomes are particularly abundant in cells that synthesize large amounts of protein. For example, the pancreas is responsible for creating several digestive enzymes and the cells that produce these enzymes contain many ribosomes. Thus, we see another example of form following function.

### Mitochondria

**Mitochondria** (singular = mitochondrion) are often called the "powerhouses" or "energy factories" of a cell because they are responsible for making adenosine triphosphate (ATP), the cell's main energy-carrying molecule. ATP represents the short-term stored energy of the cell. Cellular respiration is the process of making ATP using the chemical energy found in glucose and other nutrients. In mitochondria, this process uses oxygen and produces carbon dioxide as a waste product. In fact, the carbon dioxide that you exhale with every breath comes from the cellular reactions that produce carbon dioxide as a byproduct.

In keeping with our theme of form following function, it is important to point out that muscle cells have a very high concentration of mitochondria that produce ATP. Your muscle cells need a lot of energy to keep your body moving. When your cells don't get enough oxygen, they do not make a lot of ATP. Instead, the small amount of ATP they make in the absence of oxygen is accompanied by the production of lactic acid.

Mitochondria are oval-shaped, double membrane organelles (**Figure 5.11**) that have their own ribosomes and DNA. Each membrane is a phospholipid bilayer embedded with proteins. The inner layer has folds called cristae. The area surrounded by the folds is called the mitochondrial matrix. The cristae and the matrix have different roles in cellular respiration.



**Figure 5.11** This electron micrograph shows a mitochondrion as viewed with a transmission electron microscope. This organelle has an outer membrane and an inner membrane. The inner membrane contains folds, called cristae, which increase its surface area. The space between the two membranes is called the intermembrane space, and the space inside the inner membrane is called the mitochondrial matrix. ATP synthesis takes place on the inner membrane. (credit: modification of work by Matthew Britton; scale-bar data from Matt Russell)

#### Peroxisomes

**Peroxisomes** are small, round organelles enclosed by single membranes. They carry out oxidation reactions that break down fatty acids and amino acids. They also detoxify many poisons that may enter the body. (Many of these oxidation reactions release hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, which would be damaging to cells; however, when these reactions are confined to peroxisomes, enzymes safely break down the H<sub>2</sub>O<sub>2</sub> into oxygen and water.) For example, alcohol is detoxified by peroxisomes in liver cells. Glyoxysomes, which are specialized peroxisomes in plants, are responsible for converting stored fats into sugars.

#### Vesicles and Vacuoles

**Vesicles** and **vacuoles** are membrane-bound sacs that function in storage and transport. Other than the fact that vacuoles are somewhat larger than vesicles, there is a very subtle distinction between them: The membranes of vesicles can fuse with either the plasma membrane or other membrane systems within the cell. Additionally, some agents such as enzymes within plant vacuoles break down macromolecules. The membrane of a vacuole does not fuse with the membranes of other cellular components.

## **Animal Cells versus Plant Cells**

At this point, you know that each eukaryotic cell has a plasma membrane, cytoplasm, a nucleus, ribosomes, mitochondria, peroxisomes, and in some, vacuoles, but there are some striking differences between animal and plant cells. While both animal and plant cells have microtubule organizing centers (MTOCs), animal cells

also have centrioles associated with the MTOC: a complex called the centrosome. Animal cells each have a centrosome and lysosomes, whereas plant cells do not. Plant cells have a cell wall, chloroplasts and other specialized plastids, and a large central vacuole, whereas animal cells do not.

#### The Centrosome

The **centrosome** is a microtubule-organizing center found near the nuclei of animal cells. It contains a pair of centrioles, two structures that lie perpendicular to each other (**Figure 5.12**). Each centriole is a cylinder of nine triplets of microtubules.



**Figure 5.12** The centrosome consists of two centrioles that lie at right angles to each other. Each centriole is a cylinder made up of nine triplets of microtubules. Nontubulin proteins (indicated by the green lines) hold the microtubule triplets together.

The centrosome (the organelle where all microtubules originate) replicates itself before a cell divides, and the centrioles appear to have some role in pulling the duplicated chromosomes to opposite ends of the dividing cell. However, the exact function of the centrioles in cell division isn't clear, because cells that have had the centrosome removed can still divide, and plant cells, which lack centrosomes, are capable of cell division.

#### Lysosomes

Animal cells have another set of organelles not found in plant cells: lysosomes. The **lysosomes** are the cell's "garbage disposal." In plant cells, the digestive processes take place in vacuoles. Enzymes within the lysosomes aid the breakdown of proteins, polysaccharides, lipids, nucleic acids, and even worn-out organelles. These enzymes are active at a much lower pH than that of the cytoplasm. Therefore, the pH within lysosomes is more acidic than the pH of the cytoplasm. Many reactions that take place in the cytoplasm could not occur at a low pH, so again, the advantage of compartmentalizing the eukaryotic cell into organelles is apparent.

#### The Cell Wall

If you examine **Figure 5.5b**, the diagram of a plant cell, you will see a structure external to the plasma membrane called the cell wall. The **cell wall** is a rigid covering that protects the cell, provides structural support, and gives shape to the cell. Fungal and protistan cells also have cell walls. While the chief component of prokaryotic cell walls is peptidoglycan, the major organic molecule in the plant cell wall is cellulose (**Figure 5.13**), a polysaccharide made up of glucose units. Have you ever noticed that when you bite into a raw vegetable, like celery, it crunches? That's because you are tearing the rigid cell walls of the celery cells with your teeth.



Figure 5.13 Cellulose is a long chain of  $\beta$ -glucose molecules connected by a 1-4 linkage. The dashed lines at each end of the figure indicate a series of many more glucose units. The size of the page makes it impossible to portray an entire cellulose molecule.

#### Chloroplasts

Like the mitochondria, chloroplasts have their own DNA and ribosomes, but chloroplasts have an entirely different function. Chloroplasts are plant cell organelles that carry out photosynthesis. Photosynthesis is the

series of reactions that use carbon dioxide, water, and light energy to make glucose and oxygen. This is a major difference between plants and animals; plants (autotrophs) are able to make their own food, like sugars, while animals (heterotrophs) must ingest their food.

Like mitochondria, chloroplasts have outer and inner membranes, but within the space enclosed by a chloroplast's inner membrane is a set of interconnected and stacked fluid-filled membrane sacs called thylakoids (Figure 5.14). Each stack of thylakoids is called a granum (plural = grana). The fluid enclosed by the inner membrane that surrounds the grana is called the stroma.



**Figure 5.14** The chloroplast has an outer membrane, an inner membrane, and membrane structures called thylakoids that are stacked into grana. The space inside the thylakoid membranes is called the thylakoid space. The light harvesting reactions take place in the thylakoid membranes, and the synthesis of sugar takes place in the fluid inside the inner membrane, which is called the stroma. Chloroplasts also have their own genome, which is contained on a single circular chromosome.

The chloroplasts contain a green pigment called **chlorophyll**, which captures the light energy that drives the reactions of photosynthesis. Like plant cells, photosynthetic protists also have chloroplasts. Some bacteria perform photosynthesis, but their chlorophyll is not relegated to an organelle.

## e olution CONNECTION

## Endosymbiosis

We have mentioned that both mitochondria and chloroplasts contain DNA and ribosomes. Have you wondered why? Strong evidence points to endosymbiosis as the explanation.

Symbiosis is a relationship in which organisms from two separate species depend on each other for their survival. Endosymbiosis (endo- = "within") is a mutually beneficial relationship in which one organism lives inside the other. Endosymbiotic relationships abound in nature. We have already mentioned that microbes that produce vitamin K live inside the human gut. This relationship is beneficial for us because we are unable to synthesize vitamin K. It is also beneficial for the microbes because they are protected from other organisms and from drying out, and they receive abundant food from the environment of the large intestine.

Scientists have long noticed that bacteria, mitochondria, and chloroplasts are similar in size. We also know that bacteria have DNA and ribosomes, just as mitochondria and chloroplasts do. Scientists believe that host cells and bacteria formed an endosymbiotic relationship when the host cells ingested both aerobic and autotrophic bacteria (cyanobacteria) but did not destroy them. Through many millions of years of evolution, these ingested bacteria became more specialized in their functions, with the aerobic bacteria becoming mitochondria and the autotrophic bacteria becoming chloroplasts.

#### The Central Vacuole

Previously, we mentioned vacuoles as essential components of plant cells. If you look at **Figure 5.5b**, you will see that plant cells each have a large central vacuole that occupies most of the area of the cell. The **central vacuole** plays a key role in regulating the cell's concentration of water in changing environmental conditions. Have you ever noticed that if you forget to water a plant for a few days, it wilts? That's because as the water concentration in the soil becomes lower than the water concentration in the plant, water moves out of the central vacuoles and cytoplasm. As the central vacuole shrinks, it leaves the cell wall unsupported. This loss of support to the cell walls of plant cells results in the wilted appearance of the plant.

The central vacuole also supports the expansion of the cell. When the central vacuole holds more water, the cell gets larger without having to invest a lot of energy in synthesizing new cytoplasm.

#### **KEY TERMS**

cell theory see unified cell theory

- cell wall rigid cell covering made of various molecules that protects the cell, provides structural support, and gives shape to the cell
- **central vacuole** large plant cell organelle that regulates the cell's storage compartment, holds water, and plays a significant role in cell growth as the site of macromolecule degradation
- centrosome region in animal cells made of two centrioles
- chlorophyll green pigment that captures the light energy that drives the light reactions of photosynthesis
- chloroplast plant cell organelle that carries out photosynthesis
- chromatin protein-DNA complex that serves as the building material of chromosomes
- chromosome structure within the nucleus that is made up of chromatin that contains DNA, the hereditary material
- **cytoplasm** entire region between the plasma membrane and the nuclear envelope, consisting of organelles suspended in the gel-like cytosol, the cytoskeleton, and various chemicals
- cytosol gel-like material of the cytoplasm in which cell structures are suspended
- electron microscope an instrument that magnifies an object using a beam of electrons passed and bent through a lens system to visualize a specimen
- eukaryotic cell cell that has a membrane-bound nucleus and several other membrane-bound compartments or sacs
- **light microscope** an instrument that magnifies an object using a beam visible light passed and bent through a lens system to visualize a specimen
- **Iysosome** organelle in an animal cell that functions as the cell's digestive component; it breaks down proteins, polysaccharides, lipids, nucleic acids, and even worn-out organelles
- microscope an instrument that magnifies an object
- **mitochondria** (singular = mitochondrion) cellular organelles responsible for carrying out cellular respiration, resulting in the production of ATP, the cell's main energy-carrying molecule
- nuclear envelope double-membrane structure that constitutes the outermost portion of the nucleus
- **nucleolus** darkly staining body within the nucleus that is responsible for assembling the subunits of the ribosomes
- nucleoplasm semi-solid fluid inside the nucleus that contains the chromatin and nucleolus

nucleus cell organelle that houses the cell's DNA and directs the synthesis of ribosomes and proteins

- organelle compartment or sac within a cell
- **peroxisome** small, round organelle that contains hydrogen peroxide, oxidizes fatty acids and amino acids, and detoxifies many poisons
- **plasma membrane** phospholipid bilayer with embedded (integral) or attached (peripheral) proteins, and separates the internal content of the cell from its surrounding environment

ribosome cellular structure that carries out protein synthesis

unified cell theory a biological concept that states that all organisms are composed of one or more cells; the

cell is the basic unit of life; and new cells arise from existing cells

- vacuole membrane-bound sac, somewhat larger than a vesicle, which functions in cellular storage and transport
- **vesicle** small, membrane-bound sac that functions in cellular storage and transport; its membrane is capable of fusing with the plasma membrane and the membranes of the endoplasmic reticulum and Golgi apparatus

## CHAPTER SUMMARY

#### 5.1 Studying Cells

A cell is the smallest unit of life. Most cells are so tiny that they cannot be seen with the naked eye. Therefore, scientists use microscopes to study cells. Electron microscopes provide higher magnification, higher resolution, and more detail than light microscopes. The unified cell theory states that all organisms are composed of one or more cells, the cell is the basic unit of life, and new cells arise from existing cells.

#### 5.2 Eukaryotic Cells

Like a prokaryotic cell, a eukaryotic cell has a plasma membrane, cytoplasm, and ribosomes, but a eukaryotic cell is typically larger than a prokaryotic cell, has a true nucleus (meaning its DNA is surrounded by a membrane), and has other membrane-bound organelles that allow for compartmentalization of functions. The plasma membrane is a phospholipid bilayer embedded with proteins. The nucleus's nucleolus is the site of ribosome assembly. Ribosomes are either found in the cytoplasm or attached to the cytoplasmic side of the plasma membrane or endoplasmic reticulum. They perform protein synthesis. Mitochondria participate in cellular respiration; they are responsible for the majority of ATP produced in the cell. Peroxisomes hydrolyze fatty acids, amino acids, and some toxins. Vesicles and vacuoles are storage and transport compartments. In plant cells, vacuoles also help break down macromolecules.

Animal cells also have a centrosome and lysosomes. The centrosome has two bodies perpendicular to each other, the centrioles, and has an unknown purpose in cell division. Lysosomes are the digestive organelles of animal cells.

Plant cells and plant-like cells each have a cell wall, chloroplasts, and a central vacuole. The plant cell wall, whose primary component is cellulose, protects the cell, provides structural support, and gives shape to the cell. Photosynthesis takes place in chloroplasts. The central vacuole can expand without having to produce more cytoplasm.

## **ART CONNECTION QUESTIONS**

**1. Figure 5.5** If the nucleolus were not able to carry out its function, what other cellular organelles would

be affected?

## **REVIEW QUESTIONS**

**2.** When viewing a specimen through a light microscope, scientists use \_\_\_\_\_\_ to distinguish the individual components of cells.

- a. a beam of electrons
- b. radioactive isotopes
- c. special stains
- d. high temperatures

**3.** The \_\_\_\_\_\_ is the basic unit of life.

- a. organism
- b. cell
- c. tissue
- d. organ

**4.** Which of the following is surrounded by two phospholipid bilayers?

- a. the ribosomes
- b. the vesicles
- c. the cytoplasm
- d. the nucleoplasm

**5.** Peroxisomes got their name because hydrogen peroxide is:

- a. used in their detoxification reactions
- b. produced during their oxidation reactions
- c. incorporated into their membranes
- d. a cofactor for the organelles' enzymes

**6.** In plant cells, the function of the lysosomes is carried out by \_\_\_\_\_.

- a. vacuoles
- b. peroxisomes
- c. ribosomes
- d. nuclei

7. Which of the following is found both in eukaryotic

## **CRITICAL THINKING QUESTIONS**

8. In your everyday life, you have probably noticed that certain instruments are ideal for certain situations. For example, you would use a spoon rather than a fork to eat soup because a spoon is shaped for scooping, while soup would slip between the tines of a fork. The use of ideal instruments also applies in science. In what situation(s) would the use of a light microscope be ideal, and why?

**9.** In what situation(s) would the use of a scanning electron microscope be ideal, and why?

10. In what situation(s) would a transmission electron

and prokaryotic cells?

- a. nucleus
- b. mitochondrion
- c. vacuole
- d. ribosomes

microscope be ideal, and why?

**11.** What are the advantages and disadvantages of each of these types of microscopes?

**12.** You already know that ribosomes are abundant in red blood cells. In what other cells of the body would you find them in great abundance? Why?

**13.** What are the structural and functional similarities and differences between mitochondria and chloroplasts?

# 6 | STRUCTURE AND FUNCTION OF PLASMA MEMBRANES



**Figure 6.1** Despite its seeming hustle and bustle, Grand Central Station functions with a high level of organization: People and objects move from one location to another, they cross or are contained within certain boundaries, and they provide a constant flow as part of larger activity. Analogously, a plasma membrane's functions involve movement within the cell and across boundaries in the process of intracellular and intercellular activities. (credit: modification of work by Randy Le'Moine)

## **Chapter Outline**

6.1: Components and Structure

6.2: Passive Transport

6.3: Active Transport

#### Introduction

The plasma membrane, which is also called the cell membrane, has many functions, but the most basic one is to define the borders of the cell and keep the cell functional. The plasma membrane is selectively permeable. This means that the membrane allows some materials to freely enter or leave the cell, while other materials cannot move freely, but require the use of a specialized structure, and occasionally, even energy investment for crossing.

## 6.1 | Components and Structure

By the end of this section, you will be able to:

- · Understand the fluid mosaic model of cell membranes
- · Describe the functions of phospholipids, proteins, and carbohydrates in membranes
- Discuss membrane fluidity

A cell's plasma membrane defines the cell, outlines its borders, and determines the nature of its interaction with its environment (see **Table 6.1** for a summary). Cells exclude some substances, take in others, and excrete still others, all in controlled quantities. The plasma membrane must be very flexible to allow certain cells, such as red blood cells and white blood cells, to change shape as they pass through narrow capillaries. These are the more obvious functions of a plasma membrane. In addition, the surface of the plasma membrane carries markers that allow cells to recognize one another, which is vital for tissue and organ formation during early development, and which later plays a role in the "self" versus "non-self" distinction of the immune response.

Among the most sophisticated functions of the plasma membrane is the ability to transmit signals by means of complex, integral proteins known as receptors. These proteins act both as receivers of extracellular inputs and as activators of intracellular processes. These membrane receptors provide extracellular attachment sites for effectors like hormones and growth factors, and they activate intracellular response cascades when their effectors are bound. Occasionally, receptors are hijacked by viruses (HIV, human immunodeficiency virus, is one example) that use them to gain entry into cells, and at times, the genes encoding receptors become mutated, causing the process of signal transduction to malfunction with disastrous consequences.

### Fluid Mosaic Model

The existence of the plasma membrane was identified in the 1890s, and its chemical components were identified in 1915. The principal components identified at that time were lipids and proteins. The first widely accepted model of the plasma membrane's structure was proposed in 1935 by Hugh Davson and James Danielli; it was based on the "railroad track" appearance of the plasma membrane in early electron micrographs. They theorized that the structure of the plasma membrane resembles a sandwich, with protein being analogous to the bread, and lipids being analogous to the filling. In the 1950s, advances in microscopy, notably transmission electron microscopy (TEM), allowed researchers to see that the core of the plasma membrane consisted of a double, rather than a single, layer. A new model that better explains both the microscopic observations and the function of that plasma membrane was proposed by S.J. Singer and Garth L. Nicolson in 1972.

The explanation proposed by Singer and Nicolson is called the **fluid mosaic model**. The model has evolved somewhat over time, but it still best accounts for the structure and functions of the plasma membrane as we now understand them. The fluid mosaic model describes the structure of the plasma membrane as a mosaic of components—including phospholipids, cholesterol, proteins, and carbohydrates—that gives the membrane a fluid character. Plasma membranes range from 5 to 10 nm in thickness. For comparison, human red blood cells, visible via light microscopy, are approximately 8 µm wide, or approximately 1,000 times wider than a plasma membrane. The membrane does look a bit like a sandwich (Figure 6.2).



**Figure 6.2** The fluid mosaic model of the plasma membrane describes the plasma membrane as a fluid combination of phospholipids, cholesterol, and proteins. Carbohydrates attached to lipids (glycolipids) and to proteins (glycoproteins) extend from the outward-facing surface of the membrane.

The principal components of a plasma membrane are lipids (phospholipids and cholesterol), proteins, and carbohydrates attached to some of the lipids and some of the proteins. A phospholipid is a molecule consisting of glycerol, two fatty acids, and a phosphate-linked head group. Cholesterol, another lipid composed of four fused carbon rings, is found alongside the phospholipids in the core of the membrane. The proportions of proteins, lipids, and carbohydrates in the plasma membrane vary with cell type, but for a typical human cell, protein accounts for about 50 percent of the composition by mass, lipids (of all types) account for about 40 percent of the composition by mass, with the remaining 10 percent of the composition by mass being carbohydrates. However, the concentration of proteins and lipids varies with different cell membranes. For example, myelin, an outgrowth of the membrane of specialized cells that insulates the axons of the peripheral nerves, contains only 18 percent lipid. The plasma membrane of human red blood cells is 30 percent lipid. Carbohydrates are present only on the exterior surface of the plasma membrane and are attached to proteins, forming **glycoproteins**, or attached to lipids, forming **glycolipids**.

#### Phospholipids

The main fabric of the membrane is composed of amphiphilic, phospholipid molecules. The **hydrophilic** or "water-loving" areas of these molecules (which look like a collection of balls in an artist's rendition of the model) (Figure 6.2) are in contact with the aqueous fluid both inside and outside the cell. **Hydrophobic**, or water-hating molecules, tend to be non-polar. They interact with other non-polar molecules in chemical reactions, but generally do not interact with polar molecules. When placed in water, hydrophobic molecules tend to form a ball or cluster. The hydrophilic regions of the phospholipids tend to form hydrogen bonds with water and other polar molecules on both the exterior and interior of the cell. Thus, the membrane surfaces that face the interior and exterior of the cell are hydrophilic. In contrast, the interior of the cell membrane is hydrophobic and will not interact with water. Therefore, phospholipids form an excellent two-layer cell membrane that separates fluid within the cell from the fluid outside of the cell.

A phospholipid molecule (Figure 6.3) consists of a three-carbon glycerol backbone with two fatty acid molecules attached to carbons 1 and 2, and a phosphate-containing group attached to the third carbon. This arrangement gives the overall molecule an area described as its head (the phosphate-containing group), which has a polar character or negative charge, and an area called the tail (the fatty acids), which has no charge. The head can form hydrogen bonds, but the tail cannot. A molecule with this arrangement of a positively or negatively charged area and an uncharged, or non-polar, area is referred to as **amphiphilic** or "dual-loving."



**Figure 6.3** This phospholipid molecule is composed of a hydrophilic head and two hydrophobic tails. The hydrophilic head group consists of a phosphate-containing group attached to a glycerol molecule. The hydrophobic tails, each containing either a saturated or an unsaturated fatty acid, are long hydrocarbon chains.

This characteristic is vital to the structure of a plasma membrane because, in water, phospholipids tend to become arranged with their hydrophobic tails facing each other and their hydrophilic heads facing out. In this way, they form a lipid bilayer—a barrier composed of a double layer of phospholipids that separates the water and other materials on one side of the barrier from the water and other materials on the other side. In fact, phospholipids heated in an aqueous solution tend to spontaneously form small spheres or droplets (called micelles or liposomes), with their hydrophilic heads forming the exterior and their hydrophobic tails on the inside (**Figure 6.4**).


Figure 6.4 In an aqueous solution, phospholipids tend to arrange themselves with their polar heads facing outward and their hydrophobic tails facing inward. (credit: modification of work by Mariana Ruiz Villareal)

#### **Proteins**

Proteins make up the second major component of plasma membranes. **Integral proteins** (some specialized types are called integrins) are, as their name suggests, integrated completely into the membrane structure, and their hydrophobic membrane-spanning regions interact with the hydrophobic region of the the phospholipid bilayer (**Figure 6.2**). Single-pass integral membrane proteins usually have a hydrophobic transmembrane segment that consists of 20–25 amino acids. Some span only part of the membrane—associating with a single layer—while others stretch from one side of the membrane to the other, and are exposed on either side. Some complex proteins are composed of up to 12 segments of a single protein, which are extensively folded and embedded in the membrane (**Figure 6.5**). This type of protein has a hydrophilic region or regions, and one or several mildly hydrophobic regions. This arrangement of regions of the protein tends to orient the protein alongside the phospholipids, with the hydrophobic region of the protein adjacent to the tails of the phospholipids and the hydrophilic region or regions of the protein protein from the membrane and in contact with the cytosol or extracellular fluid.



Figure 6.5 Integral membranes proteins may have one or more alpha-helices that span the membrane (examples 1 and 2), or they may have beta-sheets that span the membrane (example 3). (credit: "Foobar"/Wikimedia Commons)

**Peripheral proteins** are found on the exterior and interior surfaces of membranes, attached either to integral proteins or to phospholipids. Peripheral proteins, along with integral proteins, may serve as enzymes, as structural attachments for the fibers of the cytoskeleton, or as part of the cell's recognition sites. These are sometimes referred to as "cell-specific" proteins. The body recognizes its own proteins and attacks foreign proteins associated with invasive pathogens.

#### Carbohydrates

Carbohydrates are the third major component of plasma membranes. They are always found on the exterior surface of cells and are bound either to proteins (forming glycoproteins) or to lipids (forming glycolipids) (**Figure 6.2**). These carbohydrate chains may consist of 2–60 monosaccharide units and can be either straight or branched. Along with peripheral proteins, carbohydrates form specialized sites on the cell surface that allow cells to recognize each other. These sites have unique patterns that allow the cell to be recognized, much the way that the facial features unique to each person allow him or her to be recognized. This recognition function is very important to cells, as it allows the immune system to differentiate between body cells (called "self") and foreign cells or tissues (called "non-self"). Similar types of glycoproteins and glycolipids are found on the surfaces of viruses and may change frequently, preventing immune cells from recognizing and attacking them.

These carbohydrates on the exterior surface of the cell—the carbohydrate components of both glycoproteins and glycolipids—are collectively referred to as the glycocalyx (meaning "sugar coating"). The glycocalyx is highly hydrophilic and attracts large amounts of water to the surface of the cell. This aids in the interaction of the cell with its watery environment and in the cell's ability to obtain substances dissolved in the water. As discussed above, the glycocalyx is also important for cell identification, self/non-self determination, and embryonic development, and is used in cell-cell attachments to form tissues.

# e olution CONNECTION

# How Viruses Infect Specific Organs

Glycoprotein and glycolipid patterns on the surfaces of cells give many viruses an opportunity for infection. HIV and hepatitis viruses infect only specific organs or cells in the human body. HIV is able to penetrate the plasma membranes of a subtype of lymphocytes called T-helper cells, as well as some monocytes and central nervous system cells. The hepatitis virus attacks liver cells.

These viruses are able to invade these cells, because the cells have binding sites on their surfaces that are specific to and compatible with certain viruses (Figure 6.6). Other recognition sites on the virus's surface interact with the human immune system, prompting the body to produce antibodies. Antibodies are made in response to the antigens or proteins associated with invasive pathogens, or in response to foreign cells, such as might occur with an organ transplant. These same sites serve as places for antibodies to attach and either destroy or inhibit the activity of the virus. Unfortunately, these recognition sites on HIV change at a rapid rate because of mutations, making the production of an effective vaccine against the virus very difficult, as the virus evolves and adapts. A person infected with HIV will quickly develop different populations, or variants, of the virus that are distinguished by differences in these recognition sites. This rapid change of surface markers decreases the effectiveness of the person's immune system in attacking the virus, because the antibodies will not recognize the new variations of the surface patterns. In the case of HIV, the problem is compounded by the fact that the virus specifically infects and destroys cells involved in the immune response, further incapacitating the host.



Figure 6.6 HIV binds to the CD4 receptor, a glycoprotein on the surfaces of T cells. (credit: modification of work by NIH, NIAID)

## **Membrane Fluidity**

The mosaic characteristic of the membrane, described in the fluid mosaic model, helps to illustrate its nature. The integral proteins and lipids exist in the membrane as separate but loosely attached molecules. These resemble the separate, multicolored tiles of a mosaic picture, and they float, moving somewhat with respect to one another. The membrane is not like a balloon, however, that can expand and contract; rather, it is fairly rigid

and can burst if penetrated or if a cell takes in too much water. However, because of its mosaic nature, a very fine needle can easily penetrate a plasma membrane without causing it to burst, and the membrane will flow and self-seal when the needle is extracted.

The mosaic characteristics of the membrane explain some but not all of its fluidity. There are two other factors that help maintain this fluid characteristic. One factor is the nature of the phospholipids themselves. In their saturated form, the fatty acids in phospholipid tails are saturated with bound hydrogen atoms. There are no double bonds between adjacent carbon atoms. This results in tails that are relatively straight. In contrast, unsaturated fatty acids do not contain a maximal number of hydrogen atoms, but they do contain some double bonds between adjacent carbon atoms; a double bond results in a bend in the string of carbons of approximately 30 degrees (Figure 6.3).

Thus, if saturated fatty acids, with their straight tails, are compressed by decreasing temperatures, they press in on each other, making a dense and fairly rigid membrane. If unsaturated fatty acids are compressed, the "kinks" in their tails elbow adjacent phospholipid molecules away, maintaining some space between the phospholipid molecules. This "elbow room" helps to maintain fluidity in the membrane at temperatures at which membranes with saturated fatty acid tails in their phospholipids would "freeze" or solidify. The relative fluidity of the membrane is particularly important in a cold environment. A cold environment tends to compress membranes composed largely of saturated fatty acids, making them less fluid and more susceptible to rupturing. Many organisms (fish are one example) are capable of adapting to cold environments by changing the proportion of unsaturated fatty acids in their membranes to "





Visit this **site (http://openstaxcollege.org/l/biological\_memb)** to see animations of the fluidity and mosaic quality of membranes.

Animals have an additional membrane constituent that assists in maintaining fluidity. Cholesterol, which lies alongside the phospholipids in the membrane, tends to dampen the effects of temperature on the membrane. Thus, this lipid functions as a buffer, preventing lower temperatures from inhibiting fluidity and preventing increased temperatures from increasing fluidity too much. Thus, cholesterol extends, in both directions, the range of temperature in which the membrane is appropriately fluid and consequently functional. Cholesterol also serves other functions, such as organizing clusters of transmembrane proteins into lipid rafts.

Component	Location
Phospholipid	Main fabric of the membrane
Cholesterol	Attached between phospholipids and between the two phospholipid layers
Integral proteins (for example, integrins)	Embedded within the phospholipid layer(s). May or may not penetrate through both layers
Peripheral proteins	On the inner or outer surface of the phospholipid bilayer; not embedded within the phospholipids
Carbohydrates (components of glycoproteins and glycolipids)	Generally attached to proteins on the outside membrane layer

#### The Components and Functions of the Plasma Membrane

#### Table 6.1



## Immunologist

The variations in peripheral proteins and carbohydrates that affect a cell's recognition sites are of prime interest in immunology. These changes are taken into consideration in vaccine development. Many infectious diseases, such as smallpox, polio, diphtheria, and tetanus, were conquered by the use of vaccines.

Immunologists are the physicians and scientists who research and develop vaccines, as well as treat and study allergies or other immune problems. Some immunologists study and treat autoimmune problems (diseases in which a person's immune system attacks his or her own cells or tissues, such as lupus) and immunodeficiencies, whether acquired (such as acquired immunodeficiency syndrome, or AIDS) or hereditary (such as severe combined immunodeficiency, or SCID). Immunologists are called in to help treat organ transplantation patients, who must have their immune systems suppressed so that their bodies will not reject a transplanted organ. Some immunologists work to understand natural immunity and the effects of a person's environment on it. Others work on questions about how the immune system affects diseases such as cancer. In the past, the importance of having a healthy immune system in preventing cancer was not at all understood.

To work as an immunologist, a PhD or MD is required. In addition, immunologists undertake at least 2–3 years of training in an accredited program and must pass an examination given by the American Board of Allergy and Immunology. Immunologists must possess knowledge of the functions of the human body as they relate to issues beyond immunization, and knowledge of pharmacology and medical technology, such as medications, therapies, test materials, and surgical procedures.

# 6.2 | Passive Transport

By the end of this section, you will be able to:

- · Explain why and how passive transport occurs
- · Understand the processes of osmosis and diffusion
- · Define tonicity and describe its relevance to passive transport

Plasma membranes must allow certain substances to enter and leave a cell, and prevent some harmful materials from entering and some essential materials from leaving. In other words, plasma membranes are **selectively permeable**—they allow some substances to pass through, but not others. If they were to lose this selectivity, the cell would no longer be able to sustain itself, and it would be destroyed. Some cells require larger amounts of specific substances than do other cells; they must have a way of obtaining these materials from extracellular fluids. This may happen passively, as certain materials move back and forth, or the cell may have special mechanisms that facilitate transport. Some materials are so important to a cell that it spends some of its energy, hydrolyzing adenosine triphosphate (ATP), to obtain these materials. Red blood cells use some of their energy doing just that. All cells spend the majority of their energy to maintain an imbalance of sodium and potassium ions between the interior and exterior of the cell.

The most direct forms of membrane transport are passive. **Passive transport** is a naturally occurring phenomenon and does not require the cell to exert any of its energy to accomplish the movement. In passive transport, substances move from an area of higher concentration to an area of lower concentration. A physical space in which there is a range of concentrations of a single substance is said to have a **concentration gradient**.

# Selective Permeability

Plasma membranes are asymmetric: the interior of the membrane is not identical to the exterior of the membrane. In fact, there is a considerable difference between the array of phospholipids and proteins between

the two leaflets that form a membrane. On the interior of the membrane, some proteins serve to anchor the membrane to fibers of the cytoskeleton. There are peripheral proteins on the exterior of the membrane that bind elements of the extracellular matrix. Carbohydrates, attached to lipids or proteins, are also found on the exterior surface of the plasma membrane. These carbohydrate complexes help the cell bind substances that the cell needs in the extracellular fluid. This adds considerably to the selective nature of plasma membranes (Figure 6.7).



Figure 6.7 The exterior surface of the plasma membrane is not identical to the interior surface of the same membrane.

Recall that plasma membranes are amphiphilic: They have hydrophilic and hydrophobic regions. This characteristic helps the movement of some materials through the membrane and hinders the movement of others. Lipid-soluble material with a low molecular weight can easily slip through the hydrophobic lipid core of the membrane. Substances such as the fat-soluble vitamins A, D, E, and K readily pass through the plasma membranes in the digestive tract and other tissues. Fat-soluble drugs and hormones also gain easy entry into cells and are readily transported into the body's tissues and organs. Molecules of oxygen and carbon dioxide have no charge and so pass through membranes by simple diffusion.

Polar substances present problems for the membrane. While some polar molecules connect easily with the outside of a cell, they cannot readily pass through the lipid core of the plasma membrane. Additionally, while small ions could easily slip through the spaces in the mosaic of the membrane, their charge prevents them from doing so. Ions such as sodium, potassium, calcium, and chloride must have special means of penetrating plasma membranes. Simple sugars and amino acids also need help with transport across plasma membranes, achieved by various transmembrane proteins (channels).

# Diffusion

**Diffusion** is a passive process of transport. A single substance tends to move from an area of high concentration to an area of low concentration until the concentration is equal across a space. You are familiar with diffusion of substances through the air. For example, think about someone opening a bottle of ammonia in a room filled with people. The ammonia gas is at its highest concentration in the bottle; its lowest concentration is at the edges of the room. The ammonia vapor will diffuse, or spread away, from the bottle, and gradually, more and more people will smell the ammonia as it spreads. Materials move within the cell's cytosol by diffusion, and certain materials move through the plasma membrane by diffusion (Figure 6.8). Diffusion expends no energy. On the contrary, concentration gradients are a form of potential energy, dissipated as the gradient is eliminated.



**Figure 6.8** Diffusion through a permeable membrane moves a substance from an area of high concentration (extracellular fluid, in this case) down its concentration gradient (into the cytoplasm). (credit: modification of work by Mariana Ruiz Villareal)

Each separate substance in a medium, such as the extracellular fluid, has its own concentration gradient, independent of the concentration gradients of other materials. In addition, each substance will diffuse according to that gradient. Within a system, there will be different rates of diffusion of the different substances in the medium.

#### Factors That Affect Diffusion

Molecules move constantly in a random manner, at a rate that depends on their mass, their environment, and the amount of thermal energy they possess, which in turn is a function of temperature. This movement accounts for the diffusion of molecules through whatever medium in which they are localized. A substance will tend to move into any space available to it until it is evenly distributed throughout it. After a substance has diffused completely through a space, removing its concentration gradient, molecules will still move around in the space, but there will be no *net* movement of the number of molecules from one area to another. This lack of a concentration gradient in which there is no net movement of a substance is known as dynamic equilibrium. While diffusion will go forward in the presence of a concentration gradient of a substance, several factors affect the rate of diffusion.

- Extent of the concentration gradient: The greater the difference in concentration, the more rapid the diffusion. The closer the distribution of the material gets to equilibrium, the slower the rate of diffusion becomes.
- Mass of the molecules diffusing: Heavier molecules move more slowly; therefore, they diffuse more slowly. The reverse is true for lighter molecules.
- Temperature: Higher temperatures increase the energy and therefore the movement of the molecules, increasing the rate of diffusion. Lower temperatures decrease the energy of the molecules, thus decreasing the rate of diffusion.
- Solvent density: As the density of a solvent increases, the rate of diffusion decreases. The molecules slow
  down because they have a more difficult time getting through the denser medium. If the medium is less
  dense, diffusion increases. Because cells primarily use diffusion to move materials within the cytoplasm,
  any increase in the cytoplasm's density will inhibit the movement of the materials. An example of this is
  a person experiencing dehydration. As the body's cells lose water, the rate of diffusion decreases in the
  cytoplasm, and the cells' functions deteriorate. Neurons tend to be very sensitive to this effect. Dehydration
  frequently leads to unconsciousness and possibly coma because of the decrease in diffusion rate within the
  cells.
- Solubility: As discussed earlier, nonpolar or lipid-soluble materials pass through plasma membranes more easily than polar materials, allowing a faster rate of diffusion.
- Surface area and thickness of the plasma membrane: Increased surface area increases the rate of diffusion, whereas a thicker membrane reduces it.
- Distance travelled: The greater the distance that a substance must travel, the slower the rate of diffusion. This places an upper limitation on cell size. A large, spherical cell will die because nutrients or waste cannot reach or leave the center of the cell, respectively. Therefore, cells must either be small in size, as in the

case of many prokaryotes, or be flattened, as with many single-celled eukaryotes.

A variation of diffusion is the process of filtration. In filtration, material moves according to its concentration gradient through a membrane; sometimes the rate of diffusion is enhanced by pressure, causing the substances to filter more rapidly. This occurs in the kidney, where blood pressure forces large amounts of water and accompanying dissolved substances, or **solutes**, out of the blood and into the renal tubules. The rate of diffusion in this instance is almost totally dependent on pressure. One of the effects of high blood pressure is the appearance of protein in the urine, which is "squeezed through" by the abnormally high pressure.

# **Facilitated transport**

In **facilitated transport**, also called facilitated diffusion, materials diffuse across the plasma membrane with the help of membrane proteins. A concentration gradient exists that would allow these materials to diffuse into the cell without expending cellular energy. However, these materials are ions are polar molecules that are repelled by the hydrophobic parts of the cell membrane. Facilitated transport proteins shield these materials from the repulsive force of the membrane, allowing them to diffuse into the cell.

The material being transported is first attached to protein or glycoprotein receptors on the exterior surface of the plasma membrane. This allows the material that is needed by the cell to be removed from the extracellular fluid. The substances are then passed to specific integral proteins that facilitate their passage. Some of these integral proteins are collections of beta pleated sheets that form a pore or channel through the phospholipid bilayer. Others are carrier proteins which bind with the substance and aid its diffusion through the membrane.

#### Channels

The integral proteins involved in facilitated transport are collectively referred to as **transport proteins**, and they function as either channels for the material or carriers. In both cases, they are transmembrane proteins. Channels are specific for the substance that is being transported. **Channel proteins** have hydrophilic domains exposed to the intracellular and extracellular fluids; they additionally have a hydrophilic channel through their core that provides a hydrated opening through the membrane layers (**Figure 6.9**). Passage through the channel allows polar compounds to avoid the nonpolar central layer of the plasma membrane that would otherwise slow or prevent their entry into the cell. **Aquaporins** are channel proteins that allow water to pass through the membrane at a very high rate.



**Figure 6.9** Facilitated transport moves substances down their concentration gradients. They may cross the plasma membrane with the aid of channel proteins. (credit: modification of work by Mariana Ruiz Villareal)

Channel proteins are either open at all times or they are "gated," which controls the opening of the channel. The attachment of a particular ion to the channel protein may control the opening, or other mechanisms or substances may be involved. In some tissues, sodium and chloride ions pass freely through open channels, whereas in other tissues a gate must be opened to allow passage. An example of this occurs in the kidney, where both forms of channels are found in different parts of the renal tubules. Cells involved in the transmission

of electrical impulses, such as nerve and muscle cells, have gated channels for sodium, potassium, and calcium in their membranes. Opening and closing of these channels changes the relative concentrations on opposing sides of the membrane of these ions, resulting in the facilitation of electrical transmission along membranes (in the case of nerve cells) or in muscle contraction (in the case of muscle cells).

#### **Carrier Proteins**

Another type of protein embedded in the plasma membrane is a **carrier protein**. This aptly named protein binds a substance and, in doing so, triggers a change of its own shape, moving the bound molecule from the outside of the cell to its interior (**Figure 6.10**); depending on the gradient, the material may move in the opposite direction. Carrier proteins are typically specific for a single substance. This selectivity adds to the overall selectivity of the plasma membrane. The exact mechanism for the change of shape is poorly understood. Proteins can change shape when their hydrogen bonds are affected, but this may not fully explain this mechanism. Each carrier protein is specific to one substance, and there are a finite number of these proteins in any membrane. This can cause problems in transporting enough of the material for the cell to function properly. When all of the proteins are bound to their ligands, they are saturated and the rate of transport is at its maximum. Increasing the concentration gradient at this point will not result in an increased rate of transport.



**Figure 6.10** Some substances are able to move down their concentration gradient across the plasma membrane with the aid of carrier proteins. Carrier proteins change shape as they move molecules across the membrane. (credit: modification of work by Mariana Ruiz Villareal)

An example of this process occurs in the kidney. Glucose, water, salts, ions, and amino acids needed by the body are filtered in one part of the kidney. This filtrate, which includes glucose, is then reabsorbed in another part of the kidney. Because there are only a finite number of carrier proteins for glucose, if more glucose is present than the proteins can handle, the excess is not transported and it is excreted from the body in the urine. In a diabetic individual, this is described as "spilling glucose into the urine." A different group of carrier proteins called glucose transport proteins, or GLUTs, are involved in transporting glucose and other hexose sugars through plasma membranes within the body.

Channel and carrier proteins transport material at different rates. Channel proteins transport much more quickly than do carrier proteins. Channel proteins facilitate diffusion at a rate of tens of millions of molecules per second, whereas carrier proteins work at a rate of a thousand to a million molecules per second.

#### Osmosis

**Osmosis** is the movement of water through a semipermeable membrane according to the concentration gradient of water across the membrane, which is inversely proportional to the concentration of solutes. While diffusion transports material across membranes and within cells, osmosis transports *only water* across a membrane and the membrane limits the diffusion of solutes in the water. Not surprisingly, the aquaporins that facilitate water movement play a large role in osmosis, most prominently in red blood cells and the membranes of kidney tubules.

#### Mechanism

Osmosis is a special case of diffusion. Water, like other substances, moves from an area of high concentration

to one of low concentration. An obvious question is what makes water move at all? Imagine a beaker with a semipermeable membrane separating the two sides or halves (Figure 6.11). On both sides of the membrane the water level is the same, but there are different concentrations of a dissolved substance, or **solute**, that cannot cross the membrane (otherwise the concentrations on each side would be balanced by the solute crossing the membrane). If the volume of the solution on both sides of the membrane is the same, but there are different amounts of water, the solvent, on either side of the membrane.



**Figure 6.11** In osmosis, water always moves from an area of higher water concentration to one of lower concentration. In the diagram shown, the solute cannot pass through the selectively permeable membrane, but the water can.

To illustrate this, imagine two full glasses of water. One has a single teaspoon of sugar in it, whereas the second one contains one-quarter cup of sugar. If the total volume of the solutions in both cups is the same, which cup contains more water? Because the large amount of sugar in the second cup takes up much more space than the teaspoon of sugar in the first cup, the first cup has more water in it.

Returning to the beaker example, recall that it has a mixture of solutes on either side of the membrane. A principle of diffusion is that the molecules move around and will spread evenly throughout the medium if they can. However, only the material capable of getting through the membrane will diffuse through it. In this example, the solute cannot diffuse through the membrane, but the water can. Water has a concentration gradient in this system. Thus, water will diffuse down its concentration gradient, crossing the membrane to the side where it is less concentrated. This diffusion of water through the membrane—osmosis—will continue until the concentration gradient of water goes to zero or until the hydrostatic pressure of the water balances the osmotic pressure. Osmosis proceeds constantly in living systems.

## Tonicity

**Tonicity** describes how an extracellular solution can change the volume of a cell by affecting osmosis. A solution's tonicity often directly correlates with the osmolarity of the solution. **Osmolarity** describes the total solute concentration of the solution. A solution with low osmolarity has a greater number of water molecules relative to the number of solute particles; a solution with high osmolarity has fewer water molecules with respect to solute particles. In a situation in which solutions of two different osmolarities are separated by a membrane permeable to water, though not to the solute, water will move from the side of the membrane with lower osmolarity (and more water) to the side with higher osmolarity (and less water). This effect makes sense if you remember that the solute cannot move across the membrane, and thus the only component in the system that can move—the water—moves along its own concentration gradient. An important distinction that concerns living systems is that osmolarity measures the number of particles (which may be molecules) in a solution. Therefore, a solution that is cloudy with cells may have a lower osmolarity than a solution that is clear, if the second solution contains more dissolved molecules than there are cells.

#### **Hypotonic Solutions**

Three terms—hypotonic, isotonic, and hypertonic—are used to relate the osmolarity of a cell to the osmolarity of the extracellular fluid that contains the cells. In a **hypotonic** situation, the extracellular fluid has lower osmolarity than the fluid inside the cell, and water enters the cell. (In living systems, the point of reference is always the cytoplasm, so the prefix *hypo*- means that the extracellular fluid has a lower concentration of solutes, or a lower osmolarity, than the cell cytoplasm.) It also means that the extracellular fluid has a higher concentration of water in the solution than does the cell. In this situation, water will follow its concentration gradient and enter the cell.

#### **Hypertonic Solutions**

As for a hypertonic solution, the prefix hyper- refers to the extracellular fluid having a higher osmolarity than

the cell's cytoplasm; therefore, the fluid contains less water than the cell does. Because the cell has a relatively higher concentration of water, water will leave the cell.

#### **Isotonic Solutions**

In an **isotonic** solution, the extracellular fluid has the same osmolarity as the cell. If the osmolarity of the cell matches that of the extracellular fluid, there will be no net movement of water into or out of the cell, although water will still move in and out. Blood cells and plant cells in hypertonic, isotonic, and hypotonic solutions take on characteristic appearances (Figure 6.12).



**Figure 6.12** Osmotic pressure changes the shape of red blood cells in hypertonic, isotonic, and hypotonic solutions. (credit: Mariana Ruiz Villareal)

A doctor injects a patient with what the doctor thinks is an isotonic saline solution. The patient dies, and an autopsy reveals that many red blood cells have been destroyed. Do you think the solution the doctor injected was really isotonic?





For a video illustrating the process of diffusion in solutions, visit this **site (http://openstaxcollege.org/l/dispersion)**.

# **Tonicity in Living Systems**

In a hypotonic environment, water enters a cell, and the cell swells. In an isotonic condition, the relative concentrations of solute and solvent are equal on both sides of the membrane. There is no net water movement; therefore, there is no change in the size of the cell. In a hypertonic solution, water leaves a cell and the cell shrinks. If either the hypo- or hyper- condition goes to excess, the cell's functions become compromised, and the cell may be destroyed.

A red blood cell will burst, or lyse, when it swells beyond the plasma membrane's capability to expand. Remember, the membrane resembles a mosaic, with discrete spaces between the molecules composing it. If the cell swells, and the spaces between the lipids and proteins become too large, the cell will break apart.

In contrast, when excessive amounts of water leave a red blood cell, the cell shrinks, or crenates. This has the effect of concentrating the solutes left in the cell, making the cytosol denser and interfering with diffusion within the cell. The cell's ability to function will be compromised and may also result in the death of the cell.

Various living things have ways of controlling the effects of osmosis—a mechanism called osmoregulation. Some organisms, such as plants, fungi, bacteria, and some protists, have cell walls that surround the plasma

membrane and prevent cell lysis in a hypotonic solution. The plasma membrane can only expand to the limit of the cell wall, so the cell will not lyse. In fact, the cytoplasm in plants is always slightly hypertonic to the cellular environment, and water will always enter a cell if water is available. This inflow of water produces turgor pressure, which stiffens the cell walls of the plant (Figure 6.13). In nonwoody plants, turgor pressure supports the plant. Conversly, if the plant is not watered, the extracellular fluid will become hypertonic, causing water to leave the cell. In this condition, the cell does not shrink because the cell wall is not flexible. However, the cell membrane detaches from the wall and constricts the cytoplasm. This is called **plasmolysis**. Plants lose turgor pressure in this condition and wilt (Figure 6.14).



Figure 6.13 The turgor pressure within a plant cell depends on the tonicity of the solution that it is bathed in. (credit: modification of work by Mariana Ruiz Villareal)



Figure 6.14 Without adequate water, the plant on the left has lost turgor pressure, visible in its wilting; the turgor pressure is restored by watering it (right). (credit: Victor M. Vicente Selvas)

Tonicity is a concern for all living things. For example, paramecia and amoebas, which are protists that lack cell walls, have contractile vacuoles. This vesicle collects excess water from the cell and pumps it out, keeping the cell from lysing as it takes on water from its environment (Figure 6.15).



**Figure 6.15** A paramecium's contractile vacuole, here visualized using bright field light microscopy at 480x magnification, continuously pumps water out of the organism's body to keep it from bursting in a hypotonic medium. (credit: modification of work by NIH; scale-bar data from Matt Russell)

Many marine invertebrates have internal salt levels matched to their environments, making them isotonic with the water in which they live. Fish, however, must spend approximately five percent of their metabolic energy maintaining osmotic homeostasis. Freshwater fish live in an environment that is hypotonic to their cells. These fish actively take in salt through their gills and excrete diluted urine to rid themselves of excess water. Saltwater fish live in the reverse environment, which is hypertonic to their cells, and they secrete salt through their gills and excrete highly concentrated urine.

In vertebrates, the kidneys regulate the amount of water in the body. Osmoreceptors are specialized cells in the brain that monitor the concentration of solutes in the blood. If the levels of solutes increase beyond a certain range, a hormone is released that retards water loss through the kidney and dilutes the blood to safer levels. Animals also have high concentrations of albumin, which is produced by the liver, in their blood. This protein is too large to pass easily through plasma membranes and is a major factor in controlling the osmotic pressures applied to tissues.

# 6.3 | Active Transport

By the end of this section, you will be able to:

- Understand how electrochemical gradients affect ions
- · Distinguish between primary active transport and secondary active transport

Active transport mechanisms require the use of the cell's energy, usually in the form of adenosine triphosphate (ATP). If a substance must move into the cell against its concentration gradient—that is, if the concentration of the substance inside the cell is greater than its concentration in the extracellular fluid (and vice versa)—the cell must use energy to move the substance. Some active transport mechanisms move small-molecular weight materials, such as ions, through the membrane. Other mechanisms transport much larger molecules.

# **Electrochemical Gradient**

We have discussed simple concentration gradients—differential concentrations of a substance across a space or a membrane—but in living systems, gradients are more complex. Because ions move into and out of cells and because cells contain proteins that do not move across the membrane and are mostly negatively charged, there is also an electrical gradient, a difference of charge, across the plasma membrane. The interior of living cells is electrically negative with respect to the extracellular fluid in which they are bathed, and at the same time, cells have higher concentrations of potassium (K<sup>+</sup>) and lower concentrations of sodium (Na<sup>+</sup>) than does the extracellular fluid. So in a living cell, the concentration gradient of Na<sup>+</sup> tends to drive it into the cell, and the electrical gradient of Na<sup>+</sup> (a positive ion) also tends to drive it inward to the negatively charged interior. The situation is more complex, however, for other elements such as potassium. The electrical gradient of K<sup>+</sup>, a positive ion, also tends to drive it into the cell, but the concentration gradient of K<sup>+</sup> tends to drive K<sup>+</sup> *out* of the cell (**Figure 6.16**). The combined gradient of concentration and electrical charge that affects an ion is called its **electrochemical gradient**.



**Figure 6.16** Electrochemical gradients arise from the combined effects of concentration gradients and electrical gradients. (credit: "Synaptitude"/Wikimedia Commons)

Injection of a potassium solution into a person's blood is lethal; this is used in capital punishment and euthanasia. Why do you think a potassium solution injection is lethal?

#### Moving Against a Gradient

To move substances against a concentration or electrochemical gradient, the cell must use energy. This energy is harvested from ATP generated through the cell's metabolism. Active transport mechanisms, collectively called **pumps**, work against electrochemical gradients. Small substances constantly pass through plasma membranes. Active transport maintains concentrations of ions and other substances needed by living cells in the face of these passive movements. Much of a cell's supply of metabolic energy may be spent maintaining these processes. (Most of a red blood cell's metabolic energy is used to maintain the imbalance between exterior and interior sodium and potassium levels required by the cell.) Because active transport mechanisms depend on a cell's metabolism for energy, they are sensitive to many metabolic poisons that interfere with the supply of ATP.

Two mechanisms exist for the transport of small-molecular weight material and small molecules. **Primary active transport** moves ions across a membrane and creates a difference in charge across that membrane, which is directly dependent on ATP. **Secondary active transport** describes the movement of material that is due to the electrochemical gradient established by primary active transport that does not directly require ATP.

#### **Carrier Proteins for Active Transport**

An important membrane adaption for active transport is the presence of specific carrier proteins or pumps to facilitate movement: there are three types of these proteins or **transporters (Figure 6.17)**. A **uniporter** carries one specific ion or molecule. A **symporter** carries two different ions or molecules, both in the same direction. An **antiporter** also carries two different ions or molecules, but in different directions. All of these transporters can also transport small, uncharged organic molecules like glucose. These three types of carrier proteins are also found in facilitated diffusion, but they do not require ATP to work in that process. Some examples of pumps for active transport are Na<sup>+</sup>-K<sup>+</sup> ATPase, which carries sodium and potassium ions, and H<sup>+</sup>-K<sup>+</sup> ATPase, which

carries hydrogen and potassium ions. Both of these are antiporter carrier proteins. Two other carrier proteins are  $Ca^{2+}$  ATPase and H<sup>+</sup> ATPase, which carry only calcium and only hydrogen ions, respectively. Both are pumps.



Figure 6.17 A uniporter carries one molecule or ion. A symporter carries two different molecules or ions, both in the same direction. An antiporter also carries two different molecules or ions, but in different directions. (credit: modification of work by "Lupask"/Wikimedia Commons)

# **Primary Active Transport**

The primary active transport that functions with the active transport of sodium and potassium allows secondary active transport to occur. The second transport method is still considered active because it depends on the use of energy as does primary transport (Figure 6.18).



Figure 6.18 Primary active transport moves ions across a membrane, creating an electrochemical gradient (electrogenic transport). (credit: modification of work by Mariana Ruiz Villareal)

One of the most important pumps in animals cells is the sodium-potassium pump ( $Na^+-K^+$  ATPase), which maintains the electrochemical gradient (and the correct concentrations of  $Na^+$  and  $K^+$ ) in living cells. The sodium-potassium pump moves  $K^+$  into the cell while moving  $Na^+$  out at the same time, at a ratio of three  $Na^+$  for every two  $K^+$  ions moved in. The  $Na^+-K^+$  ATPase exists in two forms, depending on its orientation to the interior or exterior of the cell and its affinity for either sodium or potassium ions. The process consists of the following six steps.

- 1. With the enzyme oriented towards the interior of the cell, the carrier has a high affinity for sodium ions. Three ions bind to the protein.
- 2. ATP is hydrolyzed by the protein carrier and a low-energy phosphate group attaches to it.
- 3. As a result, the carrier changes shape and re-orients itself towards the exterior of the membrane. The protein's affinity for sodium decreases and the three sodium ions leave the carrier.
- 4. The shape change increases the carrier's affinity for potassium ions, and two such ions attach to the protein. Subsequently, the low-energy phosphate group detaches from the carrier.
- 5. With the phosphate group removed and potassium ions attached, the carrier protein repositions itself towards the interior of the cell.

6. The carrier protein, in its new configuration, has a decreased affinity for potassium, and the two ions are released into the cytoplasm. The protein now has a higher affinity for sodium ions, and the process starts again.

Several things have happened as a result of this process. At this point, there are more sodium ions outside of the cell than inside and more potassium ions inside than out. For every three ions of sodium that move out, two ions of potassium move in. This results in the interior being slightly more negative relative to the exterior. This difference in charge is important in creating the conditions necessary for the secondary process. The sodium-potassium pump is, therefore, an **electrogenic pump** (a pump that creates a charge imbalance), creating an electrical imbalance across the membrane and contributing to the membrane potential.

Link to Learning



Watch this video (https://openstax.org/l/Na\_K\_ATPase) to see a simulation of active transport in a sodium-potassium ATPase.

# Secondary Active Transport (Co-transport)

Secondary active transport brings sodium ions, and possibly other compounds, into the cell. As sodium ion concentrations build outside of the plasma membrane because of the action of the primary active transport process, an electrochemical gradient is created. If a channel protein exists and is open, the sodium ions will be pulled through the membrane. This movement is used to transport other substances that can attach themselves to the transport protein through the membrane (Figure 6.19). Many amino acids, as well as glucose, enter a cell this way. This secondary process is also used to store high-energy hydrogen ions in the mitochondria of plant and animal cells for the production of ATP. The potential energy that accumulates in the stored hydrogen ions is translated into kinetic energy as the ions surge through the channel protein ATP synthase, and that energy is used to convert ADP into ATP.



**Figure 6.19** An electrochemical gradient, created by primary active transport, can move other substances against their concentration gradients, a process called co-transport or secondary active transport. (credit: modification of work by Mariana Ruiz Villareal)

If the pH outside the cell decreases, would you expect the amount of amino acids transported into the cell to increase or decrease?

## **KEY TERMS**

active transport method of transporting material that requires energy

- **amphiphilic** molecule possessing a polar or charged area and a nonpolar or uncharged area capable of interacting with both hydrophilic and hydrophobic environments
- antiporter transporter that carries two ions or small molecules in different directions
- aquaporin channel protein that allows water through the membrane at a very high rate
- carrier protein membrane protein that moves a substance across the plasma membrane by changing its own shape
- channel protein membrane protein that allows a substance to pass through its hollow core across the plasma membrane
- concentration gradient area of high concentration adjacent to an area of low concentration
- diffusion passive process of transport of low-molecular weight material according to its concentration gradient
- electrochemical gradient gradient produced by the combined forces of an electrical gradient and a chemical gradient
- electrogenic pump pump that creates a charge imbalance
- facilitated transport process by which material moves down a concentration gradient (from high to low concentration) using integral membrane proteins
- **fluid mosaic model** describes the structure of the plasma membrane as a mosaic of components including phospholipids, cholesterol, proteins, glycoproteins, and glycolipids (sugar chains attached to proteins or lipids, respectively), resulting in a fluid character (fluidity)
- glycolipid combination of carbohydrates and lipids
- glycoprotein combination of carbohydrates and proteins
- hydrophilic molecule with the ability to bond with water; "water-loving"
- hydrophobic molecule that does not have the ability to bond with water; "water-hating"
- **hypertonic** situation in which extracellular fluid has a higher osmolarity than the fluid inside the cell, resulting in water moving out of the cell
- **hypotonic** situation in which extracellular fluid has a lower osmolarity than the fluid inside the cell, resulting in water moving into the cell
- integral protein protein integrated into the membrane structure that interacts extensively with the hydrocarbon chains of membrane lipids and often spans the membrane; these proteins can be removed only by the disruption of the membrane by detergents
- **isotonic** situation in which the extracellular fluid has the same osmolarity as the fluid inside the cell, resulting in no net movement of water into or out of the cell
- osmolarity total amount of substances dissolved in a specific amount of solution
- **osmosis** transport of water through a semipermeable membrane according to the concentration gradient of water across the membrane that results from the presence of solute that cannot pass through the membrane

**passive transport** method of transporting material through a membrane that does not require energy

peripheral protein protein found at the surface of a plasma membrane either on its exterior or interior side;

these proteins can be removed (washed off of the membrane) by a high-salt wash

- **plasmolysis** detaching of the cell membrane from the cell wall and constriction of the cell membrane when a plant cell is in a hypertonic solution
- **primary active transport** active transport that moves ions or small molecules across a membrane and may create a difference in charge across that membrane

pump active transport mechanism that works against electrochemical gradients

secondary active transport movement of material that is due to the electrochemical gradient established by primary active transport

selectively permeable characteristic of a membrane that allows some substances through but not others

solute substance dissolved in a liquid to form a solution

symporter transporter that carries two different ions or small molecules, both in the same direction

tonicity amount of solute in a solution

transport protein membrane protein that facilitates passage of a substance across a membrane by binding it

transporter specific carrier proteins or pumps that facilitate movement

uniporter transporter that carries one specific ion or molecule

# **CHAPTER SUMMARY**

#### 6.1 Components and Structure

The modern understanding of the plasma membrane is referred to as the fluid mosaic model. The plasma membrane is composed of a bilayer of phospholipids, with their hydrophobic, fatty acid tails in contact with each other. The landscape of the membrane is studded with proteins, some of which span the membrane. Some of these proteins serve to transport materials into or out of the cell. Carbohydrates are attached to some of the proteins and lipids on the outward-facing surface of the membrane, forming complexes that function to identify the cell to other cells. The fluid nature of the membrane is due to temperature, the configuration of the fatty acid tails (some kinked by double bonds), the presence of cholesterol embedded in the membrane, and the mosaic nature of the proteins and protein-carbohydrate combinations, which are not firmly fixed in place. Plasma membranes enclose and define the borders of cells, but rather than being a static bag, they are dynamic and constantly in flux.

#### 6.2 Passive Transport

The passive forms of transport, diffusion and osmosis, move materials of small molecular weight across membranes. Substances diffuse from areas of high concentration to areas of lower concentration, and this process continues until the substance is evenly distributed in a system. In solutions containing more than one substance, each type of molecule diffuses according to its own concentration gradient, independent of the diffusion of other substances. Many factors can affect the rate of diffusion, including concentration gradient, size of the particles that are diffusing, temperature of the system, and so on.

In living systems, diffusion of substances into and out of cells is mediated by the plasma membrane. Some materials diffuse readily through the membrane, but others are hindered, and their passage is made possible by specialized proteins, such as channels and transporters. The chemistry of living things occurs in aqueous solutions, and balancing the concentrations of those solutions is an ongoing problem. In living systems, diffusion of some substances would be slow or difficult without membrane proteins that facilitate transport.

#### 6.3 Active Transport

The combined gradient that affects an ion includes its concentration gradient and its electrical gradient. A positive ion, for example, might tend to diffuse into a new area, down its concentration gradient, but if it is diffusing into an area of net positive charge, its diffusion will be hampered by its electrical gradient. When

dealing with ions in aqueous solutions, a combination of the electrochemical and concentration gradients, rather than just the concentration gradient alone, must be considered. Living cells need certain substances that exist inside the cell in concentrations greater than they exist in the extracellular space. Moving substances up their electrochemical gradients requires energy from the cell. Active transport uses energy stored in ATP to fuel this transport. Active transport of small molecular-sized materials uses integral proteins in the cell membrane to move the materials: These proteins are analogous to pumps. Some pumps, which carry out primary active transport, couple directly with ATP to drive their action. In co-transport (or secondary active transport), energy from primary transport can be used to move another substance into the cell and up its concentration gradient.

# **ART CONNECTION QUESTIONS**

**1. Figure 6.12** A doctor injects a patient with what the doctor thinks is an isotonic saline solution. The patient dies, and an autopsy reveals that many red blood cells have been destroyed. Do you think the solution the doctor injected was really isotonic?

2. Figure 6.16 Injection of a potassium solution into a

# **REVIEW QUESTIONS**

**4.** Which plasma membrane component can be either found on its surface or embedded in the membrane structure?

- a. protein
- b. cholesterol
- c. carbohydrate
- d. phospholipid

**5.** Which characteristic of a phospholipid contributes to the fluidity of the membrane?

- a. its head
- b. cholesterol
- c. a saturated fatty acid tail
- d. double bonds in the fatty acid tail

**6.** What is the primary function of carbohydrates attached to the exterior of cell membranes?

- a. identification of the cell
- b. flexibility of the membrane
- c. strengthening the membrane
- d. channels through membrane

7. Water moves via osmosis \_

- a. throughout the cytoplasm
- b. from an area with a high concentration of other solutes to a lower one
- c. from an area with a high concentration of water to one of lower concentration
- d. from an area with a low concentration of water to one of higher concentration

**8.** The principal force driving movement in diffusion is the

- a. temperature
- b. particle size
- c. concentration gradient
- d. membrane surface area

person's blood is lethal; this is used in capital punishment and euthanasia. Why do you think a potassium solution injection is lethal?

**3. Figure 6.19** If the pH outside the cell decreases, would you expect the amount of amino acids transported into the cell to increase or decrease?

**9.** What problem is faced by organisms that live in fresh water?

- a. Their bodies tend to take in too much water.
- b. They have no way of controlling their tonicity.
- c. Only salt water poses problems for animals that live in it.
- d. Their bodies tend to lose too much water to their environment.

**10.** Active transport must function continuously because

- a. plasma membranes wear out
- b. not all membranes are amphiphilic
- c. facilitated transport opposes active transport
- d. diffusion is constantly moving solutes in opposite directions

**11.** How does the sodium-potassium pump make the interior of the cell negatively charged?

- a. by expelling anions
- b. by pulling in anions
- c. by expelling more cations than are taken ind. by taking in and expelling an equal number
- of cations

**12.** What is the combination of an electrical gradient and a concentration gradient called?

- a. potential gradient
- b. electrical potential
- c. concentration potential
- d. electrochemical gradient

# **CRITICAL THINKING QUESTIONS**

**13.** Why is it advantageous for the cell membrane to be fluid in nature?

**14.** Why do phospholipids tend to spontaneously orient themselves into something resembling a membrane?

**15.** Discuss why the following affect the rate of diffusion: molecular size, temperature, solution density, and the distance that must be traveled.

16. Why does water move through a membrane?

**17.** Both of the regular intravenous solutions administered in medicine, normal saline and lactated Ringer's solution, are isotonic. Why is this important?

**18.** Where does the cell get energy for active transport processes?

**19.** How does the sodium-potassium pump contribute to the net negative charge of the interior of the cell?

# 7 | METABOLISM



**Figure 7.1** A hummingbird needs energy to maintain prolonged periods of flight. The bird obtains its energy from taking in food and transforming the nutrients into energy through a series of biochemical reactions. The flight muscles in birds are extremely efficient in energy production. (credit: modification of work by Cory Zanker)

# **Chapter Outline**

- 7.1: Nutrition and Energy Production
- 7.2: Digestive System Processes
- 7.3: Energy and Metabolism
- 7.4: Potential, Kinetic, Free, and Activation Energy
- 7.5: ATP: Adenosine Triphosphate
- 7.6: Overview of Photosynthesis
- 7.7: Collision Theory
- 7.8: Factors Affecting Reaction Rates
- 7.9: Enzymes

## Introduction

Virtually every task performed by living organisms requires energy. Energy is needed to perform heavy labor and exercise, but humans also use a great deal of energy while thinking, and even during sleep. In fact, the living cells of every organism constantly use energy. Nutrients and other molecules are imported, metabolized (broken down) and possibly synthesized into new molecules, modified if needed, transported around the cell, and may be distributed to the entire organism. For example, the large proteins that make up muscles are actively built from smaller molecules. Complex carbohydrates are broken down into simple sugars that the cell uses for energy. Just as energy is required to both build and demolish a building, energy is required for both the synthesis and breakdown of molecules. Additionally, signaling molecules such as hormones and neurotransmitters are transported between cells. Pathogenic bacteria and viruses are ingested and broken down by cells. Cells must also export waste and toxins to stay healthy, and many cells must swim or move surrounding materials via the beating motion of cellular appendages like cilia and flagella.

The cellular processes listed above require a steady supply of energy. From where, and in what form, does this energy come? How do living cells obtain energy, and how do they use it? This chapter will discuss different forms

of energy and the physical laws that govern energy transfer. This chapter will also describe how cells use energy and replenish it, and how chemical reactions in the cell are performed with great efficiency.



Figure 7.2 For humans, fruits and vegetables are important in maintaining a balanced diet. (credit: modification of work by Julie Rybarczyk)

### **Chapter Outline**

- 7.1: Nutrition and Energy Production
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- 7.6: Overview of Photosynthesis
- 7.7: Collision Theory
- 7.8: Factors Affecting Reaction Rates
- 7.9: Enzymes

# Introduction

All living organisms need nutrients to survive. While plants can obtain the molecules required for cellular function through the process of photosynthesis, most animals obtain their nutrients by the consumption of other organisms. At the cellular level, the biological molecules necessary for animal function are amino acids, lipid molecules, nucleotides, and simple sugars. However, the food consumed consists of protein, fat, and complex carbohydrates. Animals must convert these macromolecules into the simple molecules required for maintaining cellular functions, such as assembling new molecules, cells, and tissues. The conversion of the food consumed to the nutrients required is a multi-step process involving digestion and absorption. During digestion, food particles are broken down to smaller components, and later, they are absorbed by the body.

One of the challenges in human nutrition is maintaining a balance between food intake, storage, and energy expenditure. Imbalances can have serious health consequences. For example, eating too much food while not expending much energy leads to obesity, which in turn will increase the risk of developing illnesses

such as type-2 diabetes and cardiovascular disease. The recent rise in obesity and related diseases makes understanding the role of diet and nutrition in maintaining good health all the more important.

# 7.1 | Nutrition and Energy Production

By the end of this section, you will be able to:

- Explain why an animal's diet should be balanced and meet the needs of the body
- · Define the primary components of food
- Describe the essential nutrients required for cellular function that cannot be synthesized by the animal body
- Explain how energy is produced through diet and digestion
- Describe how excess carbohydrates and energy are stored in the body

Given the diversity of animal life on our planet, it is not surprising that the animal diet would also vary substantially. The animal diet is the source of materials needed for building DNA and other complex molecules needed for growth, maintenance, and reproduction; collectively these processes are called biosynthesis. The diet is also the source of materials for ATP production in the cells. The diet must be balanced to provide the minerals and vitamins that are required for cellular function.

# **Food Requirements**

What are the fundamental requirements of the animal diet? The animal diet should be well balanced and provide nutrients required for bodily function and the minerals and vitamins required for maintaining structure and regulation necessary for good health and reproductive capability. These requirements for a human are illustrated graphically in Figure 7.3



Figure 7.3 For humans, a balanced diet includes fruits, vegetables, grains, and protein. (credit: USDA)





The first step in ensuring that you are meeting the food requirements of your body is an awareness of the food groups and the nutrients they provide. To learn more about each food group and the recommended daily amounts, explore this **interactive site (http://openstaxcollege.org/l/food\_groups)** by the United States Department of Agriculture.

# everyday CONNECTION

# Let's Move! Campaign

Obesity is a growing epidemic and the rate of obesity among children is rapidly rising in the United States. To combat childhood obesity and ensure that children get a healthy start in life, first lady Michelle Obama has launched the Let's Move! campaign. The goal of this campaign is to educate parents and caregivers on providing healthy nutrition and encouraging active lifestyles to future generations. This program aims to involve the entire community, including parents, teachers, and healthcare providers to ensure that children have access to healthy foods—more fruits, vegetables, and whole grains—and consume fewer calories from processed foods. Another goal is to ensure that children get physical activity. With the increase in television viewing and stationary pursuits such as video games, sedentary lifestyles have become the norm. Learn more at www.letsmove.gov.

#### **Organic Precursors**

The organic molecules required for building cellular material and tissues must come from food. Carbohydrates or sugars are the primary source of organic carbons in the animal body. During digestion, digestible carbohydrates are ultimately broken down into glucose and used to provide energy through metabolic pathways. Complex carbohydrates, including polysaccharides, can be broken down into glucose through biochemical modification; however, humans do not produce the enzyme cellulase and lack the ability to derive glucose from the polysaccharide cellulose. In humans, these molecules provide the fiber required for moving waste through the large intestine and a healthy colon. The intestinal flora in the human gut are able to extract some nutrition from these plant fibers. The excess sugars in the body are converted into glycogen and stored in the liver and muscles for later use. Glycogen stores are used to fuel prolonged exertions, such as long-distance running, and to provide energy during food shortage. Excess glycogen can be converted to fats, which are stored in the lower layer of the skin of mammals for insulation and energy storage. Excess digestible carbohydrates are stored by mammals in order to survive famine and aid in mobility.

Another important requirement is that of nitrogen. Protein catabolism provides a source of organic nitrogen. Amino acids are the building blocks of proteins and protein breakdown provides amino acids that are used for cellular function. The carbon and nitrogen derived from these become the building block for nucleotides, nucleic acids, proteins, cells, and tissues. Excess nitrogen must be excreted as it is toxic. Fats add flavor to food and promote a sense of satiety or fullness. Fatty foods are also significant sources of energy because one gram of fat contains nine calories. Fats are required in the diet to aid the absorption of fat-soluble vitamins and the production of fat-soluble hormones.

#### **Essential Nutrients**

While the animal body can synthesize many of the molecules required for function from the organic precursors, there are some nutrients that need to be consumed from food. These nutrients are termed **essential nutrients**, meaning they must be eaten, and the body cannot produce them.

The omega-3 alpha-linolenic acid and the omega-6 linoleic acid are essential fatty acids needed to make some membrane phospholipids. **Vitamins** are another class of essential organic molecules that are required in small quantities for many enzymes to function and, for this reason, are considered to be co-enzymes. Absence or low levels of vitamins can have a dramatic effect on health, as outlined in **Table 7.1** and **Table 7.2**. Both fat-soluble

and water-soluble vitamins must be obtained from food. **Minerals**, listed in **Table 7.3**, are inorganic essential nutrients that must be obtained from food. Among their many functions, minerals help in structure and regulation and are considered co-factors. Certain amino acids also must be procured from food and cannot be synthesized by the body. These amino acids are the "essential" amino acids. The human body can synthesize only 11 of the 20 required amino acids; the rest must be obtained from food. The essential amino acids are listed in **Table 7.4**.

Vitamin	Function	Deficiencies Can Lead To	Sources
Vitamin B <sub>1</sub> (Thiamine)	Needed by the body to process lipids, proteins, and carbohydrates Coenzyme removes CO <sub>2</sub> from organic compounds	Muscle weakness, Beriberi: reduced heart function, CNS problems	Milk, meat, dried beans, whole grains
Vitamin B <sub>2</sub> (Riboflavin)	Takes an active role in metabolism, aiding in the conversion of food to energy (FAD and FMN)	Cracks or sores on the outer surface of the lips (cheliosis); inflammation and redness of the tongue; moist, scaly skin inflammation (seborrheic dermatitis)	Meat, eggs, enriched grains, vegetables
Vitamin B <sub>3</sub> (Niacin)	Used by the body to release energy from carbohydrates and to process alcohol; required for the synthesis of sex hormones; component of coenzyme NAD <sup>+</sup> and NADP <sup>+</sup>	Pellagra, which can result in dermatitis, diarrhea, dementia, and death	Meat, eggs, grains, nuts, potatoes
Vitamin B5 (Pantothenic acid)	Assists in producing energy from foods (lipids, in particular); component of coenzyme A	Fatigue, poor coordination, retarded growth, numbness, tingling of hands and feet	Meat, whole grains, milk, fruits, vegetables
Vitamin B <sub>6</sub> (Pyridoxine)	The principal vitamin for processing amino acids and lipids; also helps convert nutrients into energy	Irritability, depression, confusion, mouth sores or ulcers, anemia, muscular twitching	Meat, dairy products, whole grains, orange juice
Vitamin B7 (Biotin)	Used in energy and amino acid metabolism, fat synthesis, and fat breakdown; helps the body use blood sugar	Hair loss, dermatitis, depression, numbness and tingling in the extremities; neuromuscular disorders	Meat, eggs, legumes and other vegetables
Vitamin B9 (Folic acid)	Assists the normal development of cells, especially during fetal development; helps metabolize nucleic and amino acids	Deficiency during pregnancy is associated with birth defects, such as neural tube defects and anemia	Leafy green vegetables, whole wheat, fruits, nuts, legumes
Vitamin B <sub>12</sub> (Cobalamin)	Maintains healthy nervous system and assists with blood cell formation; coenzyme in nucleic acid metabolism	Anemia, neurological disorders, numbness, loss of balance	Meat, eggs, animal products
Vitamin C (Ascorbic acid)	Helps maintain connective tissue: bone, cartilage, and dentin; boosts the immune system	Scurvy, which results in bleeding, hair and tooth loss; joint pain and swelling; delayed wound healing	Citrus fruits, broccoli, tomatoes, red sweet bell peppers

#### Water-soluble Essential Vitamins

Table 7.1

Vitamin	Function	Deficiencies Can Lead To	Sources
Vitamin A (Retinol)	Critical to the development of bones, teeth, and skin; helps maintain eyesight, enhances the immune system, fetal development, gene expression	Night-blindness, skin disorders, impaired immunity	Dark green leafy vegetables, yellow- orange vegetables fruits, milk, butter
Vitamin D	Critical for calcium absorption for bone development and strength; maintains a stable nervous system; maintains a normal and strong heartbeat; helps in blood clotting	Rickets, osteomalacia, immunity	Cod liver oil, milk, egg yolk
Vitamin E (Tocopherol)	Lessens oxidative damage of cells,and prevents lung damage from pollutants; vital to the immune system	Deficiency is rare; anemia, nervous system degeneration	Wheat germ oil, unrefined vegetable oils, nuts, seeds, grains
Vitamin K (Phylloquinone)	Essential to blood clotting	Bleeding and easy bruising	Leafy green vegetables, tea

### **Fat-soluble Essential Vitamins**

#### Table 7.2



Figure 7.4 A healthy diet should include a variety of foods to ensure that needs for essential nutrients are met. (credit: Keith Weller, USDA ARS)

# Minerals and Their Function in the Human Body

Mineral	Function	Deficiencies Can Lead To	Sources
*Calcium	Needed for muscle and neuron function; heart health; builds bone and supports synthesis and function of blood cells; nerve function	Osteoporosis, rickets, muscle spasms, impaired growth	Milk, yogurt, fish, green leafy vegetables, legumes

Mineral	Function	Deficiencies Can Lead To	Sources
*Chlorine	Needed for production of hydrochloric acid (HCl) in the stomach and nerve function; osmotic balance	Muscle cramps, mood disturbances, reduced appetite	Table salt
Copper (trace amounts)	Required component of many redox enzymes, including cytochrome c oxidase; cofactor for hemoglobin synthesis	Copper deficiency is rare	Liver, oysters, cocoa, chocolate, sesame, nuts
lodine	Required for the synthesis of thyroid hormones	Goiter	Seafood, iodized salt, dairy products
Iron	Required for many proteins and enzymes, notably hemoglobin, to prevent anemia	Anemia, which causes poor concentration, fatigue, and poor immune function	Red meat, leafy green vegetables, fish (tuna, salmon), eggs, dried fruits, beans, whole grains
*Magnesium	Required co-factor for ATP formation; bone formation; normal membrane functions; muscle function	Mood disturbances, muscle spasms	Whole grains, leafy green vegetables
Manganese (trace amounts)	A cofactor in enzyme functions; trace amounts are required	Manganese deficiency is rare	Common in most foods
Molybdenum (trace amounts)	Acts as a cofactor for three essential enzymes in humans: sulfite oxidase, xanthine oxidase, and aldehyde oxidase	Molybdenum deficiency is rare	
*Phosphorus	A component of bones and teeth; helps regulate acid-base balance; nucleotide synthesis	Weakness, bone abnormalities, calcium loss	Milk, hard cheese, whole grains, meats
*Potassium	Vital for muscles, heart, and nerve function	Cardiac rhythm disturbance, muscle weakness	Legumes, potato skin, tomatoes, bananas
Selenium (trace amounts)	A cofactor essential to activity of antioxidant enzymes like glutathione peroxidase; trace amounts are required	Selenium deficiency is rare	Common in most foods
*Sodium	Systemic electrolyte required for many functions; acid-base balance; water balance; nerve function	Muscle cramps, fatigue, reduced appetite	Table salt
Zinc (trace amounts)	Required for several enzymes such as carboxypeptidase, liver alcohol dehydrogenase, and carbonic anhydrase	Anemia, poor wound healing, can lead to short stature	Common in most foods
*Greater than	200mg/day required		

# Minerals and Their Function in the Human Body

Table 7.3

Amino acids that must be consumed	Amino acids anabolized by the body
isoleucine	alanine
leucine	selenocysteine
lysine	aspartate
methionine	cysteine
phenylalanine	glutamate
tryptophan	glycine
valine	proline
histidine*	serine
threonine	tyrosine
arginine*	asparagine

#### **Essential Amino Acids**

\*The human body can synthesize histidine and arginine, but not in the quantities required, especially for growing children.

Table 7.4

# Food Energy and ATP

Animals need food to obtain energy and maintain homeostasis. Homeostasis is the ability of a system to maintain a stable internal environment even in the face of external changes to the environment. For example, the normal body temperature of humans is 37°C (98.6°F). Humans maintain this temperature even when the external temperature is hot or cold. It takes energy to maintain this body temperature, and animals obtain this energy from food.

The primary source of energy for animals is carbohydrates, mainly glucose. Glucose is called the body's fuel. The digestible carbohydrates in an animal's diet are converted to glucose molecules through a series of catabolic chemical reactions.

Adenosine triphosphate, or ATP, is the primary energy currency in cells; ATP stores energy in phosphate ester bonds. ATP releases energy when the phosphodiester bonds are broken and ATP is converted to ADP and a phosphate group. ATP is produced by the oxidative reactions in the cytoplasm and mitochondrion of the cell, where carbohydrates, proteins, and fats undergo a series of metabolic reactions collectively called cellular respiration. For example, glycolysis is a series of reactions in which glucose is converted to pyruvic acid and some of its chemical potential energy is transferred to NADH and ATP.

ATP is required for all cellular functions. It is used to build the organic molecules that are required for cells and tissues; it provides energy for muscle contraction and for the transmission of electrical signals in the nervous system. When the amount of ATP is available in excess of the body's requirements, the liver uses the excess ATP and excess glucose to produce molecules called glycogen. Glycogen is a polymeric form of glucose and is stored in the liver and skeletal muscle cells. When blood sugar drops, the liver releases glucose from stores of glycogen. Skeletal muscle converts glycogen to glucose during intense exercise. The process of converting glucose and excess ATP to glycogen and the storage of excess energy is an evolutionarily important step in helping animals deal with mobility, food shortages, and famine.

# everyday CONNECTION

# Obesity

Obesity is a major health concern in the United States, and there is a growing focus on reducing obesity and the diseases it may lead to, such as type-2 diabetes, cancers of the colon and breast, and cardiovascular disease. How does the food consumed contribute to obesity?

Fatty foods are calorie-dense, meaning that they have more calories per unit mass than carbohydrates or proteins. One gram of carbohydrates has four calories, one gram of protein has four calories, and one gram of fat has nine calories. Animals tend to seek lipid-rich food for their higher energy content.

The signals of hunger ("time to eat") and satiety ("time to stop eating") are controlled in the hypothalamus region of the brain. Foods that are rich in fatty acids tend to promote satiety more than foods that are rich only in carbohydrates.

Excess carbohydrate and ATP are used by the liver to synthesize glycogen. The pyruvate produced during glycolysis is used to synthesize fatty acids. When there is more glucose in the body than required, the resulting excess pyruvate is converted into molecules that eventually result in the synthesis of fatty acids within the body. These fatty acids are stored in adipose cells—the fat cells in the mammalian body whose primary role is to store fat for later use.

It is important to note that some animals benefit from obesity. Polar bears and seals need body fat for insulation and to keep them from losing body heat during Arctic winters. When food is scarce, stored body fat provides energy for maintaining homeostasis. Fats prevent famine in mammals, allowing them to access energy when food is not available on a daily basis; fats are stored when a large kill is made or lots of food is available.

# 7.2 | Digestive System Processes

By the end of this section, you will be able to:

- · Describe the process of digestion
- · Detail the steps involved in digestion and absorption
- Define elimination
- Explain the role of both the small and large intestines in absorption

Obtaining nutrition and energy from food is a multi-step process. For true animals, the first step is ingestion, the act of taking in food. This is followed by digestion, absorption, and elimination. In the following sections, each of these steps will be discussed in detail.

# Ingestion

The large molecules found in intact food cannot pass through the cell membranes. Food needs to be broken into smaller particles so that animals can harness the nutrients and organic molecules. The first step in this process is **ingestion**. Ingestion is the process of taking in food through the mouth. In vertebrates, the teeth, saliva, and tongue play important roles in mastication (preparing the food into bolus). While the food is being mechanically broken down, the enzymes in saliva begin to chemically process the food as well. The combined action of these processes modifies the food from large particles to a soft mass that can be swallowed and can travel the length of the esophagus.

# **Digestion and Absorption**

**Digestion** is the mechanical and chemical break down of food into small organic fragments. It is important to break down macromolecules into smaller fragments that are of suitable size for absorption across the digestive epithelium. Large, complex molecules of proteins, polysaccharides, and lipids must be reduced to simpler particles such as simple sugar before they can be absorbed by the digestive epithelial cells. Different organs play

specific roles in the digestive process. The animal diet needs carbohydrates, protein, and fat, as well as vitamins and inorganic components for nutritional balance. How each of these components is digested is discussed in the following sections.

#### Carbohydrates

The digestion of carbohydrates begins in the mouth. The salivary enzyme amylase begins the breakdown of food starches into maltose, a disaccharide. As the bolus of food travels through the esophagus to the stomach, no significant digestion of carbohydrates takes place. The esophagus produces no digestive enzymes but does produce mucous for lubrication. The acidic environment in the stomach stops the action of the amylase enzyme.

The next step of carbohydrate digestion takes place in the duodenum. Recall that the chyme from the stomach enters the duodenum and mixes with the digestive secretion from the pancreas, liver, and gallbladder. Pancreatic juices also contain amylase, which continues the breakdown of starch and glycogen into maltose, a disaccharide. The disaccharides are broken down into monosaccharides by enzymes called **maltases**, **sucrases**, and **lactases**, which are also present in the brush border of the small intestinal wall. Maltase breaks down maltose into glucose. Other disaccharides, such as sucrose and lactose are broken down by sucrase and lactase, respectively. Sucrase breaks down sucrose (or "table sugar") into glucose and fructose, and lactase breaks down lactose (or "milk sugar") into glucose and galactose. The monosaccharides (glucose) thus produced are absorbed and then can be used in metabolic pathways to harness energy. The monosaccharides are transported across the intestinal epithelium into the bloodstream to be transported to the different cells in the body. The steps in carbohydrate digestion are summarized in Figure 7.5 and Table 7.5.



Figure 7.5 Digestion of carbohydrates is performed by several enzymes. Starch and glycogen are broken down into glucose by amylase and maltase. Sucrose (table sugar) and lactose (milk sugar) are broken down by sucrase and lactase, respectively.

#### **Digestion of Carbohydrates**

Enzyme	Produced By	Site of Action	Substrate Acting On	End Products
Salivary amylase	Salivary glands	Mouth	Polysaccharides (Starch)	Disaccharides (maltose), oligosaccharides
Pancreatic amylase	Pancreas	Small intestine	Polysaccharides (starch)	Disaccharides (maltose), monosaccharides
Oligosaccharidases	Lining of the intestine; brush border membrane	Small intestine	Disaccharides	Monosaccharides (e.g., glucose, fructose, galactose)

#### Table 7.5

#### Protein

A large part of protein digestion takes place in the stomach. The enzyme pepsin plays an important role in the digestion of proteins by breaking down the intact protein to peptides, which are short chains of four to nine amino acids. In the duodenum, other enzymes— **trypsin**, **elastase**, and **chymotrypsin**—act on the peptides reducing them to smaller peptides. Trypsin elastase, carboxypeptidase, and chymotrypsin are produced by the pancreas and released into the duodenum where they act on the chyme. Further breakdown of peptides to single amino acids is aided by enzymes called peptidases (those that break down peptides). Specifically, **carboxypeptidase**,

**dipeptidase**, and **aminopeptidase** play important roles in reducing the peptides to free amino acids. The amino acids are absorbed into the bloodstream through the small intestines. The steps in protein digestion are summarized in Figure 7.6 and Table 7.6.



Figure 7.6 Protein digestion is a multistep process that begins in the stomach and continues through the intestines.

### **Digestion of Protein**

Enzyme	Produced By	Site of Action	Substrate Acting On	End Products
Pepsin	Stomach chief cells	Stomach	Proteins	Peptides
Trypsin Elastase Chymotrypsin	Pancreas	Small intestine	Proteins	Peptides
Carboxypeptidase	Pancreas	Small intestine	Peptides	Amino acids and peptides

Table 7.6

#### **Digestion of Protein**

Enzyme	Produced By	Site of Action	Substrate Acting On	End Products
Aminopeptidase Dipeptidase	Lining of intestine	Small intestine	Peptides	Amino acids

#### Table 7.6

#### Lipids

Lipid digestion begins in the stomach with the aid of lingual lipase and gastric lipase. However, the bulk of lipid digestion occurs in the small intestine due to pancreatic lipase. When chyme enters the duodenum, the hormonal responses trigger the release of bile, which is produced in the liver and stored in the gallbladder. Bile aids in the digestion of lipids, primarily triglycerides by emulsification. Emulsification is a process in which large lipid globules are broken down into several small lipid globules. These small globules are more widely distributed in the chyme rather than forming large aggregates. Lipids are hydrophobic substances: in the presence of water, they will aggregate to form globules to minimize exposure to water. Bile contains bile salts, which are amphipathic, meaning they contain hydrophobic and hydrophilic parts. Thus, the bile salts hydrophilic side can interface with water on one side and the hydrophobic side interfaces with lipids on the other. By doing so, bile salts emulsify large lipid globules into small lipid globules.

Why is emulsification important for digestion of lipids? Pancreatic juices contain enzymes called lipases (enzymes that break down lipids). If the lipid in the chyme aggregates into large globules, very little surface area of the lipids is available for the lipases to act on, leaving lipid digestion incomplete. By forming an emulsion, bile salts increase the available surface area of the lipids many fold. The pancreatic lipases can then act on the lipids more efficiently and digest them, as detailed in Figure 7.7. Lipases break down the lipids into fatty acids and glycerides. These molecules can pass through the plasma membrane of the cell and enter the epithelial cells of the intestinal lining. The bile salts surround long-chain fatty acids and monoglycerides forming tiny spheres called micelles. The micelles move into the brush border of the small intestine absorptive cells where the long-chain fatty acids and monoglycerides diffuse out of the micelles into the absorptive cells leaving the micelles behind in the chyme. The long-chain fatty acids and monoglycerides recombine in the absorptive cells to form triglycerides, which aggregate into globules and become coated with proteins. These large spheres are called **chylomicrons**. Chylomicrons contain triglycerides, cholesterol, and other lipids and have proteins on their surface. The surface is also composed of the hydrophilic phosphate "heads" of phospholipids. Together, they enable the chylomicron to move in an aqueous environment without exposing the lipids to water. Chylomicrons leave the absorptive cells via exocytosis. Chylomicrons enter the lymphatic vessels, and then enter the blood in the subclavian vein.



Figure 7.7 Lipids are digested and absorbed in the small intestine.

#### Vitamins

Vitamins can be either water-soluble or lipid-soluble. Fat soluble vitamins are absorbed in the same manner as lipids. It is important to consume some amount of dietary lipid to aid the absorption of lipid-soluble vitamins. Water-soluble vitamins can be directly at stream from the intestine.





This website (http://openstaxcollege.org/l/digest\_enzymes) has an overview of the digestion of protein, fat, and carbohydrates.



Figure 7.8 Mechanical and chemical digestion of food takes place in many steps, beginning in the mouth and ending in the rectum.

Which of the following statements about digestive processes is true?

- a. Amylase, maltase, and lactase in the mouth digest carbohydrates.
- b. Trypsin and lipase in the stomach digest protein.
- c. Bile emulsifies lipids in the small intestine.
- d. No food is absorbed until the small intestine.

## Elimination

The final step in digestion is the elimination of undigested food content and waste products. The undigested food material enters the colon, where most of the water is reabsorbed. Recall that the colon is also home to the microflora called "intestinal flora" that aid in the digestion process. The semi-solid waste is moved through the colon by peristaltic movements of the muscle and is stored in the rectum. As the rectum expands in response to storage of fecal matter, it triggers the neural signals required to set up the urge to eliminate. The solid waste is eliminated through the anus using peristaltic movements of the rectum.

#### **Common Problems with Elimination**

Diarrhea and constipation are some of the most common health concerns that affect digestion. Constipation is
a condition where the feces are hardened because of excess water removal in the colon. In contrast, if enough water is not removed from the feces, it results in diarrhea. Many bacteria, including the ones that cause cholera, affect the proteins involved in water reabsorption in the colon and result in excessive diarrhea.

#### Emesis

Emesis, or vomiting, is elimination of food by forceful expulsion through the mouth. It is often in response to an irritant that affects the digestive tract, including but not limited to viruses, bacteria, emotions, sights, and food poisoning. This forceful expulsion of the food is due to the strong contractions produced by the stomach muscles. The process of emesis is regulated by the medulla.

# 7.3 | Energy and Metabolism

By the end of this section, you will be able to:

- Explain what metabolic pathways are and describe the two major types of metabolic pathways
- · Discuss how chemical reactions play a role in energy transfer

Scientists use the term **bioenergetics** to discuss the concept of energy flow (Figure 7.9) through living systems, such as cells. Cellular processes such as the building and breaking down of complex molecules occur through stepwise chemical reactions. Some of these chemical reactions are spontaneous and release energy, whereas others require energy to proceed. Just as living things must continually consume food to replenish what has been used, cells must continually produce more energy to replenish that used by the many energy-requiring chemical reactions that constantly take place. All of the chemical reactions that take place inside cells, including those that use energy and those that release energy, are the cell's **metabolism**.



Figure 7.9 Most life forms on earth get their energy from the sun. Plants use photosynthesis to capture sunlight, and herbivores eat those plants to obtain energy. Carnivores eat the herbivores, and decomposers digest plant and animal matter.

### Metabolism of Carbohydrates

The metabolism of sugar (a simple carbohydrate) is a classic example of the many cellular processes that use and produce energy. Living things consume sugar as a major energy source, because sugar molecules have a great deal of energy stored within their bonds. The breakdown of glucose, a simple sugar, is described by the equation:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy$$

Carbohydrates that are consumed have their origins in photosynthesizing organisms like plants (Figure 7.10). During photosynthesis, plants use the energy of sunlight to convert carbon dioxide gas (CO<sub>2</sub>) into sugar molecules, like glucose ( $C_6H_{12}O_6$ ). Because this process involves synthesizing a larger, energy-storing molecule, it requires an input of energy to proceed. The synthesis of glucose is described by this equation (notice that it is the reverse of the previous equation):

$$6CO_2 + 6H_2O + energy \rightarrow C_6H_{12}O_6 + 6O_2$$

During the chemical reactions of photosynthesis, energy is provided in the form of a very high-energy molecule called ATP, or adenosine triphosphate, which is the primary energy currency of all cells. Just as the dollar is used as currency to buy goods, cells use molecules of ATP as energy currency to perform immediate work. The sugar (glucose) is stored as starch or glycogen. Energy-storing polymers like these are broken down into glucose to supply molecules of ATP.

Solar energy is required to synthesize a molecule of glucose during the reactions of photosynthesis. In photosynthesis, light energy from the sun is initially transformed into chemical energy that is temporally stored in the energy carrier molecules ATP and NADPH (nicotinamide adenine dinucleotide phosphate). The stored energy in ATP and NADPH is then used later in photosynthesis to build one molecule of glucose from six molecules of CO<sub>2</sub>. This process is analogous to eating breakfast in the morning to acquire energy for your body that can be used later in the day. Under ideal conditions, energy from 18 molecules of ATP is required to synthesize one molecule of glucose during the reactions of photosynthesis. Glucose molecules can also be combined with and converted into other types of sugars. When sugars are consumed, molecules of glucose eventually make their way into each living cell of the organism. Inside the cell, each sugar molecule is broken down through a complex series of chemical reactions. The goal of these reactions is to harvest the energy stored inside the sugar molecules. The harvested energy is used to make high-energy ATP molecules, which can be used to perform work, powering many chemical reactions in the cell. The amount of energy needed to make one molecule of glucose from six molecules of carbon dioxide is 18 molecules of ATP and 12 molecules of NADPH (each one of which is energetically equivalent to three molecules of ATP), or a total of 54 molecule equivalents required for the synthesis of one molecule of glucose. This process is a fundamental and efficient way for cells to generate the molecular energy that they require.



**Figure 7.10** Plants, like this oak tree and acorn, use energy from sunlight to make sugar and other organic molecules. Both plants and animals (like this squirrel) use cellular respiration to derive energy from the organic molecules originally produced by plants. (credit "acorn": modification of work by Noel Reynolds; credit "squirrel": modification of work by Dawn Huczek)

## **Metabolic Pathways**

The processes of making and breaking down sugar molecules illustrate two types of metabolic pathways. A metabolic pathway is a series of interconnected biochemical reactions that convert a substrate molecule or molecules, step-by-step, through a series of metabolic intermediates, eventually yielding a final product or products. In the case of sugar metabolism, the first metabolic pathway synthesized sugar from smaller molecules, and the other pathway broke sugar down into smaller molecules. These two opposite processes—the first requiring energy and the second producing energy—are referred to as anabolic (building) and catabolic (breaking down) pathways, respectively. Consequently, metabolism is composed of building (anabolism) and degradation (catabolism).



**Figure 7.11** This tree shows the evolution of the various branches of life. The vertical dimension is time. Early life forms, in blue, used anaerobic metabolism to obtain energy from their surroundings.

## **Evolution of Metabolic Pathways**

There is more to the complexity of metabolism than understanding the metabolic pathways alone. Metabolic complexity varies from organism to organism. Photosynthesis is the primary pathway in which photosynthetic organisms like plants (the majority of global synthesis is done by planktonic algae) harvest the sun's energy and convert it into carbohydrates. The by-product of photosynthesis is oxygen, required by some cells to carry out cellular respiration. During cellular respiration, oxygen aids in the catabolic breakdown of carbon compounds, like carbohydrates. Among the products of this catabolism are CO<sub>2</sub> and ATP. In addition, some eukaryotes perform catabolic processes without oxygen (fermentation); that is, they perform or use anaerobic metabolism.

Organisms probably evolved anaerobic metabolism to survive (living organisms came into existence about 3.8 billion years ago, when the atmosphere lacked oxygen). Despite the differences between organisms and the complexity of metabolism, researchers have found that all branches of life share some of the same metabolic pathways, suggesting that all organisms evolved from the same ancient common ancestor (Figure 7.11). Evidence indicates that over time, the pathways diverged, adding specialized enzymes to allow organisms to better adapt to their environment, thus increasing their chance to survive. However, the underlying principle remains that all organisms must harvest energy from their environment and convert it to ATP to carry out cellular functions.

#### Anabolic and Catabolic Pathways

**Anabolic** pathways require an input of energy to synthesize complex molecules from simpler ones. Synthesizing sugar from CO<sub>2</sub> is one example. Other examples are the synthesis of large proteins from amino acid building blocks, and the synthesis of new DNA strands from nucleic acid building blocks. These biosynthetic processes are critical to the life of the cell, take place constantly, and demand energy provided by ATP and other high-

energy molecules like NADH (nicotinamide adenine dinucleotide) and NADPH (Figure 7.12).

ATP is an important molecule for cells to have in sufficient supply at all times. The breakdown of sugars illustrates how a single molecule of glucose can store enough energy to make a great deal of ATP, 36 to 38 molecules. This is a **catabolic** pathway. Catabolic pathways involve the degradation (or breakdown) of complex molecules into simpler ones. Molecular energy stored in the bonds of complex molecules is released in catabolic pathways and harvested in such a way that it can be used to produce ATP. Other energy-storing molecules, such as fats, are also broken down through similar catabolic reactions to release energy and make ATP (Figure 7.12).

It is important to know that the chemical reactions of metabolic pathways don't take place spontaneously. Each reaction step is facilitated, or catalyzed, by a protein called an enzyme. Enzymes are important for catalyzing all types of biological reactions—those that require energy as well as those that release energy.

#### Metabolic pathways



**Figure 7.12** Anabolic pathways are those that require energy to synthesize larger molecules. Catabolic pathways are those that generate energy by breaking down larger molecules. Both types of pathways are required for maintaining the cell's energy balance.

## 7.4 | Potential, Kinetic, Free, and Activation Energy

By the end of this section, you will be able to:

- Define "energy"
- Explain the difference between kinetic and potential energy
- Discuss the concepts of free energy and activation energy
- Describe endergonic and exergonic reactions

Energy is defined as the ability to do work. As you've learned, energy exists in different forms. For example, electrical energy, light energy, and heat energy are all different types of energy. While these are all familiar types of energy that one can see or feel, there is another type of energy that is much less tangible. This energy is associated with something as simple as an object held above the ground. In order to appreciate the way energy flows into and out of biological systems, it is important to understand more about the different types of energy that exist in the physical world.

## Types of Energy

When an object is in motion, there is energy associated with that object. In the example of an airplane in flight, there is a great deal of energy associated with the motion of the airplane. This is because moving objects are capable of enacting a change, or doing work. Think of a wrecking ball. Even a slow-moving wrecking ball can do a great deal of damage to other objects. However, a wrecking ball that is not in motion is incapable of performing work. Energy associated with objects in motion is called **kinetic energy**. A speeding bullet, a walking person, the rapid movement of molecules in the air (which produces heat), and electromagnetic radiation like light all have kinetic energy.

Now what if that same motionless wrecking ball is lifted two stories above a car with a crane? If the suspended wrecking ball is unmoving, is there energy associated with it? The answer is yes. The suspended wrecking ball has energy associated with it that is fundamentally different from the kinetic energy of objects in motion. This form of energy results from the fact that there is the *potential* for the wrecking ball to do work. If it is released, indeed it would do work. Because this type of energy refers to the potential to do work, it is called **potential energy**. Objects transfer their energy between kinetic and potential in the following way: As the wrecking ball

hangs motionless, it has 0 kinetic and 100 percent potential energy. Once it is released, its kinetic energy begins to increase because it builds speed due to gravity. At the same time, as it nears the ground, it loses potential energy. Somewhere mid-fall it has 50 percent kinetic and 50 percent potential energy. Just before it hits the ground, the ball has nearly lost its potential energy and has near-maximal kinetic energy. Other examples of potential energy include the energy of water held behind a dam (Figure 7.13), or a person about to skydive out of an airplane.



**Figure 7.13** Water behind a dam has potential energy. Moving water, such as in a waterfall or a rapidly flowing river, has kinetic energy. (credit "dam": modification of work by "Pascal"/Flickr; credit "waterfall": modification of work by Frank Gualtieri)

Potential energy is not only associated with the location of matter (such as a child sitting on a tree branch), but also with the structure of matter. A spring on the ground has potential energy if it is compressed; so does a rubber band that is pulled taut. The very existence of living cells relies heavily on structural potential energy. On a chemical level, the bonds that hold the atoms of molecules together have potential energy. Remember that anabolic cellular pathways require energy to synthesize complex molecules from simpler ones, and catabolic pathways release energy when complex molecules are broken down. The fact that energy can be released by the breakdown of certain chemical bonds implies that those bonds have potential energy. In fact, there is potential energy stored within the bonds of all the food molecules we eat, which is eventually harnessed for use. This is because these bonds can release energy when broken. The type of potential energy (Figure 7.14). Chemical energy is responsible for providing living cells with energy from food. The release of energy is brought about by breaking the molecular bonds within fuel molecules.



**Figure 7.14** The molecules in gasoline (octane, the chemical formula shown) contain chemical energy within the chemical bonds. This energy is transformed into kinetic energy that allows a car to race on a racetrack. (credit "car": modification of work by Russell Trow)





Visit this **site (http://openstaxcollege.org/l/simple\_pendulum)** and select "A simple pendulum" on the menu (under "Harmonic Motion") to see the shifting kinetic (K) and potential energy (U) of a pendulum in motion.

## **Free Energy**

After learning that chemical reactions release energy when energy-storing bonds are broken, an important next question is how is the energy associated with chemical reactions quantified and expressed? How can the energy released from one reaction be compared to that of another reaction? A measurement of **free energy** is used to quantitate these energy transfers. Free energy is called Gibbs free energy (abbreviated with the letter G) after Josiah Willard Gibbs, the scientist who developed the measurement. Recall that according to the second law of thermodynamics, all energy transfers involve the loss of some amount of energy in an unusable form such as heat, resulting in entropy. Gibbs free energy specifically refers to the energy associated with a chemical reaction that is available after entropy is accounted for. In other words, Gibbs free energy is usable energy, or energy that is available to do work.

Every chemical reaction involves a change in free energy, called delta G ( $\Delta$ G). The change in free energy can be calculated for any system that undergoes such a change, such as a chemical reaction. To calculate  $\Delta$ G, subtract the amount of energy lost to entropy (denoted as  $\Delta$ S) from the total energy change of the system. This total energy change in the system is called **enthalpy** and is denoted as  $\Delta$ H. The formula for calculating  $\Delta$ G is as follows, where the symbol T refers to absolute temperature in Kelvin (degrees Celsius + 273):

#### $\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$

The standard free energy change of a chemical reaction is expressed as an amount of energy per mole of the reaction product (either in kilojoules or kilocalories, kJ/mol or kcal/mol; 1 kJ = 0.239 kcal) under

standard pH, temperature, and pressure conditions. Standard pH, temperature, and pressure conditions are generally calculated at pH 7.0 in biological systems, 25 degrees Celsius, and 100 kilopascals (1 atm pressure), respectively. It is important to note that cellular conditions vary considerably from these standard conditions, and so standard calculated  $\Delta G$  values for biological reactions will be different inside the cell.

#### **Endergonic Reactions and Exergonic Reactions**

If energy is released during a chemical reaction, then the resulting value from the above equation will be a negative number. In other words, reactions that release energy have a  $\Delta G < 0$ . A negative  $\Delta G$  also means that the products of the reaction have less free energy than the reactants, because they gave off some free energy during the reaction. Reactions that have a negative  $\Delta G$  and consequently release free energy are called **exergonic reactions**. Think: exergonic means energy is exiting the system. These reactions are also referred to as spontaneous reactions, because they can occur without the addition of energy into the system. Understanding which chemical reactions are spontaneous and release free energy is extremely useful for biologists, because these reactions can be harnessed to perform work inside the cell. An important distinction must be drawn between the term spontaneous and the idea of a chemical reaction that occurs immediately. Contrary to the everyday use of the term, a spontaneous reaction is not one that suddenly or quickly occurs. The rusting of iron is an example of a spontaneous reaction that occurs slowly, little by little, over time.

If a chemical reaction requires an input of energy rather than releasing energy, then the  $\Delta G$  for that reaction will be a positive value. In this case, the products have more free energy than the reactants. Thus, the products of these reactions can be thought of as energy-storing molecules. These chemical reactions are called **endergonic reactions**, and they are non-spontaneous. An endergonic reaction will not take place on its own without the addition of free energy.

Let's revisit the example of the synthesis and breakdown of the food molecule, glucose. Remember that the building of complex molecules, such as sugars, from simpler ones is an anabolic process and requires energy. Therefore, the chemical reactions involved in anabolic processes are endergonic reactions. On the other hand, the catabolic process of breaking sugar down into simpler molecules releases energy in a series of exergonic reactions. Like the example of rust above, the breakdown of sugar involves spontaneous reactions, but these reactions don't occur instantaneously. **Figure 7.15** shows some other examples of endergonic and exergonic reactions. Later sections will provide more information about what else is required to make even spontaneous reactions happen more efficiently.

# visual 💽 CONNECTION





**Figure 7.15** Shown are some examples of endergonic processes (ones that require energy) and exergonic processes (ones that release energy). These include (a) a compost pile decomposing, (b) a chick hatching from a fertilized egg, (c) sand art being destroyed, and (d) a ball rolling down a hill. (credit a: modification of work by Natalie Maynor; credit b: modification of work by USDA; credit c: modification of work by "Athlex"/Flickr; credit d: modification of work by Harry Malsch)

Look at each of the processes shown, and decide if it is endergonic or exergonic. In each case, does enthalpy increase or decrease, and does entropy increase or decrease?

An important concept in the study of metabolism and energy is that of chemical equilibrium. Most chemical reactions are reversible. They can proceed in both directions, releasing energy into their environment in one direction, and absorbing it from the environment in the other direction (**Figure 7.16**). The same is true for the chemical reactions involved in cell metabolism, such as the breaking down and building up of proteins into and from individual amino acids, respectively. Reactants within a closed system will undergo chemical reactions in both directions until a state of equilibrium is reached. This state of equilibrium is one of the lowest possible free energy and a state of maximal entropy. Energy must be put into the system to push the reactants and products away from a state of equilibrium. Either reactants or products must be added, removed, or changed. If a cell were a closed system, its chemical reactions would reach equilibrium, and it would die because there would be insufficient free energy left to perform the work needed to maintain life. In a living cell, chemical reactions are constantly moving towards equilibrium, but never reach it. This is because a living cell is an open system. Materials pass in and out, the cell recycles the products of certain chemical reactions into other reactions, and chemical equilibrium and entropy. This constant supply of energy ultimately comes from sunlight, which is used to produce nutrients in the process of photosynthesis.



Figure 7.16 Exergonic and endergonic reactions result in changes in Gibbs free energy. Exergonic reactions release energy; endergonic reactions require energy to proceed.

## **Activation Energy**

There is another important concept that must be considered regarding endergonic and exergonic reactions. Even exergonic reactions require a small amount of energy input to get going before they can proceed with their energy-releasing steps. These reactions have a net release of energy, but still require some energy in the beginning. This small amount of energy input necessary for all chemical reactions to occur is called the **activation energy** (or free energy of activation) and is abbreviated  $E_A$  (Figure 7.17).

Why would an energy-releasing, negative  $\Delta G$  reaction actually require some energy to proceed? The reason lies in the steps that take place during a chemical reaction. During chemical reactions, certain chemical bonds are broken and new ones are formed. For example, when a glucose molecule is broken down, bonds between the carbon atoms of the molecule are broken. Since these are energy-storing bonds, they release energy when broken. However, to get them into a state that allows the bonds to break, the molecule must be somewhat contorted. A small energy input is required to achieve this contorted state. This contorted state is called the **transition state**, and it is a high-energy, unstable state. For this reason, reactant molecules don't last long in their transition state, but very quickly proceed to the next steps of the chemical reaction. Free energy diagrams illustrate the energy profiles for a given reaction. Whether the reaction is exergonic or endergonic determines whether the products in the diagram will exist at a lower or higher energy state than both the reactants and the products. However, regardless of this measure, the transition state of the reaction exists at a higher energy state than the reactants, and thus,  $E_A$  is alway<sup>2</sup> and the transition state of the reaction exists at a higher energy state than the reactants.





Watch an animation of the move from free energy to transition state at this (http://openstaxcollege.org/l/ energy\_reaction) site.

Where does the activation energy required by chemical reactants come from? The source of the activation energy needed to push reactions forward is typically heat energy from the surroundings. **Heat energy** (the total bond energy of reactants or products in a chemical reaction) speeds up the motion of molecules, increasing the frequency and force with which they collide; it also moves atoms and bonds within the molecule slightly, helping them reach their transition state. For this reason, heating up a system will cause chemical reactants within that system to react more frequently. Increasing the pressure on a system has the same effect. Once reactants have absorbed enough heat energy from their surroundings to reach the transition state, the reaction will proceed.

The activation energy of a particular reaction determines the rate at which it will proceed. The higher the activation energy, the slower the chemical reaction will be. The example of iron rusting illustrates an inherently slow reaction. This reaction occurs slowly over time because of its high  $E_A$ . Additionally, the burning of many fuels, which is strongly exergonic, will take place at a negligible rate unless their activation energy is overcome by sufficient heat from a spark. Once they begin to burn, however, the chemical reactions release enough heat

to continue the burning process, supplying the activation energy for surrounding fuel molecules. Like these reactions outside of cells, the activation energy for most cellular reactions is too high for heat energy to overcome at efficient rates. In other words, in order for important cellular reactions to occur at appreciable rates (number of reactions per unit time), their activation energies must be lowered (Figure 7.17); this is referred to as catalysis. This is a very good thing as far as living cells are concerned. Important macromolecules, such as proteins, DNA, and RNA, store considerable energy, and their breakdown is exergonic. If cellular temperatures alone provided enough heat energy for these exergonic reactions to overcome their activation barriers, the essential components of a cell would disintegrate.



**Figure 7.17** Activation energy is the energy required for a reaction to proceed, and it is lower if the reaction is catalyzed. The horizontal axis of this diagram describes the sequence of events in time.

If no activation energy were required to break down sucrose (table sugar), would you be able to store it in a sugar bowl?

## 7.5 | ATP: Adenosine Triphosphate

By the end of this section, you will be able to:

- Explain the role of ATP as the cellular energy currency
- Describe how energy is released through hydrolysis of ATP

Even exergonic, energy-releasing reactions require a small amount of activation energy in order to proceed. However, consider endergonic reactions, which require much more energy input, because their products have more free energy than their reactants. Within the cell, where does energy to power such reactions come from? The answer lies with an energy-supplying molecule called **adenosine triphosphate**, or **ATP**. ATP is a small, relatively simple molecule (**Figure 7.18**), but within some of its bonds, it contains the potential for a quick burst of energy that can be harnessed to perform cellular work. This molecule can be thought of as the primary energy currency of cells in much the same way that money is the currency that people exchange for things they need. ATP is used to power the majority of energy-requiring cellular reactions.



Figure 7.18 ATP is the primary energy currency of the cell. It has an adenosine backbone with three phosphate groups attached.

As its name suggests, adenosine triphosphate is comprised of adenosine bound to three phosphate groups (Figure 7.18). Adenosine is a nucleoside consisting of the nitrogenous base adenine and a five-carbon sugar, ribose. The three phosphate groups, in order of closest to furthest from the ribose sugar, are labeled alpha, beta, and gamma. Together, these chemical groups constitute an energy powerhouse. However, not all bonds within this molecule exist in a particularly high-energy state. Both bonds that link the phosphates are equally high-energy bonds ( **phosphoanhydride bonds**) that, when broken, release sufficient energy to power a variety of cellular reactions and processes. These high-energy bonds are the bonds between the second and third (or beta and gamma) phosphate groups and between the first and second phosphate groups. The reason that these bonds are considered "high-energy" is because the products of such bond breaking—adenosine diphosphate (ADP) and one inorganic phosphate group (Pi)—have considerably lower free energy than the reactants: ATP and a water molecule. Because this reaction takes place with the use of a water molecule, it is considered a hydrolysis reaction. In other words, ATP is hydrolyzed into ADP in the following reaction:

$$ATP + H_2O \rightarrow ADP + P_i + free energy$$

Like most chemical reactions, the hydrolysis of ATP to ADP is reversible. The reverse reaction regenerates ATP from ADP +  $P_i$ . Indeed, cells rely on the regeneration of ATP just as people rely on the regeneration of spent money through some sort of income. Since ATP hydrolysis releases energy, ATP regeneration must require an input of free energy. The formation of ATP is expressed in this equation:

$$ADP + P_i + free energy \rightarrow ATP + H_2O$$

Two prominent questions remain with regard to the use of ATP as an energy source. Exactly how much free energy is released with the hydrolysis of ATP, and how is that free energy used to do cellular work? The calculated  $\Delta G$  for the hydrolysis of one mole of ATP into ADP and P<sub>i</sub> is -7.3 kcal/mole (-30.5 kJ/mol). Since this calculation is true under standard conditions, it would be expected that a different value exists under cellular conditions. In fact, the  $\Delta G$  for the hydrolysis of one mole of ATP in a living cell is almost double the value at standard conditions: -14 kcal/mol (-57 kJ/mol).

ATP is a highly unstable molecule. Unless quickly used to perform work, ATP spontaneously dissociates into ADP + P<sub>i</sub>, and the free energy released during this process is lost as heat. The second question posed above, that is, how the energy released by ATP hydrolysis is used to perform work inside the cell, depends on a strategy called energy coupling. Cells couple the exergonic reaction of ATP hydrolysis with endergonic reactions, allowing them to proceed. One example of energy coupling using ATP involves a transmembrane ion pump that is extremely important for cellular function. This sodium-potassium pump (Na<sup>+</sup>/K<sup>+</sup> pump) drives sodium out of the cell and potassium into the cell (**Figure 7.19**). A large percentage of a cell's ATP is spent powering this pump, because cellular processes bring a great deal of sodium into the cell and potassium out of the cell. The pump works constantly to stabilize cellular concentrations of sodium and potassium. In order for the pump to turn one cycle (exporting three Na+ ions and importing two K<sup>+</sup> ions), one molecule of ATP must be hydrolyzed. When ATP is hydrolyzed, its gamma phosphate doesn't simply float away, but is actually transferred onto the pump protein. This process of a phosphate group binding to a molecule is called phosphorylation. As with most cases of ATP hydrolysis, a phosphate from ATP is transferred onto another molecule. In a phosphorylated state, the Na<sup>+</sup>/K<sup>+</sup> pump has more free energy and is triggered to undergo a conformational change. This change allows it to release Na<sup>+</sup> to the outside of the cell. It then binds extracellular K<sup>+</sup>, which, through another conformational

change, causes the phosphate to detach from the pump. This release of phosphate triggers the  $K^+$  to be released to the inside of the cell. Essentially, the energy released from the hydrolysis of ATP is coupled with the energy required to power the pump and transport Na<sup>+</sup> and K<sup>+</sup> ions. ATP performs cellular work using this basic form of energy coupling through phosphorylation.



**Figure 7.19** The sodium-potassium pump is an example of energy coupling. The energy derived from exergonic ATP hydrolysis is used to pump sodium and potassium ions across the cell membrane.

The hydrolysis of one ATP molecule releases 7.3 kcal/mol of energy ( $\Delta G = -7.3$  kcal/mol of energy). If it takes 2.1 kcal/mol of energy to move one Na<sup>+</sup> across the membrane ( $\Delta G = +2.1$  kcal/mol of energy), how many sodium ions could be moved by the hydrolysis of one ATP molecule?

Often during cellular metabolic reactions, such as the synthesis and breakdown of nutrients, certain molecules must be altered slightly in their conformation to become substrates for the next step in the reaction series. One example is during the very first steps of cellular respiration, when a molecule of the sugar glucose is broken down in the process of glycolysis. In the first step of this process, ATP is required for the phosphorylation of glucose, creating a high-energy but unstable intermediate. This phosphorylation reaction powers a conformational change that allows the phosphorylated glucose molecule to be converted to the phosphorylated sugar fructose. Fructose is a necessary intermediate for glycolysis to move forward. Here, the exergonic reaction of ATP hydrolysis is coupled with the endergonic reaction of converting glucose into a phosphorylated intermediate in the pathway. Once again, the energy released by breaking a phosphate bond within ATP was used for the phosphorylation of another molecule, creating an unstable ir





See an interactive animation of the ATP-producing glycolysis process at this site (http://openstaxcollege.org/ l/glycolysis\_stgs).

# 7.6 | Overview of Photosynthesis

By the end of this section, you will be able to:

- Explain the relevance of photosynthesis to other living things
- · Describe the main structures involved in photosynthesis
- Identify the substrates and products of photosynthesis
- · Summarize the process of photosynthesis

Photosynthesis is essential to all life on earth; both plants and animals depend on it. It is the only biological process that can capture energy that originates in outer space (sunlight) and convert it into chemical compounds (carbohydrates) that every organism uses to power its metabolism. In brief, the energy of sunlight is captured and used to energize electrons, which are then stored in the covalent bonds of sugar molecules. How long lasting and stable are those covalent bonds? The energy extracted today by the burning of coal and petroleum products represents sunlight energy captured and stored by photosynthesis almost 200 million years ago.

Plants, algae, and a group of bacteria called cyanobacteria are the only organisms capable of performing photosynthesis (Figure 7.20). Because they use light to manufacture their own food, they are called **photoautotrophs** (literally, "self-feeders using light"). Other organisms, such as animals, fungi, and most other bacteria, are termed **heterotrophs** ("other feeders"), because they must rely on the sugars produced by photosynthetic organisms for their energy needs. A third very interesting group of bacteria synthesize sugars, not by using sunlight's energy, but by extracting energy from inorganic chemical compounds; hence, they are referred to as **chemoautotrophs**.



(a)

(b)

(C)



**Figure 7.20** Photoautotrophs including (a) plants, (b) algae, and (c) cyanobacteria synthesize their organic compounds via photosynthesis using sunlight as an energy source. Cyanobacteria and planktonic algae can grow over enormous areas in water, at times completely covering the surface. In a (d) deep sea vent, chemoautotrophs, such as these (e) thermophilic bacteria, capture energy from inorganic compounds to produce organic compounds. The ecosystem surrounding the vents has a diverse array of animals, such as tubeworms, crustaceans, and octopi that derive energy from the bacteria. (credit a: modification of work by Steve Hillebrand, U.S. Fish and Wildlife Service; credit b: modification of work by "eutrophication&hypoxia"/Flickr; credit c: modification of work by NASA; credit d: University of Washington, NOAA; credit e: modification of work by Mark Amend, West Coast and Polar Regions Undersea Research Center, UAF, NOAA)

The importance of photosynthesis is not just that it can capture sunlight's energy. A lizard sunning itself on a cold day can use the sun's energy to warm up. Photosynthesis is vital because it evolved as a way to store the energy in solar radiation (the "photo-" part) as high-energy electrons in the carbon-carbon bonds of carbohydrate

molecules (the "-synthesis" part). Those carbohydrates are the energy source that heterotrophs use to power the synthesis of ATP via respiration. Therefore, photosynthesis powers 99 percent of Earth's ecosystems. When a top predator, such as a wolf, preys on a deer (Figure 7.21), the wolf is at the end of an energy path that went from nuclear reactions on the surface of the sun, to light, to photosynthesis, to vegetation, to deer, and finally to wolf.



**Figure 7.21** The energy stored in carbohydrate molecules from photosynthesis passes through the food chain. The predator that eats these deer receives a portion of the energy that originated in the photosynthetic vegetation that the deer consumed. (credit: modification of work by Steve VanRiper, U.S. Fish and Wildlife Service)

### Main Structures and Summary of Photosynthesis

Photosynthesis is a multi-step process that requires sunlight, carbon dioxide (which is low in energy), and water as substrates (Figure 7.22). After the process is complete, it releases oxygen and produces glyceraldehyde-3-phosphate (GA3P), simple carbohydrate molecules (which are high in energy) that can subsequently be converted into glucose, sucrose, or any of dozens of other sugar molecules. These sugar molecules contain energy and the energized carbon that all living things need to survive.



Figure 7.22 Photosynthesis uses solar energy, carbon dioxide, and water to produce energy-storing carbohydrates. Oxygen is generated as a waste product of photosynthesis.

The following is the chemical equation for photosynthesis (Figure 7.23):



**Figure 7.23** The basic equation for photosynthesis is deceptively simple. In reality, the process takes place in many steps involving intermediate reactants and products. Glucose, the primary energy source in cells, is made from two three-carbon GA3Ps.

Although the equation looks simple, the many steps that take place during photosynthesis are actually quite complex. Before learning the details of how photoautotrophs turn sunlight into food, it is important to become familiar with the structures involved.

In plants, photosynthesis generally takes place in leaves, which consist of several layers of cells. The process of photosynthesis occurs in a middle layer called the **mesophyll**. The gas exchange of carbon dioxide and oxygen occurs through small, regulated openings called **stomata** (singular: stoma), which also play roles in the regulation of gas exchange and water balance. The stomata are typically located on the underside of the leaf, which helps to minimize water loss. Each stoma is flanked by guard cells that regulate the opening and closing of the stomata by swelling or shrinking in response to osmotic changes.

In all autotrophic eukaryotes, photosynthesis takes place inside an organelle called a **chloroplast**. For plants, chloroplast-containing cells exist in the mesophyll. Chloroplasts have a double membrane envelope (composed of an outer membrane and an inner membrane). Within the chloroplast are stacked, disc-shaped structures called **thylakoids**. Embedded in the thylakoid membrane is chlorophyll, a **pigment** (molecule that absorbs light) responsible for the initial interaction between light and plant material, and numerous proteins that make up the electron transport chain. The thylakoid membrane encloses an internal space called the **thylakoid lumen**. As shown in **Figure 7.24**, a stack of thylakoids is called a **granum**, and the liquid-filled space surrounding the granum is called **stroma** or "bed" (not to be confused with stoma or "mouth," an opening on the leaf epidermis).



**Figure 7.24** Photosynthesis takes place in chloroplasts, which have an outer membrane and an inner membrane. Stacks of thylakoids called grana form a third membrane layer.

On a hot, dry day, plants close their stomata to conserve water. What impact will this have on photosynthesis?

## The Two Parts of Photosynthesis

Photosynthesis takes place in two sequential stages: the light-dependent reactions and the light independent reactions. In the **light-dependent reactions**, energy from sunlight is absorbed by chlorophyll and that energy is converted into stored chemical energy. In the **light-independent reactions**, the chemical energy harvested

during the light-dependent reactions drive the assembly of sugar molecules from carbon dioxide. Therefore, although the light-independent reactions do not use light as a reactant, they require the products of the light-dependent reactions to function. In addition, several enzymes of the light-independent reactions are activated by light. The light-dependent reactions utilize certain molecules to temporarily store the energy: These are referred to as energy carriers. The energy carriers that move energy from light-dependent reactions to light-independent reactions can be thought of as "full" because they are rich in energy. After the energy is released, the "empty" energy carriers return to the light-dependent reaction to obtain more energy. Figure 7.25 illustrates the components inside the chloroplast where the light-dependent and light-independent reactions take place.



**Figure 7.25** Photosynthesis takes place in two stages: light dependent reactions and the Calvin cycle. Light-dependent reactions, which take place in the thylakoid membrane, use light energy to make ATP and NADPH. The Calvin cycle, which takes place in the stroma, uses energy derived from these compounds to make GA3P from CO<sub>2</sub>.





Click the link (http://openstaxcollege.org/l/photosynthesis) to learn more about photosynthesis.

# everyday CONNECTION

## **Photosynthesis at the Grocery Store**



Figure 7.26 Foods that humans consume originate from photosynthesis. (credit: Associação Brasileira de Supermercados)

Major grocery stores in the United States are organized into departments, such as dairy, meats, produce, bread, cereals, and so forth. Each aisle (Figure 7.26) contains hundreds, if not thousands, of different products for customers to buy and consume.

Although there is a large variety, each item links back to photosynthesis. Meats and dairy link, because the animals were fed plant-based foods. The breads, cereals, and pastas come largely from starchy grains, which are the seeds of photosynthesis-dependent plants. What about desserts and drinks? All of these products contain sugar—sucrose is a plant product, a disaccharide, a carbohydrate molecule, which is built directly from photosynthesis. Moreover, many items are less obviously derived from plants: For instance, paper goods are generally plant products, and many plastics (abundant as products and packaging) are derived from algae. Virtually every spice and flavoring in the spice aisle was produced by a plant as a leaf, root, bark, flower, fruit, or stem. Ultimately, photosynthesis connects to every meal and every food a person consumes.

# 7.7 | Collision Theory

By the end of this section, you will be able to:

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- · Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

reaction rate 
$$\propto \frac{\# \text{ collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.

3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2 \operatorname{CO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{CO}_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure 7.27. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (O = C = O). This is a rather simple example of

how important the orientation of the collision is in terms of creating the desired product of the reaction.



Figure 7.27 Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. As an example, **Figure 7.28** depicts the structure of possible transitions states in the reaction between CO and O<sub>2</sub> to form CO<sub>2</sub>.

0=C···0=0 0---C···0=0 0=C···0···0

**Figure 7.28** Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third "extra" oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

## Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy** ( $E_a$ ). The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

**Figure 7.29** shows the energy relationships for the general reaction of a molecule of *A* with a molecule of *B* to form molecules of *C* and *D*:

$$A + B \longrightarrow C + D$$

The figure shows that the energy of the transition state is higher than that of the reactants *A* and *B* by an amount equal to  $E_a$ , the activation energy. Thus, the sum of the kinetic energies of *A* and *B* must be equal to or greater than  $E_a$  to reach the transition state. After the transition state has been reached, and as *C* and *D* begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules *A* and *B*) therefore tends to take place readily once the reaction has started. In **Figure 7.29**,  $\Delta H$  represents the difference in enthalpy between the reactants (*A* and *B*) and the products (*C* and *D*). The sum of  $E_a$  and  $\Delta H$  represents the activation energy for the reverse reaction:

$$C + D \longrightarrow A + B$$



## Extent of reaction

**Figure 7.29** This graph shows the potential energy relationships for the reaction  $A + B \longrightarrow C + D$ . The dashed portion of the curve represents the energy of the system with a molecule of *A* and a molecule of *B* present, and the solid portion represents the energy of the system with a molecule of *C* and a molecule of *D* present. The activation energy for the forward reaction is represented by  $E_a$ . The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to  $\Delta H$ . The curve's peak represents the transition state.

We can use the **Arrhenius equation** to relate the activation energy and the rate constant, *k*, of a given reaction:

$$k = Ae^{-E_a/RT}$$

In this equation, R is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale,  $E_a$  is the activation energy in joules per mole, e is the constant 2.7183, and A is a constant called the **frequency factor**, which is related to the frequency of collisions and the orientation of the reacting molecules.

The postulates of collision theory are accommodated in the Arrhenius equation. The frequency factor *A* is related to the rate at which collisions having the correct *orientation* occur. The exponential term,  $e^{-E_a/RT}$ , is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of  $E_a$  results in a smaller value for  $e^{-E_a/RT}$ , reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller  $E_a$  has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of  $e^{-E_a/RT}$ , a larger rate constant, and a faster rate for the reaction. An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure 7.30), as indicated by an increase in the value of  $e^{-E_a/RT}$ . The rate constant is also directly proportional to the frequency factor,

A. Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in A and, consequently, an increase in k.



**Figure 7.30** (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature,  $T_2$ , more molecules have kinetic energies greater than  $E_a$ , as shown by the yellow shaded area.

A convenient approach for determining  $E_a$  for a reaction involves the measurement of k at different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$
$$y = mx + b$$

Thus, a plot of ln *k* versus  $\frac{1}{T}$  gives a straight line with the slope  $\frac{-E_a}{R}$ , from which  $E_a$  may be determined. The intercept gives the value of ln *A*.

#### Example 7.1

#### Determination of Ea

The variation of the rate constant with temperature for the decomposition of HI(g) to  $H_2(g)$  and  $I_2(g)$  is given here. What is the activation energy for the reaction?

$$2\mathrm{HI}(g) \longrightarrow \mathrm{H}_{2}(g) + \mathrm{I}_{2}(g)$$

<i>Т</i> (К)	k (L/mol/s)
555	$3.52 \times 10^{-7}$
575	$1.22 \times 10^{-6}$
645	$8.59 \times 10^{-5}$
700	$1.16 \times 10^{-3}$
781	$3.95 \times 10^{-2}$

#### Solution

Values of  $\frac{1}{T}$  and ln *k* are:

$\frac{1}{T}$ (K <sup>-1</sup> )		ln <i>k</i>	
1.80	×	10 <sup>-3</sup>	-14.860
1.74	×	10 <sup>-3</sup>	-13.617
1.55	×	10 <sup>-3</sup>	-9.362
1.43	×	10 <sup>-3</sup>	-6.759
1.28	×	10 <sup>-3</sup>	-3.231

**Figure 7.31** is a graph of ln *k* versus  $\frac{1}{T}$ . To determine the slope of the line, we need two values of ln *k*, which are determined from the line at two values of  $\frac{1}{T}$  (one near each end of the line is preferable). For example, the value of ln *k* determined from the line when  $\frac{1}{T} = 1.25 \times 10^{-3}$  is -2.593; the value when  $\frac{1}{T} = 1.78 \times 10^{-3}$  is -14.447.



**Figure 7.31** This graph shows the linear relationship between  $\ln k$  and  $\frac{1}{T}$  for the reaction  $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$  according to the Arrhenius equation.

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The slope of this line is given by the following expression:

Slope = 
$$\frac{\Delta(\ln k)}{\Delta(\frac{1}{T})}$$
  
=  $\frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3} \text{ K}^{-1}) - (1.25 \times 10^{-3} \text{ K}^{-1})}$   
=  $\frac{-11.854}{0.53 \times 10^{-3} \text{ K}^{-1}} = 2.2 \times 10^4 \text{ K}$   
=  $-\frac{E_a}{R}$ 

Thus:

$$E_a = -\text{slope} \times R = -(-2.2 \times 10^4 \text{ K} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$
  
 $E_a = 1.8 \times 10^5 \text{ J mol}$ 

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

$$\ln k = \left(\frac{-E_{a}}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

can be rearranged as shown to give:

$$\frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} = -\frac{E_{a}}{R}$$

or

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

$$E_{a} = -R\left(\frac{\ln k_{2} - \ln k_{1}}{\left(\frac{1}{T_{2}}\right) - \left(\frac{1}{T_{1}}\right)}\right)$$

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

<i>Т</i> (К)	k (L/mol/s)	$\frac{1}{T}$ (K <sup>-1</sup> )	ln <i>k</i>
555	$3.52 \times 10^{-7}$	$1.80 \times 10^{-3}$	-14.860
781	$3.95 \times 10^{-2}$	$1.28 \times 10^{-3}$	-3.231

After calculating  $\frac{1}{T}$  and ln *k*, we can substitute into the equation:

$$E_{\rm a} = -8.314 \,\mathrm{J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1} \left( \frac{-3.231 - (-14.860)}{1.28 \times 10^{-3}\,\mathrm{K}^{-1} - 1.80 \times 10^{-3}\,\mathrm{K}^{-1}} \right)$$

and the result is  $E_a = 185,900 \text{ J/mol}$ .

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

#### **Check Your Learning**

The rate constant for the rate of decomposition of  $N_2O_5$  to NO and  $O_2$  in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2N_2O_5(g) \longrightarrow 4NO(g) + 3O_2(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer:

113,000 J/mol

## **Key Equations**

- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} \frac{1}{T_1} \right)$

## **Chemistry End of Chapter Exercises**

#### Exercise 7.1

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

#### Solution

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

#### Exercise 7.2

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

#### Exercise 7.3

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

#### Solution

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

#### Exercise 7.4

Account for the relationship between the rate of a reaction and its activation energy.

#### Exercise 7.5

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

#### Solution

After finding k at several different temperatures, a plot of ln k versus  $\frac{1}{T}$ , gives a straight line with the slope  $\frac{-E_a}{R}$ 

from which  $E_a$  may be determined.

Exercise 7.6

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

#### Exercise 7.7

The rate of a certain reaction doubles for every 10 °C rise in temperature.

(a) How much faster does the reaction proceed at 45 °C than at 25 °C?

(b) How much faster does the reaction proceed at 95 °C than at 25 °C?

#### Solution

(a) 4-times faster (b) 128-times faster

#### Exercise 7.8

In an experiment, a sample of NaClO<sub>3</sub> was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)

#### Exercise 7.9

The rate constant at 325 °C for the decomposition reaction  $C_4H_8 \longrightarrow 2C_2H_4$  is 6.1 × 10<sup>-8</sup> s<sup>-1</sup>, and the activation energy is 261 kJ per mole of C<sub>4</sub>H<sub>8</sub>. Determine the frequency factor for the reaction.

#### Solution

 $3.9 \times 10^{15} \text{ s}^{-1}$ 

#### Exercise 7.10

The rate constant for the decomposition of acetaldehyde, CH<sub>3</sub>CHO, to methane, CH<sub>4</sub>, and carbon monoxide, CO, in the gas phase is  $1.1 \times 10^{-2}$  L/mol/s at 703 K and 4.95 L/mol/s at 865 K. Determine the activation energy for this decomposition.

#### Exercise 7.11

An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

#### Solution

43.0 kJ/mol

#### Exercise 7.12

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

- (a) the change in free energy per second
- (b) the change in temperature per second
- (c) the number of collisions per second
- (d) the number of product molecules

#### Exercise 7.13

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen,  $H_2$ , and iodine,  $I_2$ . The value of the rate constant, k, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	$k (M^{-1} \text{ s}^{-1})$
555	$6.23 \times 10^{-7}$
575	$2.42 \times 10^{-6}$
645	$1.44 \times 10^{-4}$
700	$2.01 \times 10^{-3}$

What is the value of the activation energy (in kJ/mol) for this reaction?

#### Solution

177 kJ/mol

#### Exercise 7.14

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

<i>Т</i> (К)	<i>k</i> (s <sup>-1</sup> )
293	0.054
298	0.100

#### Exercise 7.15

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows a first-order rate equation for the disappearance of sucrose: Rate =  $k[C_{12}H_{22}O_{11}]$  (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

(a) In neutral solution,  $k = 2.1 \times 10^{-11} \text{ s}^{-1}$  at 27 °C and 8.5  $\times 10^{-11} \text{ s}^{-1}$  at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).

(b) When a solution of sucrose with an initial concentration of 0.150 *M* reaches equilibrium, the concentration of sucrose is  $1.65 \times 10^{-7}$  *M*. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.

(c) Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

#### Solution

 $E_a = 108 \text{ kJ}$   $A = 2.0 \times 10^8 \text{ s}^{-1}$  $k = 3.2 \times 10^{-10} \text{ s}^{-1}$ 

(b)  $1.81 \times 10^8$  h or  $7.6 \times 10^6$  day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

#### Exercise 7.16

Use the PhET Reactions & Rates interactive simulation (http://openstax.org/l/16PHETreaction) to simulate

a system. On the "Single collision" tab of the simulation applet, enable the "Energy view" by clicking the "+" icon. Select the first  $A + BC \longrightarrow AB + C$  reaction (A is yellow, B is purple, and C is navy blue). Using the "straight shot" default option, try launching the A atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

#### Exercise 7.17

Use the **PhET Reactions & Rates interactive simulation (http://openstax.org/l/16PHETreaction)** to simulate a system. On the "Single collision" tab of the simulation applet, enable the "Energy view" by clicking the "+" icon. Select the first  $A + BC \rightarrow AB + C$  reaction (A is yellow, B is purple, and C is navy blue). Using the "angled shot" option, try launching the A atom with varying angles, but with more Total energy than the transition state. What happens when the A atom hits the BC molecule from different directions? Why?

#### Solution

The *A* atom has enough energy to react with *BC*; however, the different angles at which it bounces off of *BC* without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

## 7.8 | Factors Affecting Reaction Rates

By the end of this section, you will be able to:

Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

### The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

## The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure 7.32). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



**Figure 7.32** (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total surface area:  $2Fe(s) + 6HCl(aq) \rightarrow 2FeCl_3(aq) + 3H_2(g)$ . (b) An iron nail reacts more slowly.



Watch this video (http://openstax.org/l/16cesium) to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

## **Temperature of the Reactants**

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

### **Concentrations of the Reactants**

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate (CaCO<sub>3</sub>) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 7.33). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$SO_2(g) + H_2O(g) \longrightarrow H_2SO_3(aq)$$

Calcium carbonate reacts with sulfurous acid as follows:

$$CaCO_3(s) + H_2SO_3(aq) \longrightarrow CaSO_3(aq) + CO_2(g) + H_2O(l)$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



**Figure 7.33** Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)



Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video (http://openstax.org/l/16phosphor) to see an example.

## The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (Figure 7.34). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.



#### **Reaction coordinate**





Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the **PhET Reactions** & **Rates interactive (http://openstax.org/l/16PHETreaction)** to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

## **Chemistry End of Chapter Exercises**

#### Exercise 7.18

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

#### Solution

Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because more reactive surface exists.

#### Exercise 7.19

Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

Exercise 7.20

Go to the **PhET Reactions & Rates (http://openstax.org/l/16PHETreaction)** interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on "Reload Launcher" and change to "Angled shot" to see the difference.

(a) What happens when the angle of the collision is changed?

(b) Explain how this is relevant to rate of reaction.

#### Solution

(a) Depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other. (b) Particles of reactant must come into contact with each other before they can react.

#### Exercise 7.21

In the **PhET Reactions & Rates (http://openstax.org/l/16PHETreaction)** interactive, use the "Many Collisions" tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select "Show bonds" under Options. How is the rate of the reaction affected by concentration and temperature?

#### Exercise 7.22

In the **PhET Reactions & Rates (http://openstax.org/l/16PHETreaction)** interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select "Show Bonds" under Options.

(a) Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?

(b) Click "Pause" and then "Reset All," and then enter 15 molecules of A and 10 molecules of BC once again. Select "Show Bonds" under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

#### Solution

(a) very slow; (b) As the temperature is increased, the reaction proceeds at a faster rate. The amount of reactants decreases, and the amount of products increases. After a while, there is a roughly equal amount of *BC*, *AB*, and *C* in the mixture and a slight excess of *A*.

# 7.9 | Enzymes

By the end of this section, you will be able to:

- · Describe the role of enzymes in metabolic pathways
- Explain how enzymes function as molecular catalysts
- Discuss enzyme regulation by various factors

A substance that helps a chemical reaction to occur is a catalyst, and the special molecules that catalyze biochemical reactions are called enzymes. Almost all enzymes are proteins, made up of chains of amino acids, and they perform the critical task of lowering the activation energies of chemical reactions inside the cell. Enzymes do this by binding to the reactant molecules, and holding them in such a way as to make the chemical bond-breaking and bond-forming processes take place more readily. It is important to remember that enzymes don't change the  $\Delta G$  of a reaction. In other words, they don't change whether a reaction is exergonic (spontaneous) or endergonic. This is because they don't change the free energy of the reactants or products. They only reduce the activation energy required to reach the transition state (Figure 7.35).



Figure 7.35 Enzymes lower the activation energy of the reaction but do not change the free energy of the reaction.

## Enzyme Active Site and Substrate Specificity

The chemical reactants to which an enzyme binds are the enzyme's **substrates**. There may be one or more substrates, depending on the particular chemical reaction. In some reactions, a single-reactant substrate is broken down into multiple products. In others, two substrates may come together to create one larger molecule. Two reactants might also enter a reaction, both become modified, and leave the reaction as two products. The location within the enzyme where the substrate binds is called the enzyme's **active site**. The active site is where the "action" happens, so to speak. Since enzymes are proteins, there is a unique combination of amino acid residues (also called side chains, or R groups) within the active site. Each residue is characterized by different properties. Residues can be large or small, weakly acidic or basic, hydrophilic or hydrophobic, positively or negatively charged, or neutral. The unique combination of amino acid residues, their positions, sequences, structures, and properties, creates a very specific chemical environment within the active site. This specific environment is suited to bind, albeit briefly, to a specific chemical substrate (or substrates). Due to this jigsaw puzzle-like match between an enzyme and its substrates (which adapts to find the best fit between the transition state and the active site), enzymes are known for their specificity. The "best fit" results from the shape and the amino acid functional group's attraction to the substrate. There is a specifically matched enzyme for each substrate and, thus, for each chemical reaction; however, there is flexibility as well.

The fact that active sites are so perfectly suited to provide specific environmental conditions also means that they are subject to influences by the local environment. It is true that increasing the environmental temperature generally increases reaction rates, enzyme-catalyzed or otherwise. However, increasing or decreasing the temperature outside of an optimal range can affect chemical bonds within the active site in such a way that they are less well suited to bind substrates. High temperatures will eventually cause enzymes, like other biological molecules, to **denature**, a process that changes the natural properties of a substance. Likewise, the pH of the local environment can also affect enzyme function. Active site amino acid residues have their own acidic or basic properties that are optimal for catalysis. These residues are sensitive to changes in pH that can impair the way substrate molecules bind. Enzymes are suited to function best within a certain pH range, and, as with temperature, extreme pH values (acidic or basic) of the environment can cause enzymes to denature.

#### Induced Fit and Enzyme Function

For many years, scientists thought that enzyme-substrate binding took place in a simple "lock-and-key" fashion. This model asserted that the enzyme and substrate fit together perfectly in one instantaneous step. However, current research supports a more refined view called **induced fit** (Figure 7.36). The induced-fit model expands upon the lock-and-key model by describing a more dynamic interaction between enzyme and substrate. As the enzyme and substrate come together, their interaction causes a mild shift in the enzyme's structure that confirms an ideal binding arrangement between the enzyme and the transition state of the substrate. This ideal binding maximizes the enzyme's ability to catalyze its reaction.

LINK T



View an animation of induced fit at this website (http://openstaxcollege.org/l/hexokinase) .

LEARNING

When an enzyme binds its substrate, an enzyme-substrate complex is formed. This complex lowers the activation energy of the reaction and promotes its rapid progression in one of many ways. On a basic level, enzymes promote chemical reactions that involve more than one substrate by bringing the substrates together in an optimal orientation. The appropriate region (atoms and bonds) of one molecule is juxtaposed to the appropriate region of the other molecule with which it must react. Another way in which enzymes promote the reaction of their substrates is by creating an optimal environment within the active site for the reaction to occur. Certain chemical reactions might proceed best in a slightly acidic or non-polar environment. The chemical properties that emerge from the particular arrangement of amino acid residues within an active site create the perfect environment for an enzyme's specific substrates to react.

You've learned that the activation energy required for many reactions includes the energy involved in manipulating or slightly contorting chemical bonds so that they can easily break and allow others to reform. Enzymatic action can aid this process. The enzyme-substrate complex can lower the activation energy by contorting substrate molecules in such a way as to facilitate bond-breaking, helping to reach the transition state. Finally, enzymes can also lower activation energies by taking part in the chemical reaction itself. The amino acid residues can provide certain ions or chemical groups that actually form covalent bonds with substrate molecules as a necessary step of the reaction process. In these cases, it is important to remember that the enzyme will always return to its original state at the completion of the reaction. One of the hallmark properties of enzymes is that they remain ultimately unchanged by the reactions they catalyze. After an enzyme is done catalyzing a reaction, it releases its product(s).



Figure 7.36 According to the induced-fit model, both enzyme and substrate undergo dynamic conformational changes upon binding. The enzyme contorts the substrate into its transition state, thereby increasing the rate of the reaction.

## **Control of Metabolism Through Enzyme Regulation**

It would seem ideal to have a scenario in which all of the enzymes encoded in an organism's genome existed in abundant supply and functioned optimally under all cellular conditions, in all cells, at all times. In reality, this is far from the case. A variety of mechanisms ensure that this does not happen. Cellular needs and conditions vary from cell to cell, and change within individual cells over time. The required enzymes and energetic demands of stomach cells are different from those of fat storage cells, skin cells, blood cells, and nerve cells. Furthermore, a digestive cell works much harder to process and break down nutrients during the time that closely follows a meal compared with many hours after a meal. As these cellular demands and conditions vary, so do the amounts and functionality of different enzymes.

Since the rates of biochemical reactions are controlled by activation energy, and enzymes lower and determine activation energies for chemical reactions, the relative amounts and functioning of the variety of enzymes within a cell ultimately determine which reactions will proceed and at which rates. This determination is tightly

controlled. In certain cellular environments, enzyme activity is partly controlled by environmental factors, like pH and temperature. There are other mechanisms through which cells control the activity of enzymes and determine the rates at which various biochemical reactions will occur.

#### **Regulation of Enzymes by Molecules**

Enzymes can be regulated in ways that either promote or reduce their activity. There are many different kinds of molecules that inhibit or promote enzyme function, and various mechanisms exist for doing so. In some cases of enzyme inhibition, for example, an inhibitor molecule is similar enough to a substrate that it can bind to the active site and simply block the substrate from binding. When this happens, the enzyme is inhibited through **competitive inhibition**, because an inhibitor molecule competes with the substrate for active site binding (Figure 7.37). On the other hand, in noncompetitive inhibition, an inhibitor molecule binds to the enzyme in a location other than an allosteric site and still manages to block substrate binding to the active site.



Figure 7.37 Competitive and noncompetitive inhibition affect the rate of reaction differently. Competitive inhibitors affect the initial rate but do not affect the maximal rate, whereas noncompetitive inhibitors affect the maximal rate.

Some inhibitor molecules bind to enzymes in a location where their binding induces a conformational change that reduces the affinity of the enzyme for its substrate. This type of inhibition is called **allosteric inhibition** (Figure 7.38). Most allosterically regulated enzymes are made up of more than one polypeptide, meaning that they have more than one protein subunit. When an allosteric inhibitor binds to an enzyme, all active sites on the protein subunits are changed slightly such that they bind their substrates with less efficiency. There are allosteric activators as well as inhibitors. Allosteric activators bind to locations on an enzyme away from the active site, inducing a conformational change that increases the affinity of the enzyme's active site(s) for its substrate(s).



**Figure 7.38** Allosteric inhibitors modify the active site of the enzyme so that substrate binding is reduced or prevented. In contrast, allosteric activators modify the active site of the enzyme so that the affinity for the substrate increases.

# everyday CONNECTION



Figure 7.39 Have you ever wondered how pharmaceutical drugs are developed? (credit: Deborah Austin)

# Drug Discovery by Looking for Inhibitors of Key Enzymes in Specific Pathways

Enzymes are key components of metabolic pathways. Understanding how enzymes work and how they can be regulated is a key principle behind the development of many of the pharmaceutical drugs (Figure 7.39) on the market today. Biologists working in this field collaborate with other scientists, usually chemists, to design drugs.

Consider statins for example—which is the name given to the class of drugs that reduces cholesterol levels. These compounds are essentially inhibitors of the enzyme HMG-CoA reductase. HMG-CoA reductase is the enzyme that synthesizes cholesterol from lipids in the body. By inhibiting this enzyme, the levels of cholesterol synthesized in the body can be reduced. Similarly, acetaminophen, popularly marketed under the brand name Tylenol, is an inhibitor of the enzyme cyclooxygenase. While it is effective in providing relief from fever and inflammation (pain), its mechanism of action is still not completely understood.

How are drugs developed? One of the first challenges in drug development is identifying the specific molecule that the drug is intended to target. In the case of statins, HMG-CoA reductase is the drug target. Drug targets are identified through painstaking research in the laboratory. Identifying the target alone is not sufficient; scientists also need to know how the target acts inside the cell and which reactions go awry in the case of disease. Once the target and the pathway are identified, then the actual process of drug design begins. During this stage, chemists and biologists work together to design and synthesize molecules that can either block or activate a particular reaction. However, this is only the beginning: both if and when a drug prototype is successful in performing its function, then it must undergo many tests from in vitro experiments to clinical trials before it can get FDA approval to be on the market.

Many enzymes don't work optimally, or even at all, unless bound to other specific non-protein helper molecules, either temporarily through ionic or hydrogen bonds or permanently through stronger covalent bonds. Two types of helper molecules are **cofactors** and **coenzymes**. Binding to these molecules promotes optimal conformation and function for their respective enzymes. Cofactors are inorganic ions such as iron (Fe++) and magnesium (Mg++). One example of an enzyme that requires a metal ion as a cofactor is the enzyme that builds DNA molecules, DNA polymerase, which requires bound zinc ion (Zn++) to function. Coenzymes are organic helper molecules, with a basic atomic structure made up of carbon and hydrogen, which are required for enzyme action. The most common sources of coenzymes are dietary vitamins (Figure 7.40). Some vitamins are precursors to coenzymes and others act directly as coenzymes. Vitamin C is a coenzyme for multiple enzymes that take part in building the important connective tissue component, collagen. An important step in the breakdown of glucose to yield energy is catalysis by a multi-enzyme complex called pyruvate dehydrogenase. Pyruvate dehydrogenase is a complex of several enzymes that actually requires one cofactor (a magnesium ion) and five different organic coenzymes to catalyze its specific chemical reaction. Therefore, enzyme function is, in part, regulated by an abundance of various cofactors and coenzymes, which are supplied primarily by the diets of most organisms.



Figure 7.40 Vitamins are important coenzymes or precursors of coenzymes, and are required for enzymes to function properly. Multivitamin capsules usually contain mixtures of all the vitamins at different percentages.

#### Enzyme Compartmentalization

In eukaryotic cells, molecules such as enzymes are usually compartmentalized into different organelles. This allows for yet another level of regulation of enzyme activity. Enzymes required only for certain cellular processes can be housed separately along with their substrates, allowing for more efficient chemical reactions. Examples of this sort of enzyme regulation based on location and proximity include the enzymes involved in the latter stages of cellular respiration, which take place exclusively in the mitochondria, and the enzymes involved in the digestion of cellular debris and foreign materials, located within lysosomes.

#### Feedback Inhibition in Metabolic Pathways

Molecules can regulate enzyme function in many ways. A major question remains, however: What are these molecules and where do they come from? Some are cofactors and coenzymes, ions, and organic molecules, as you've learned. What other molecules in the cell provide enzymatic regulation, such as allosteric modulation, and competitive and noncompetitive inhibition? The answer is that a wide variety of molecules can perform these roles. Some of these molecules include pharmaceutical and non-pharmaceutical drugs, toxins, and poisons from the environment. Perhaps the most relevant sources of enzyme regulatory molecules, with respect to cellular metabolism, are the products of the cellular metabolic reactions themselves. In a most efficient and elegant way, cells have evolved to use the products of their own reactions for feedback inhibition of enzyme activity. **Feedback inhibition** involves the use of a reaction product to regulate its own further production (**Figure 7.41**). The cell responds to the abundance of specific products by slowing down production during anabolic or catabolic reactions. Such reaction products may inhibit the enzymes that catalyzed their production through the mechanisms described above.


Figure 7.41 Metabolic pathways are a series of reactions catalyzed by multiple enzymes. Feedback inhibition, where the end product of the pathway inhibits an upstream step, is an important regulatory mechanism in cells.

The production of both amino acids and nucleotides is controlled through feedback inhibition. Additionally, ATP is an allosteric regulator of some of the enzymes involved in the catabolic breakdown of sugar, the process that produces ATP. In this way, when ATP is abundant, the cell can prevent its further production. Remember that ATP is an unstable molecule that can spontaneously dissociate into ADP. If too much ATP were present in a cell, much of it would go to waste. On the other hand, ADP serves as a positive allosteric regulator (an allosteric activator) for some of the same enzymes that are inhibited by ATP. Thus, when relative levels of ADP are high compared to ATP, the cell is triggered to produce more ATP through the catabolism of sugar.

## **KEY TERMS**

- activated complex (also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system
- activation energy energy necessary for reactions to occur
- activation energy (*E*<sub>a</sub>) energy necessary in order for a reaction to take place
- active site specific region of the enzyme to which the substrate binds
- **allosteric inhibition** inhibition by a binding event at a site different from the active site, which induces a conformational change and reduces the affinity of the enzyme for its substrate
- aminopeptidase protease that breaks down peptides to single amino acids; secreted by the brush border of small intestine
- **anabolic** (also, anabolism) pathways that require an input of energy to synthesize complex molecules from simpler ones
- Arrhenius equation mathematical relationship between the rate constant and the activation energy of a reaction
- **ATP** adenosine triphosphate, the cell's energy currency
- bioenergetics study of energy flowing through living systems
- carboxypeptidase protease that breaks down peptides to single amino acids; secreted by the brush border of the small intestine
- catabolic (also, catabolism) pathways in which complex molecules are broken down into simpler ones
- catalyst substance that increases the rate of a reaction without itself being consumed by the reaction

chemical energy potential energy in chemical bonds that is released when those bonds are broken

- **chemoautotroph** organism that can build organic molecules using energy derived from inorganic chemicals instead of sunlight
- chloroplast organelle in which photosynthesis takes place
- chylomicron small lipid globule
- chymotrypsin pancreatic protease
- **coenzyme** small organic molecule, such as a vitamin or its derivative, which is required to enhance the activity of an enzyme
- cofactor inorganic ion, such as iron and magnesium ions, required for optimal regulation of enzyme activity
- **collision theory** model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics
- **competitive inhibition** type of inhibition in which the inhibitor competes with the substrate molecule by binding to the active site of the enzyme
- denature process that changes the natural properties of a substance
- digestion mechanical and chemical break down of food into small organic fragments
- dipeptidase protease that breaks down peptides to single amino acids; secreted by the brush border of small intestine

elastase pancreatic protease

endergonic describes chemical reactions that require energy input

enthalpy total energy of a system

essential nutrient nutrient that cannot be synthesized by the body; it must be obtained from food

exergonic describes chemical reactions that release free energy

**feedback inhibition** effect of a product of a reaction sequence to decrease its further production by inhibiting the activity of the first enzyme in the pathway that produces it

free energy Gibbs free energy is the usable energy, or energy that is available to do work.

frequency factor (A) proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

granum stack of thylakoids located inside a chloroplast

heat energy total bond energy of reactants or products in a chemical reaction

**heterotroph** organism that consumes organic substances or other organisms for food

induced fit dynamic fit between the enzyme and its substrate, in which both components modify their structures to allow for ideal binding

ingestion act of taking in food

**kinetic energy** type of energy associated with objects or particles in motion

lactase enzyme that breaks down lactose into glucose and galactose

**light-dependent reaction** first stage of photosynthesis where certain wavelengths of the visible light are absorbed to form two energy-carrying molecules (ATP and NADPH)

**light-independent reaction** second stage of photosynthesis, though which carbon dioxide is used to build carbohydrate molecules using energy from ATP and NADPH

maltase enzyme that breaks down maltose into glucose

mesophyll middle layer of chlorophyll-rich cells in a leaf

metabolism all the chemical reactions that take place inside cells, including anabolism and catabolism

mineral inorganic, elemental molecule that carries out important roles in the body

phosphoanhydride bond bond that connects phosphates in an ATP molecule

photoautotroph organism capable of producing its own organic compounds from sunlight

**pigment** molecule that is capable of absorbing certain wavelengths of light and reflecting others (which accounts for its color)

potential energy type of energy that has the potential to do work; stored energy

- **stoma** opening that regulates gas exchange and water evaporation between leaves and the environment, typically situated on the underside of leaves
- **stroma** fluid-filled space surrounding the grana inside a chloroplast where the light-independent reactions of photosynthesis take place

substrate molecule on which the enzyme acts

sucrase enzyme that breaks down sucrose into glucose and fructose

- **thylakoid** disc-shaped, membrane-bound structure inside a chloroplast where the light-dependent reactions of photosynthesis take place; stacks of thylakoids are called grana
- thylakoid lumen aqueous space bound by a thylakoid membrane where protons accumulate during light-driven electron transport
- transition state high-energy, unstable state (an intermediate form between the substrate and the product) occurring during a chemical reaction
- trypsin pancreatic protease that breaks down protein

vitamin organic substance necessary in small amounts to sustain life

## **CHAPTER SUMMARY**

#### 7.2 Nutrition and Energy Production

Animal diet should be balanced and meet the needs of the body. Carbohydrates, proteins, and fats are the primary components of food. Some essential nutrients are required for cellular function but cannot be produced by the animal body. These include vitamins, minerals, some fatty acids, and some amino acids. Food intake in more than necessary amounts is stored as glycogen in the liver and muscle cells, and in fat cells. Excess adipose storage can lead to obesity and serious health problems. ATP is the energy currency of the cell and is obtained from the metabolic pathways. Excess carbohydrates and energy are stored as glycogen in the body.

## 7.3 Digestive System Processes

Digestion begins with ingestion, where the food is taken in the mouth. Digestion and absorption take place in a series of steps with special enzymes playing important roles in digesting carbohydrates, proteins, and lipids. Elimination describes removal of undigested food contents and waste products from the body. While most absorption occurs in the small intestines, the large intestine is responsible for the final removal of water that remains after the absorptive process of the small intestines. The cells that line the large intestine absorb some vitamins as well as any leftover salts and water. The large intestine (colon) is also where feces is formed.

#### 7.4 Energy and Metabolism

Cells perform the functions of life through various chemical reactions. A cell's metabolism refers to the chemical reactions that take place within it. There are metabolic reactions that involve the breaking down of complex chemicals into simpler ones, such as the breakdown of large macromolecules. This process is referred to as catabolism, and such reactions are associated with a release of energy. On the other end of the spectrum, anabolism refers to metabolic processes that build complex molecules out of simpler ones, such as the synthesis of macromolecules. Anabolic processes require energy. Glucose synthesis and glucose breakdown are examples of anabolic and catabolic pathways, respectively.

#### 7.5 Potential, Kinetic, Free, and Activation Energy

Energy comes in many different forms. Objects in motion do physical work, and kinetic energy is the energy of objects in motion. Objects that are not in motion may have the potential to do work, and thus, have potential energy. Molecules also have potential energy because the breaking of molecular bonds has the potential to release energy. Living cells depend on the harvesting of potential energy from molecular bonds to perform work. Free energy is a measure of energy that is available to do work. The free energy of a system changes during energy transfers such as chemical reactions, and this change is referred to as  $\Delta G$ .

The  $\Delta G$  of a reaction can be negative or positive, meaning that the reaction releases energy or consumes energy, respectively. A reaction with a negative  $\Delta G$  that gives off energy is called an exergonic reaction. One with a positive  $\Delta G$  that requires energy input is called an endergonic reaction. Exergonic reactions are said to be spontaneous, because their products have less energy than their reactants. The products of endergonic reactions have a higher energy state than the reactants, and so these are nonspontaneous reactions. However, all reactions (including spontaneous - $\Delta G$  reactions) require an initial input of energy in order to reach the transition state, at which they'll proceed. This initial input of energy is called the activation energy.

## 7.6 ATP: Adenosine Triphosphate

ATP is the primary energy-supplying molecule for living cells. ATP is made up of a nucleotide, a five-carbon sugar, and three phosphate groups. The bonds that connect the phosphates (phosphoanhydride bonds) have high-energy content. The energy released from the hydrolysis of ATP into ADP +  $P_i$  is used to perform cellular work. Cells use ATP to perform work by coupling the exergonic reaction of ATP hydrolysis with endergonic reactions. ATP donates its phosphate group to another molecule via a process known as phosphorylation. The phosphorylated molecule is at a higher-energy state and is less stable than its unphosphorylated form, and this added energy from the addition of the phosphate allows the molecule to undergo its endergonic reaction.

## 7.7 Overview of Photosynthesis

The process of photosynthesis transformed life on Earth. By harnessing energy from the sun, photosynthesis evolved to allow living things access to enormous amounts of energy. Because of photosynthesis, living things gained access to sufficient energy that allowed them to build new structures and achieve the biodiversity evident today.

Only certain organisms, called photoautotrophs, can perform photosynthesis; they require the presence of chlorophyll, a specialized pigment that absorbs certain portions of the visible spectrum and can capture energy from sunlight. Photosynthesis uses carbon dioxide and water to assemble carbohydrate molecules and release oxygen as a waste product into the atmosphere. Eukaryotic autotrophs, such as plants and algae, have organelles called chloroplasts in which photosynthesis takes place, and starch accumulates. In prokaryotes, such as cyanobacteria, the process is less localized and occurs within folded membranes, extensions of the plasma membrane, and in the cytoplasm.

## 7.8 Collision Theory

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant and its activation energy, temperature, and dependence on collision orientation.

## 7.9 Factors Affecting Reaction Rates

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

## 7.10 Enzymes

Enzymes are chemical catalysts that accelerate chemical reactions at physiological temperatures by lowering their activation energy. Enzymes are usually proteins consisting of one or more polypeptide chains. Enzymes have an active site that provides a unique chemical environment, made up of certain amino acid R groups (residues). This unique environment is perfectly suited to convert particular chemical reactants for that enzyme, called substrates, into unstable intermediates called transition states. Enzymes and substrates are thought to bind with an induced fit, which means that enzymes undergo slight conformational adjustments upon substrate contact, leading to full, optimal binding. Enzymes bind to substrates and catalyze reactions in four different ways: bringing substrates together in an optimal orientation, compromising the bond structures of substrates so that bonds can be more easily broken, providing optimal environmental conditions for a reaction to occur, or participating directly in their chemical reaction by forming transient covalent bonds with the substrates.

Enzyme action must be regulated so that in a given cell at a given time, the desired reactions are being catalyzed and the undesired reactions are not. Enzymes are regulated by cellular conditions, such as temperature and pH. They are also regulated through their location within a cell, sometimes being compartmentalized so that they can only catalyze reactions under certain circumstances. Inhibition and activation of enzymes via other molecules are other important ways that enzymes are regulated. Inhibitors can act competitively, noncompetitively, or allosterically; noncompetitive inhibitors are usually allosteric. Activators can also enhance the function of enzymes allosterically. The most common method by which cells regulate the enzymes in metabolic pathways is through feedback inhibition. During feedback inhibition, the products of a

metabolic pathway serve as inhibitors (usually allosteric) of one or more of the enzymes (usually the first committed enzyme of the pathway) involved in the pathway that produces them.

## **ART CONNECTION QUESTIONS**

**23.** Figure 7.8 Which of the following statements about digestive processes is true?

- Amylase, maltase and lactase in the mouth digest carbohydrates.
- b. Trypsin and lipase in the stomach digest protein.
- c. Bile emulsifies lipids in the small intestine.
- d. No food is absorbed until the small intestine.

**24. Figure 7.15** Look at each of the processes shown, and decide if it is endergonic or exergonic. In each case, does enthalpy increase or decrease, and does entropy increase or decrease?

25. Figure 7.17 If no activation energy were required

## **REVIEW QUESTIONS**

28. Which of the following statements is not true?

- a. Essential nutrients can be synthesized by the body.
- b. Vitamins are required in small quantities for bodily function.
- c. Some amino acids can be synthesized by the body, while others need to be obtained from diet.
- d. Vitamins come in two categories: fat-soluble and water-soluble.
- 29. Which of the following is a water-soluble vitamin?
  - a. vitamin A
  - b. vitamin E
  - c. vitamin K
  - d. vitamin C
- 30. What is the primary fuel for the body?
  - a. carbohydrates
  - b. lipids
  - c. protein
  - d. glycogen
- **31.** Excess glucose is stored as \_\_\_\_\_
  - a. fat
  - b. glucagon
  - c. glycogen
  - d. it is not stored in the body

**32.** Where does the majority of protein digestion take place?

- a. stomach
- b. duodenum
- c. mouth
- d. jejunum

33. Lipases are enzymes that break down \_\_\_\_\_

to break down sucrose (table sugar), would you be able to store it in a sugar bowl?

**26.** Figure 7.19 The hydrolysis of one ATP molecule releases 7.3 kcal/mol of energy ( $\Delta G = -7.3$  kcal/mol of energy). If it takes 2.1 kcal/mol of energy to move one Na<sup>+</sup> across the membrane ( $\Delta G = +2.1$  kcal/mol of energy), how many sodium ions could be moved by the hydrolysis of one ATP molecule?

**27. Figure 7.24** On a hot, dry day, plants close their stomata to conserve water. What impact will this have on photosynthesis?

- a. disaccharides
- b. lipids
- c. proteins
- d. cellulose

**34.** Energy is stored long-term in the bonds of \_\_\_\_\_ and used short-term to perform work from a(n) \_\_\_\_\_ molecule.

- a. ATP : glucose
- b. an anabolic molecule : catabolic molecule
- c. glucose : ATP
- d. a catabolic molecule : anabolic molecule

**35.** DNA replication involves unwinding two strands of parent DNA, copying each strand to synthesize complementary strands, and releasing the parent and daughter DNA. Which of the following accurately describes this process?

- a. This is an anabolic process
- b. This is a catabolic process
- c. This is both anabolic and catabolic
- d. This is a metabolic process but is neither anabolic nor catabolic

**36.** Consider a pendulum swinging. Which type(s) of energy is/are associated with the pendulum in the following instances: i. the moment at which it completes one cycle, just before it begins to fall back towards the other end, ii. the moment that it is in the middle between the two ends, iii. just before it reaches the end of one cycle (just before instant i.).

- a. i. potential and kinetic, ii. potential and kinetic, iii. kinetic
- b. i. potential, ii. potential and kinetic, iii. potential and kinetic
- c. i. potential, ii. kinetic, iii. potential and kinetic
- d. i. potential and kinetic, ii. kinetic iii. kinetic

**37.** Which of the following comparisons or contrasts between endergonic and exergonic reactions is false?

- a. Endergonic reactions have a positive  $\Delta G$  and exergonic reactions have a negative  $\Delta G$
- b. Endergonic reactions consume energy and exergonic reactions release energy
- c. Both endergonic and exergonic reactions require a small amount of energy to overcome an activation barrier
- d. Endergonic reactions take place slowly and exergonic reactions take place quickly

**38.** Which of the following is the best way to judge the relative activation energies between two given chemical reactions?

- a. Compare the  $\Delta G$  values between the two reactions
- b. Compare their reaction rates
- c. Compare their ideal environmental conditions
- d. Compare the spontaneity between the two reactions
- 39. The energy released by the hydrolysis of ATP is
  - a. primarily stored between the alpha and beta phosphates
  - b. equal to -57 kcal/mol
  - c. harnessed as heat energy by the cell to perform work
  - d. providing energy to coupled reactions

**40.** Which of the following molecules is likely to have the most potential energy?

- a. sucrose
- b. ATP
- c. glucose
- d. ADP

**41.** Which of the following components is *not* used by both plants and cyanobacteria to carry out photosynthesis?

- a. chloroplasts
- b. chlorophyll
- c. carbon dioxide
- d. water

**42.** What two main products result from photosynthesis?

## **CRITICAL THINKING QUESTIONS**

- 48. What are essential nutrients?
- 49. What is the role of minerals in maintaining good

- a. oxygen and carbon dioxide
- b. chlorophyll and oxygen
- c. sugars/carbohydrates and oxygen
- d. sugars/carbohydrates and carbon dioxide

**43.** In which compartment of the plant cell do the light-independent reactions of photosynthesis take place?

- a. thylakoid
- b. stroma
- c. outer membrane
- d. mesophyll

**44.** Which statement about thylakoids in eukaryotes is *not* correct?

- a. Thylakoids are assembled into stacks.
- b. Thylakoids exist as a maze of folded membranes.
- c. The space surrounding thylakoids is called stroma.
- d. Thylakoids contain chlorophyll.
- 45. Which of the following is not true about enzymes:
  - a. They increase  $\Delta G$  of reactions
  - b. They are usually made of amino acids
  - c. They lower the activation energy of chemical reactions
  - d. Each one is specific to the particular substrate(s) to which it binds
- 46. An allosteric inhibitor does which of the following?
  - Binds to an enzyme away from the active site and changes the conformation of the active site, increasing its affinity for substrate binding
  - b. Binds to the active site and blocks it from binding substrate
  - c. Binds to an enzyme away from the active site and changes the conformation of the active site, decreasing its affinity for the substrate
  - d. Binds directly to the active site and mimics the substrate

**47.** Which of the following analogies best describe the induced-fit model of enzyme-substrate binding?

- a. A hug between two people
- b. A key fitting into a lock
- c. A square peg fitting through the square hole and a round peg fitting through the round hole of a children's toy
- d. The fitting together of two jigsaw puzzle pieces.

health?

**50.** Discuss why obesity is a growing epidemic.

**51.** There are several nations where malnourishment is a common occurrence. What may be some of the health challenges posed by malnutrition?

**52.** Explain why some dietary lipid is a necessary part of a balanced diet.

**53.** Does physical exercise involve anabolic and/or catabolic processes? Give evidence for your answer.

**54.** Name two different cellular functions that require energy that parallel human energy-requiring functions.

**55.** Explain in your own words the difference between a spontaneous reaction and one that occurs instantaneously, and what causes this difference.

**56.** Describe the position of the transition state on a vertical energy scale, from low to high, relative to the

## CHAPTER SUMMARY

7.2 Nutrition and Energy Production

position of the reactants and products, for both endergonic and exergonic reactions.

**57.** Do you think that the E<sub>A</sub> for ATP hydrolysis is relatively low or high? Explain your reasoning.

**58.** What is the overall outcome of the light reactions in photosynthesis?

**59.** Why are carnivores, such as lions, dependent on photosynthesis to survive?

**60.** Why are energy carriers thought of as either "full" or "empty"?

**61.** With regard to enzymes, why are vitamins necessary for good health? Give examples.

**62.** Explain in your own words how enzyme feedback inhibition benefits a cell.

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The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

## 7.10 Enzymes

Enzymes are chemical catalysts that accelerate chemical reactions at physiological temperatures by lowering their activation energy. Enzymes are usually proteins consisting of one or more polypeptide chains. Enzymes have an active site that provides a unique chemical environment, made up of certain amino acid R groups (residues). This unique environment is perfectly suited to convert particular chemical reactants for that enzyme, called substrates, into unstable intermediates called transition states. Enzymes and substrates are thought to bind with an induced fit, which means that enzymes undergo slight conformational adjustments upon substrate contact, leading to full, optimal binding. Enzymes bind to substrates and catalyze reactions in four different ways: bringing substrates together in an optimal orientation, compromising the bond structures of substrates so that bonds can be more easily broken, providing optimal environmental conditions for a reaction to occur, or participating directly in their chemical reaction by forming transient covalent bonds with the substrates.

Enzyme action must be regulated so that in a given cell at a given time, the desired reactions are being catalyzed and the undesired reactions are not. Enzymes are regulated by cellular conditions, such as temperature and pH. They are also regulated through their location within a cell, sometimes being compartmentalized so that they can only catalyze reactions under certain circumstances. Inhibition and

activation of enzymes via other molecules are other important ways that enzymes are regulated. Inhibitors can act competitively, noncompetitively, or allosterically; noncompetitive inhibitors are usually allosteric. Activators can also enhance the function of enzymes allosterically. The most common method by which cells regulate the enzymes in metabolic pathways is through feedback inhibition. During feedback inhibition, the products of a metabolic pathway serve as inhibitors (usually allosteric) of one or more of the enzymes (usually the first committed enzyme of the pathway) involved in the pathway that produces them.

## **ART CONNECTION QUESTIONS**

**63.** Figure 7.8 Which of the following statements about digestive processes is true?

- a. Amylase, maltase and lactase in the mouth digest carbohydrates.
- b. Trypsin and lipase in the stomach digest protein.
- c. Bile emulsifies lipids in the small intestine.
- d. No food is absorbed until the small intestine.

**64.** Figure 7.15 Look at each of the processes shown, and decide if it is endergonic or exergonic. In each case, does enthalpy increase or decrease, and does entropy increase or decrease?

65. Figure 7.17 If no activation energy were required

## **REVIEW QUESTIONS**

68. Which of the following statements is not true?

- a. Essential nutrients can be synthesized by the body.
- b. Vitamins are required in small quantities for bodily function.
- c. Some amino acids can be synthesized by the body, while others need to be obtained from diet.
- d. Vitamins come in two categories: fat-soluble and water-soluble.

69. Which of the following is a water-soluble vitamin?

- a. vitamin A
- b. vitamin E
- c. vitamin K
- d. vitamin C
- 70. What is the primary fuel for the body?
  - a. carbohydrates
  - b. lipids
  - c. protein
  - d. glycogen
- 71. Excess glucose is stored as \_\_\_\_\_
  - a. fat
  - b. glucagon
  - c. glycogen
  - d. it is not stored in the body

**72.** Where does the majority of protein digestion take place?

to break down sucrose (table sugar), would you be able to store it in a sugar bowl?

**66.** Figure 7.19 The hydrolysis of one ATP molecule releases 7.3 kcal/mol of energy ( $\Delta G = -7.3$  kcal/mol of energy). If it takes 2.1 kcal/mol of energy to move one Na<sup>+</sup> across the membrane ( $\Delta G = +2.1$  kcal/mol of energy), how many sodium ions could be moved by the hydrolysis of one ATP molecule?

**67.** Figure 7.24 On a hot, dry day, plants close their stomata to conserve water. What impact will this have on photosynthesis?

- a. stomach
- b. duodenum
- c. mouth
- d. jejunum
- 73. Lipases are enzymes that break down \_\_\_\_\_
  - a. disaccharides
  - b. lipids
  - c. proteins
  - d. cellulose

**74.** Energy is stored long-term in the bonds of \_\_\_\_\_ and used short-term to perform work from a(n) \_\_\_\_\_ molecule.

- a. ATP : glucose
- b. an anabolic molecule : catabolic molecule
- c. glucose : ATP
- d. a catabolic molecule : anabolic molecule

**75.** DNA replication involves unwinding two strands of parent DNA, copying each strand to synthesize complementary strands, and releasing the parent and daughter DNA. Which of the following accurately describes this process?

- a. This is an anabolic process
- b. This is a catabolic process
- c. This is both anabolic and catabolic
- d. This is a metabolic process but is neither anabolic nor catabolic

**76.** Consider a pendulum swinging. Which type(s) of energy is/are associated with the pendulum in the following instances: i. the moment at which it completes one cycle, just before it begins to fall back

towards the other end, ii. the moment that it is in the middle between the two ends, iii. just before it reaches the end of one cycle (just before instant i.).

- a. i. potential and kinetic, ii. potential and kinetic, iii. kinetic
- b. i. potential, ii. potential and kinetic, iii. potential and kinetic
- c. i. potential, ii. kinetic, iii. potential and kinetic
- d. i. potential and kinetic, ii. kinetic iii. kinetic

**77.** Which of the following comparisons or contrasts between endergonic and exergonic reactions is false?

- a. Endergonic reactions have a positive  $\Delta G$  and exergonic reactions have a negative  $\Delta G$
- b. Endergonic reactions consume energy and exergonic reactions release energy
- c. Both endergonic and exergonic reactions require a small amount of energy to overcome an activation barrier
- d. Endergonic reactions take place slowly and exergonic reactions take place quickly

**78.** Which of the following is the best way to judge the relative activation energies between two given chemical reactions?

- a. Compare the  $\Delta G$  values between the two reactions
- b. Compare their reaction rates
- c. Compare their ideal environmental conditions
- d. Compare the spontaneity between the two reactions
- 79. The energy released by the hydrolysis of ATP is
  - a. primarily stored between the alpha and beta phosphates
  - b. equal to -57 kcal/mol
  - c. harnessed as heat energy by the cell to perform work
  - d. providing energy to coupled reactions

**80.** Which of the following molecules is likely to have the most potential energy?

- a. sucrose
- b. ATP
- c. glucose
- d. ADP

**81.** Which of the following components is *not* used by both plants and cyanobacteria to carry out photosynthesis?

- a. chloroplasts
- b. chlorophyll
- c. carbon dioxide
- d. water

**82.** What two main products result from photosynthesis?

- a. oxygen and carbon dioxide
- b. chlorophyll and oxygen
- c. sugars/carbohydrates and oxygen
- d. sugars/carbohydrates and carbon dioxide

**83.** In which compartment of the plant cell do the light-independent reactions of photosynthesis take place?

- a. thylakoid
- b. stroma
- c. outer membrane
- d. mesophyll

**84.** Which statement about thylakoids in eukaryotes is *not* correct?

- a. Thylakoids are assembled into stacks.
- b. Thylakoids exist as a maze of folded membranes.
- c. The space surrounding thylakoids is called stroma.
- d. Thylakoids contain chlorophyll.

85. Which of the following is not true about enzymes:

- a. They increase  $\Delta G$  of reactions
- b. They are usually made of amino acids
- c. They lower the activation energy of chemical reactions
- d. Each one is specific to the particular substrate(s) to which it binds
- 86. An allosteric inhibitor does which of the following?
  - Binds to an enzyme away from the active site and changes the conformation of the active site, increasing its affinity for substrate binding
  - b. Binds to the active site and blocks it from binding substrate
  - c. Binds to an enzyme away from the active site and changes the conformation of the active site, decreasing its affinity for the substrate
  - d. Binds directly to the active site and mimics the substrate

**87.** Which of the following analogies best describe the induced-fit model of enzyme-substrate binding?

- a. A hug between two people
- b. A key fitting into a lock
- c. A square peg fitting through the square hole and a round peg fitting through the round hole of a children's toy
- d. The fitting together of two jigsaw puzzle pieces.

## **CRITICAL THINKING QUESTIONS**

88. What are essential nutrients?

**89.** What is the role of minerals in maintaining good health?

**90.** Discuss why obesity is a growing epidemic.

**91.** There are several nations where malnourishment is a common occurrence. What may be some of the health challenges posed by malnutrition?

**92.** Explain why some dietary lipid is a necessary part of a balanced diet.

**93.** Does physical exercise involve anabolic and/or catabolic processes? Give evidence for your answer.

**94.** Name two different cellular functions that require energy that parallel human energy-requiring functions.

**95.** Explain in your own words the difference between a spontaneous reaction and one that occurs instantaneously, and what causes this difference.

**96.** Describe the position of the transition state on a vertical energy scale, from low to high, relative to the position of the reactants and products, for both endergonic and exergonic reactions.

**97.** Do you think that the E<sub>A</sub> for ATP hydrolysis is relatively low or high? Explain your reasoning.

**98.** What is the overall outcome of the light reactions in photosynthesis?

**99.** Why are carnivores, such as lions, dependent on photosynthesis to survive?

**100.** Why are energy carriers thought of as either "full" or "empty"?

**101.** With regard to enzymes, why are vitamins necessary for good health? Give examples.

**102.** Explain in your own words how enzyme feedback inhibition benefits a cell.

# 8 | DNA, GENES, AND PROTEINS



Figure 8.1 Dolly the sheep was the first large mammal to be cloned.



## Introduction

The three letters "DNA" have now become synonymous with crime solving, paternity testing, human identification, and genetic testing. DNA can be retrieved from hair, blood, or saliva. Each person's DNA is unique, and it is possible to detect differences between individuals within a species on the basis of these unique features.

DNA analysis has many practical applications beyond forensics. In humans, DNA testing is applied to numerous uses: determining paternity, tracing genealogy, identifying pathogens, archeological research, tracing disease outbreaks, and studying human migration patterns. In the medical field, DNA is used in diagnostics, new vaccine development, and cancer therapy. It is now possible to determine predisposition to diseases by looking at genes.

Each human cell has 23 pairs of chromosomes: one set of chromosomes is inherited from the mother and the other set is inherited from the father. There is also a mitochondrial genome, inherited exclusively from the mother, which can be involved in inherited genetic disorders. On each chromosome, there are thousands of genes that are responsible for determining the genotype and phenotype of the individual. A gene is defined as a sequence of DNA that codes for a functional product. The human haploid genome contains 3 billion base pairs and has between 20,000 and 25,000 functional genes.



**Figure 8.2** Genes, which are carried on (a) chromosomes, are linearly organized instructions for making the RNA and protein molecules that are necessary for all of processes of life. The (b) interleukin-2 protein and (c) alpha-2u-globulin protein are just two examples of the array of different molecular structures that are encoded by genes. (credit "chromosome: National Human Genome Research Institute; credit "interleukin-2": Ramin Herati/Created from PDB 1M47 and rendered with Pymol; credit "alpha-2u-globulin": Darren Logan/rendered with AISMIG)

## **Chapter Outline**

- 8.1: DNA Structure and Sequencing
- 8.2: The Genetic Code
- 8.3: Eukaryotic Transcription
- 8.4: Ribosomes and Protein Synthesis

## Introduction

Since the rediscovery of Mendel's work in 1900, the definition of the gene has progressed from an abstract unit of heredity to a tangible molecular entity capable of replication, expression, and mutation (Figure 8.2). Genes are composed of DNA and are linearly arranged on chromosomes. Genes specify the sequences of amino acids, which are the building blocks of proteins. In turn, proteins are responsible for orchestrating nearly every function of the cell. Both genes and the proteins they encode are absolutely essential to life as we know it.

# 8.1 | DNA Structure and Sequencing

By the end of this section, you will be able to:

- Describe the structure of DNA
- Explain the Sanger method of DNA sequencing
- · Discuss the similarities and differences between eukaryotic and prokaryotic DNA

The building blocks of DNA are nucleotides. The important components of the nucleotide are a nitrogenous base, deoxyribose (5-carbon sugar), and a phosphate group (Figure 8.3). The nucleotide is named depending on the nitrogenous base. The nitrogenous base can be a purine such as adenine (A) and guanine (G), or a pyrimidine such as cytosine (C) and thymine (T).



Figure 8.3 Each nucleotide is made up of a sugar, a phosphate group, and a nitrogenous base. The sugar is deoxyribose in DNA and ribose in RNA.

The nucleotides combine with each other by covalent bonds known as phosphodiester bonds or linkages. The purines have a double ring structure with a six-membered ring fused to a five-membered ring. Pyrimidines are smaller in size; they have a single six-membered ring structure. The carbon atoms of the five-carbon sugar are numbered 1', 2', 3', 4', and 5' (1' is read as "one prime"). The phosphate residue is attached to the hydroxyl group of the 5' carbon of one sugar of one nucleotide and the hydroxyl group of the 3' carbon of the sugar of the next nucleotide, thereby forming a 5'-3' phosphodiester bond.

In the 1950s, Francis Crick and James Watson worked together to determine the structure of DNA at the University of Cambridge, England. Other scientists like Linus Pauling and Maurice Wilkins were also actively exploring this field. Pauling had discovered the secondary structure of proteins using X-ray crystallography. In Wilkins' lab, researcher Rosalind Franklin was using X-ray diffraction methods to understand the structure of DNA. Watson and Crick were able to piece together the puzzle of the DNA molecule on the basis of Franklin's data because Crick had also studied X-ray diffraction (Figure 8.4). In 1962, James Watson, Francis Crick, and Maurice Wilkins were awarded the Nobel Prize in Medicine. Unfortunately, by then Franklin had died, and Nobel prizes are not awarded posthumously.



Figure 8.4 The work of pioneering scientists (a) James Watson, Francis Crick, and Maclyn McCarty led to our present day understanding of DNA. Scientist Rosalind Franklin discovered (b) the X-ray diffraction pattern of DNA, which helped to elucidate its double helix structure. (credit a: modification of work by Marjorie McCarty, Public Library of Science)

Watson and Crick proposed that DNA is made up of two strands that are twisted around each other to form a right-handed helix. Base pairing takes place between a purine and pyrimidine; namely, A pairs with T and G pairs with C. Adenine and thymine are complementary base pairs, and cytosine and guanine are also complementary base pairs. The base pairs are stabilized by hydrogen bonds; adenine and thymine form two hydrogen bonds

and cytosine and guanine form three hydrogen bonds. The two strands are anti-parallel in nature; that is, the 3' end of one strand faces the 5' end of the other strand. The sugar and phosphate of the nucleotides form the backbone of the structure, whereas the nitrogenous bases are stacked inside. Each base pair is separated from the other base pair by a distance of 0.34 nm, and each turn of the helix measures 3.4 nm. Therefore, ten base pairs are present per turn of the helix. The diameter of the DNA double helix is 2 nm, and it is uniform throughout. Only the pairing between a purine and pyrimidine can explain the uniform diameter. The twisting of the two strands around each other results in the formation of uniformly spaced major and minor grooves (Figure 8.5).



Figure 8.5 DNA has (a) a double helix structure and (b) phosphodiester bonds. The (c) major and minor grooves are binding sites for DNA binding proteins during processes such as transcription (the copying of RNA from DNA) and replication.

## **DNA Sequencing Techniques**

Until the 1990s, the sequencing of DNA (reading the sequence of DNA) was a relatively expensive and long process. Using radiolabeled nucleotides also compounded the problem through safety concerns. With currently available technology and automated machines, the process is cheap, safer, and can be completed in a matter of hours. Fred Sanger developed the sequencing method used for the human genome sequencing project, which is widely used today (Figure 8.6).





Visit this site (http://openstaxcollege.org/l/DNA\_sequencing) to watch a video explaining the DNA sequence reading technique that resulted from Sanger's work.

The method is known as the dideoxy chain termination method. The sequencing method is based on the use of chain terminators, the dideoxynucleotides (ddNTPs). The dideoxynucleotides, or ddNTPSs, differ from the deoxynucleotides by the lack of a free 3' OH group on the five-carbon sugar. If a ddNTP is added to a growing a DNA strand, the chain is not extended any further because the free 3' OH group needed to add another nucleotide is not available. By using a predetermined ratio of deoxyribonucleotides to dideoxynucleotides, it is possible to generate DNA fragments of different sizes.



Dye–labeled dideoxynucleotides are used to generate DNA fragments of different lengths

GAT AAAT CT GGTCT TATT TCC

**Figure 8.6** In Frederick Sanger's dideoxy chain termination method, dye-labeled dideoxynucleotides are used to generate DNA fragments that terminate at different points. The DNA is separated by capillary electrophoresis on the basis of size, and from the order of fragments formed, the DNA sequence can be read. The DNA sequence readout is shown on an electropherogram that is generated by a laser scanner.

The DNA sample to be sequenced is denatured or separated into two strands by heating it to high temperatures. The DNA is divided into four tubes in which a primer, DNA polymerase, and all four nucleotides (A, T, G, and C) are added. In addition to each of the four tubes, limited quantities of one of the four dideoxynucleotides are added to each tube respectively. The tubes are labeled as A, T, G, and C according to the ddNTP added. For detection purposes, each of the four dideoxynucleotides carries a different fluorescent label. Chain elongation continues until a fluorescent dideoxy nucleotide is incorporated, after which no further elongation takes place. After the reaction is over, electrophoresis is performed. Even a difference in length of a single base can be detected. The sequence is read from a laser scanner. For his work on DNA sequencing, Sanger received a Nobel Prize in chemistry in 1980.





Sanger's genome sequencing has led to a race to sequence human genomes at a rapid speed and low cost, often referred to as the \$1000 in one day sequence. Learn more by selecting the Sequencing at Speed animation here (http://openstaxcollege.org/l/DNA\_and\_genomes).

Gel **electrophoresis** is a technique used to separate DNA fragments of different sizes. Usually the gel is made of a chemical called agarose. Agarose powder is added to a buffer and heated. After cooling, the gel solution is poured into a casting tray. Once the gel has solidified, the DNA is loaded on the gel and electric current is applied. The DNA has a net negative charge and moves from the negative electrode toward the positive electrode. The electric current is applied for sufficient time to let the DNA separate according to size; the smallest fragments will be farthest from the well (where the DNA was loaded), and the heavier molecular weight fragments will be closest to the well. Once the DNA is separated, the gel is stained with a DNA-specific dye for viewing it (Figure 8.7).



Figure 8.7 DNA can be separated on the basis of size using gel electrophoresis. (credit: James Jacob, Tompkins Cortland Community College)

# e olution CONNECTION

## Neanderthal Genome: How Are We Related?

The first draft sequence of the Neanderthal genome was recently published by Richard E. Green et al. in 2010.<sup>[1]</sup> Neanderthals are the closest ancestors of present-day humans. They were known to have lived in Europe and Western Asia before they disappeared from fossil records approximately 30,000 years ago. Green's team studied almost 40,000-year-old fossil remains that were selected from sites across the world. Extremely sophisticated means of sample preparation and DNA sequencing were employed because of the fragile nature of the bones and heavy microbial contamination. In their study, the scientists were able to sequence some four billion base pairs. The Neanderthal sequence was compared with that of present-day humans from across the world. After comparing the sequences, the researchers found that the Neanderthal genome had 2 to 3 percent greater similarity to people living outside Africa than to people in Africa. While current theories have suggested that all present-day humans can be traced to a small ancestral population in Africa, the data from the Neanderthal genome may contradict this view. Green and his colleagues also discovered DNA segments among people in Europe and Asia that are more similar to Neanderthal sequences than to other contemporary human sequences. Another interesting observation was that Neanderthals are as closely related to people from Papua New Guinea as to those from China or France. This is surprising because Neanderthal fossil remains have been located only in Europe and West Asia. Most likely, genetic exchange took place between Neanderthals and modern humans as modern humans emerged out of Africa, before the divergence of Europeans, East Asians, and Papua New Guineans.

Several genes seem to have undergone changes from Neanderthals during the evolution of presentday humans. These genes are involved in cranial structure, metabolism, skin morphology, and cognitive development. One of the genes that is of particular interest is *RUNX2*, which is different in modern day humans and Neanderthals. This gene is responsible for the prominent frontal bone, bell-shaped rib cage, and dental differences seen in Neanderthals. It is speculated that an evolutionary change in *RUNX2* was important in the origin of modern-day humans, and this affected the cranium and the upper body.





Watch **Svante Pääbo's talk (http://openstaxcollege.org/l/neanderthal)** explaining the Neanderthal genome research at the 2011 annual TED (Technology, Entertainment, Design) conference.

## DNA Packaging in Cells

When comparing prokaryotic cells to eukaryotic cells, prokaryotes are much simpler than eukaryotes in many of their features (Figure 8.8). Most prokaryotes contain a single, circular chromosome that is found in an area of the cytoplasm called the nucleoid.





In eukaryotic cells, DNA and RNA synthesis occur in a separate compartment from protein synthesis. In prokaryotic cells, both processes occur together. What advantages might there be to separating the processes? What advantages might there be to having them occur together?

The size of the genome in one of the most well-studied prokaryotes, *E.coli*, is 4.6 million base pairs (approximately 1.1 mm, if cut and stretched out). So how does this fit inside a small bacterial cell? The DNA is twisted by what is known as supercoiling. Supercoiling means that DNA is either under-wound (less than one turn of the helix per 10 base pairs) or over-wound (more than 1 turn per 10 base pairs) from its normal relaxed state. Some proteins are known to be involved in the supercoiling; other proteins and enzymes such as DNA gyrase help in maintaining the supercoiled structure.

Eukaryotes, whose chromosomes each consist of a linear DNA molecule, employ a different type of packing strategy to fit their DNA inside the nucleus (Figure 8.9). At the most basic level, DNA is wrapped around proteins known as histones to form structures called nucleosomes. The histones are evolutionarily conserved proteins that are rich in basic amino acids and form an octamer. The DNA (which is negatively charged because of the phosphate groups) is wrapped tightly around the histone core. This nucleosome is linked to the next one with the help of a linker DNA. This is also known as the "beads on a string" structure. This is further compacted into a 30 nm fiber, which is the diameter of the structure. At the metaphase stage, the chromosomes are at their most compact, are approximately 700 nm in width, and are found in association with scaffold proteins.

In interphase, eukaryotic chromosomes have two distinct regions that can be distinguished by staining. The tightly packaged region is known as heterochromatin, and the less dense region is known as euchromatin. Heterochromatin usually contains genes that are not expressed, and is found in the regions of the centromere and telomeres. The euchromatin usually contains genes that are transcribed, with DNA packaged around nucleosomes but not further compacted.



Figure 8.9 These figures illustrate the compaction of the eukaryotic chromosome.

# 8.2 | The Genetic Code

By the end of this section, you will be able to:

- Explain the "central dogma" of protein synthesis
- Describe the genetic code and how the nucleotide sequence prescribes the amino acid and the protein sequence

The cellular process of transcription generates messenger RNA (mRNA), a mobile molecular copy of one or more genes with an alphabet of A, C, G, and uracil (U). Translation of the mRNA template converts nucleotidebased genetic information into a protein product. Protein sequences consist of 20 commonly occurring amino acids; therefore, it can be said that the protein alphabet consists of 20 letters (Figure 8.10). Each amino acid is defined by a three-nucleotide sequence called the triplet codon. Different amino acids have different chemistries (such as acidic versus basic, or polar and nonpolar) and different structural constraints. Variation in amino acid sequence gives rise to enormous variation in protein structure and function.



**Figure 8.10** Structures of the 20 amino acids found in proteins are shown. Each amino acid is composed of an amino group ( $NH_3^+$ ), a carboxyl group (COO<sup>-</sup>), and a side chain (blue). The side chain may be nonpolar, polar, or charged, as well as large or small. It is the variety of amino acid side chains that gives rise to the incredible variation of protein structure and function.

## The Central Dogma: DNA Encodes RNA; RNA Encodes Protein

The flow of genetic information in cells from DNA to mRNA to protein is described by the **Central Dogma (Figure 8.11**), which states that genes specify the sequence of mRNAs, which in turn specify the sequence of proteins. The decoding of one molecule to another is performed by specific proteins and RNAs. Because the information stored in DNA is so central to cellular function, it makes intuitive sense that the cell would make mRNA copies of this information for protein synthesis, while keeping the DNA itself intact and protected. The copying of DNA to RNA is relatively straightforward, with one nucleotide being added to the mRNA strand for every nucleotide read in the DNA strand. The translation to protein is a bit more complex because three mRNA nucleotides correspond to one amino acid in the polypeptide sequence. However, the translation to protein is still systematic and **colinear**, such that nucleotides 1 to 3 correspond to amino acid 1, nucleotides 4 to 6 correspond to amino acid 2, and so on.



Figure 8.11 Instructions on DNA are transcribed onto messenger RNA. Ribosomes are able to read the genetic information inscribed on a strand of messenger RNA and use this information to string amino acids together into a protein.

#### The Genetic Code Is Degenerate and Universal

Given the different numbers of "letters" in the mRNA and protein "alphabets," scientists theorized that combinations of nucleotides corresponded to single amino acids. Nucleotide doublets would not be sufficient to specify every amino acid because there are only 16 possible two-nucleotide combinations (4<sup>2</sup>). In contrast, there are 64 possible nucleotide triplets (4<sup>3</sup>), which is far more than the number of amino acids. Scientists theorized that amino acids were encoded by nucleotide triplets and that the genetic code was **degenerate**. In other words, a given amino acid could be encoded by more than one nucleotide triplet. This was later confirmed experimentally; Francis Crick and Sydney Brenner used the chemical mutagen proflavin to insert one, two, or three nucleotides into the gene of a virus. When one or two nucleotides were inserted, protein synthesis was completely abolished. When three nucleotides were inserted, the protein was synthesized and functional. This demonstrated that three nucleotides completely changed the triplet **reading frame**, thereby altering the message for every subsequent amino acid (**Figure 8.13**). Though insertion of three nucleotides caused an extra amino acid to be inserted during translation, the integrity of the rest of the protein was maintained.

Scientists painstakingly solved the genetic code by translating synthetic mRNAs in vitro and sequencing the proteins they specified (Figure 8.12).

Second letter							
		U	с	А	G		
First letter	υ	UUU UUC UUA UUA UUG	UCU UCC UCA UCG	UAU UAC UAA Stop UAG Stop	UGU UGC UGA UGG Trp	U C A G	
	с	CUU CUC CUA CUG	CCU CCC CCA CCG	CAU CAC CAA CAG GIn	CGU CGC CGA CGG	UCAG	letter
	A	AUU AUC AUA AUG Met	ACU ACC ACA ACG	AAU AAC AAA AAG Lys	AGU }Ser AGC }Arg AGA }Arg	U C A G	Third
	G	GUU GUC GUA GUG	GCU GCC GCA GCG	GAU GAC GAA GAG Glu	GGU GGC GGA GGG	U C A G	

Cocond latton

Figure 8.12 This figure shows the genetic code for translating each nucleotide triplet in mRNA into an amino acid or a termination signal in a nascent protein. (credit: modification of work by NIH)

In addition to instructing the addition of a specific amino acid to a polypeptide chain, three of the 64 codons terminate protein synthesis and release the polypeptide from the translation machinery. These triplets are called **nonsense codons**, or stop codons. Another codon, AUG, also has a special function. In addition to specifying the amino acid methionine, it also serves as the start codon to initiate translation. The reading frame for translation is set by the AUG start codon near the 5' end of the mRNA.

The genetic code is universal. With a few exceptions, virtually all species use the same genetic code for protein synthesis. Conservation of codons means that a purified mRNA encoding the globin protein in horses could be transferred to a tulip cell, and the tulip would synthesize horse globin. That there is only one genetic code is powerful evidence that all of life on Earth shares a common origin, especially considering that there are about

10<sup>84</sup> possible combinations of 20 amino a





Transcribe a gene and translate it to protein using complementary pairing and the genetic code at this **site** (http://openstaxcollege.org/l/create\_protein).

Frameshift Mutations								
Ser	Val	Pro	Tyr		Ser	Ala	Leu	Leu

**Figure 8.13** The deletion of two nucleotides shifts the reading frame of an mRNA and changes the entire protein message, creating a nonfunctional protein or terminating protein synthesis altogether.

Degeneracy is believed to be a cellular mechanism to reduce the negative impact of random mutations. Codons that specify the same amino acid typically only differ by one nucleotide. In addition, amino acids with chemically similar side chains are encoded by similar codons. This nuance of the genetic code ensures that a single-nucleotide substitution mutation might either specify the same amino acid but have no effect or specify a similar amino acid, preventing the protein from being rendered completely nonfunctional.

# scientific methed CONNECTION

## Which Has More DNA: A Kiwi or a Strawberry?



**Figure 8.14** Do you think that a kiwi or a strawberry has more DNA per fruit? (credit "kiwi": "Kelbv"/Flickr; credit: "strawberry": Alisdair McDiarmid)

**Question**: Would a kiwifruit and strawberry that are approximately the same size (Figure 8.14) also have approximately the same amount of DNA?

**Background**: Genes are carried on chromosomes and are made of DNA. All mammals are diploid, meaning they have two copies of each chromosome. However, not all plants are diploid. The common strawberry is octoploid (8*n*) and the cultivated kiwi is hexaploid (6*n*). Research the total number of chromosomes in the cells of each of these fruits and think about how this might correspond to the amount of DNA in these fruits' cell nuclei. Read about the technique of DNA isolation to understand how each step in the isolation protocol helps liberate and precipitate DNA.

**Hypothesis**: Hypothesize whether you would be able to detect a difference in DNA quantity from similarly sized strawberries and kiwis. Which fruit do you think would yield more DNA?

**Test your hypothesis**: Isolate the DNA from a strawberry and a kiwi that are similarly sized. Perform the experiment in at least triplicate for each fruit.

- 1. Prepare a bottle of DNA extraction buffer from 900 mL water, 50 mL dish detergent, and two teaspoons of table salt. Mix by inversion (cap it and turn it upside down a few times).
- 2. Grind a strawberry and a kiwifruit by hand in a plastic bag, or using a mortar and pestle, or with a metal bowl and the end of a blunt instrument. Grind for at least two minutes per fruit.
- 3. Add 10 mL of the DNA extraction buffer to each fruit, and mix well for at least one minute.
- 4. Remove cellular debris by filtering each fruit mixture through cheesecloth or porous cloth and into a funnel placed in a test tube or an appropriate container.
- 5. Pour ice-cold ethanol or isopropanol (rubbing alcohol) into the test tube. You should observe white, precipitated DNA.
- 6. Gather the DNA from each fruit by winding it around separate glass rods.

**Record your observations**: Because you are not quantitatively measuring DNA volume, you can record for each trial whether the two fruits produced the same or different amounts of DNA as observed by eye. If one or the other fruit produced noticeably more DNA, record this as well. Determine whether your observations are consistent with several pieces of each fruit.

**Analyze your data**: Did you notice an obvious difference in the amount of DNA produced by each fruit? Were your results reproducible?

**Draw a conclusion**: Given what you know about the number of chromosomes in each fruit, can you conclude that chromosome number necessarily correlates to DNA amount? Can you identify any drawbacks to this procedure? If you had access to a laboratory, how could you standardize your comparison and make it more quantitative?

# 8.3 | Eukaryotic Transcription

By the end of this section, you will be able to:

- · List the steps in eukaryotic transcription
- Discuss the role of RNA polymerases in transcription
- · Compare and contrast the three RNA polymerases
- Explain the significance of transcription factors

Prokaryotes and eukaryotes perform fundamentally the same process of transcription, with a few key differences. The most important difference between prokaryotes and eukaryotes is the latter's membrane-bound nucleus and organelles. With the genes bound in a nucleus, the eukaryotic cell must be able to transport its mRNA to the cytoplasm and must protect its mRNA from degrading before it is translated. Eukaryotes also employ three different polymerases that each transcribe a different subset of genes. Eukaryotic mRNAs are usually monogenic, meaning that they specify a single protein.

## Initiation of Transcription in Eukaryotes

Unlike the prokaryotic polymerase that can bind to a DNA template on its own, eukaryotes require several other proteins, called transcription factors, to first bind to the promoter region and then help recruit the appropriate polymerase.

#### The Three Eukaryotic RNA Polymerases

The features of eukaryotic mRNA synthesis are markedly more complex those of prokaryotes. Instead of a single polymerase comprising five subunits, the eukaryotes have three polymerases that are each made up of 10 subunits or more. Each eukaryotic polymerase also requires a distinct set of transcription factors to bring it to the DNA template.

RNA polymerase I is located in the nucleolus, a specialized nuclear substructure in which ribosomal RNA (rRNA) is transcribed, processed, and assembled into ribosomes (**Table 8.1**). The rRNA molecules are considered structural RNAs because they have a cellular role but are not translated into protein. The rRNAs are components of the ribosome and are essential to the process of translation. RNA polymerase I synthesizes all of the rRNAs except for the 5S rRNA molecule. The "S" designation applies to "Svedberg" units, a nonadditive value that characterizes the speed at which a particle sediments during centrifugation.

RNA Polymerase	Cellular Compartment	Product of Transcription	α-Amanitin Sensitivity
I	Nucleolus	All rRNAs except 5S rRNA	Insensitive
II	Nucleus	All protein-coding nuclear pre- mRNAs	Extremely sensitive
	Nucleus	5S rRNA, tRNAs, and small nuclear RNAs	Moderately sensitive

## Locations, Products, and Sensitivities of the Three Eukaryotic RNA Polymerases

#### Table 8.1

RNA polymerase II is located in the nucleus and synthesizes all protein-coding nuclear pre-mRNAs. Eukaryotic pre-mRNAs undergo extensive processing after transcription but before translation. For clarity, this module's discussion of transcription and translation in eukaryotes will use the term "mRNAs" to describe only the mature, processed molecules that are ready to be translated. RNA polymerase II is responsible for transcribing the overwhelming majority of eukaryotic genes.

RNA polymerase III is also located in the nucleus. This polymerase transcribes a variety of structural RNAs

that includes the 5S pre-rRNA, transfer pre-RNAs (pre-tRNAs), and **small nuclear** pre- **RNAs**. The tRNAs have a critical role in translation; they serve as the adaptor molecules between the mRNA template and the growing polypeptide chain. Small nuclear RNAs have a variety of functions, including "splicing" pre-mRNAs and regulating transcription factors.

A scientist characterizing a new gene can determine which polymerase transcribes it by testing whether the gene is expressed in the presence of a particular mushroom poison,  $\alpha$ -amanitin (**Table 8.1**). Interestingly,  $\alpha$ -amanitin produced by *Amanita phalloides*, the Death Cap mushroom, affects the three polymerases very differently. RNA polymerase I is completely insensitive to  $\alpha$ -amanitin, meaning that the polymerase can transcribe DNA in vitro in the presence of this poison. In contrast, RNA polymerase II is extremely sensitive to  $\alpha$ -amanitin, and RNA polymerase III is moderately sensitive. Knowing the transcribing polymerase can clue a researcher into the general function of the gene being studied. Because RNA polymerase II transcribes the vast majority of genes, we will focus on this polymerase in our subsequent discussions about eukaryotic transcription factors and promoters.

#### Structure of an RNA Polymerase II Promoter

Eukaryotic promoters are much larger and more complex than prokaryotic promoters, but both have a TATA box. For example, in the mouse thymidine kinase gene, the TATA box is located at approximately -30 relative to the initiation (+1) site (Figure 8.15). For this gene, the exact TATA box sequence is TATAAAA, as read in the 5' to 3' direction on the nontemplate strand. This sequence is not identical to the *E. coli* TATA box, but it conserves the A–T rich element. The thermostability of A–T bonds is low and this helps the DNA template to locally unwind in preparation for transcription.



**Figure 8.15** A generalized promoter of a gene transcribed by RNA polymerase II is shown. Transcription factors recognize the promoter. RNA polymerase II then binds and forms the transcription initiation complex.



Figure 8.16 Eukaryotic mRNA contains introns that must be spliced out. A 5' cap and 3' poly-A tail are also added.

A scientist splices a eukaryotic promoter in front of a bacterial gene and inserts the gene in a bacterial chromosome. Would you expect the bacteria to transcribe the gene?

The mouse genome includes one gene and two pseudogenes for cytoplasmic thymidine kinase. Pseudogenes are genes that have lost their protein-coding ability or are no longer expressed by the cell. These pseudogenes are copied from mRNA and incorporated into the chromosome. For example, the mouse thymidine kinase promoter also has a conserved **CAAT box** (GGCCAATCT) at approximately -80. This sequence is essential and is involved in binding transcription factors. Further upstream of the TATA box, eukaryotic promoters may also contain one or more **GC-rich boxes** (GGCG) or **octamer boxes** (ATTTGCAT). These elements bind cellular factors that increase the efficiency of transcription initiation and are often identified in more "active" genes that are constantly being expressed by the cell.

## Transcription Factors for RNA Polymerase II

The complexity of eukaryotic transcription does not end with the polymerases and promoters. An army of basal transcription factors, enhancers, and silencers also help to regulate the frequency with which pre-mRNA is synthesized from a gene. Enhancers and silencers affect the efficiency of transcription but are not necessary for transcription to proceed. Basal transcription factors are crucial in the formation of a **preinitiation complex** on the DNA template that subsequently recruits RNA polymerase II for transcription initiation.

The names of the basal transcription factors begin with "TFII" (this is the transcription factor for RNA polymerase II) and are specified with the letters A–J. The transcription factors systematically fall into place on the DNA template, with each one further stabilizing the preinitiation complex and contributing to the recruitment of RNA polymerase II.

The processes of bringing RNA polymerases I and III to the DNA template involve slightly less complex collections of transcription factors, but the general theme is the same. Eukaryotic transcription is a tightly regulated process that requires a variety of proteins to interact with each other and with the DNA strand. Although the process of transcription in eukaryotes involves a greater metabolic investment than in prokaryotes, it ensures that the cell transcribes precisely the pre-mRNAs that it needs for protein synthesis.



## **The Evolution of Promoters**

The evolution of genes may be a familiar concept. Mutations can occur in genes during DNA replication, and the result may or may not be beneficial to the cell. By altering an enzyme, structural protein, or some other factor, the process of mutation can transform functions or physical features. However, eukaryotic promoters and other gene regulatory sequences may evolve as well. For instance, consider a gene that, over many generations, becomes more valuable to the cell. Maybe the gene encodes a structural protein that the cell needs to synthesize in abundance for a certain function. If this is the case, it would be beneficial to the cell for that gene's promoter to recruit transcription factors more efficiently and increase gene expression.

Scientists examining the evolution of promoter sequences have reported varying results. In part, this is because it is difficult to infer exactly where a eukaryotic promoter begins and ends. Some promoters occur within genes; others are located very far upstream, or even downstream, of the genes they are regulating. However, when researchers limited their examination to human core promoter sequences that were defined experimentally as sequences that bind the preinitiation complex, they found that promoters evolve even faster than protein-coding genes.

It is still unclear how promoter evolution might correspond to the evolution of humans or other higher organisms. However, the evolution of a promoter to effectively make more or less of a given gene product is an intriguing alternative to the evolution of the genes themselves.<sup>[2]</sup>

#### Promoter Structures for RNA Polymerases I and III

In eukaryotes, the conserved promoter elements differ for genes transcribed by RNA polymerases I, II, and III. RNA polymerase I transcribes genes that have two GC-rich promoter sequences in the -45 to +20 region. These sequences alone are sufficient for transcription initiation to occur, but promoters with additional sequences in the region from -180 to -105 upstream of the initiation site will further enhance initiation. Genes that are transcribed by RNA polymerase III have upstream promoters or promoters that occur within the genes themselves.

## **Eukaryotic Elongation and Termination**

Following the formation of the preinitiation complex, the polymerase is released from the other transcription factors, and elongation is allowed to proceed as it does in prokaryotes with the polymerase synthesizing premRNA in the 5' to 3' direction. As discussed previously, RNA polymerase II transcribes the major share of eukaryotic genes, so this section will focus on how this polymerase accomplishes elongation and termination.

Although the enzymatic process of elongation is essentially the same in eukaryotes and prokaryotes, the DNA template is more complex. When eukaryotic cells are not dividing, their genes exist as a diffuse mass of DNA and proteins called chromatin. The DNA is tightly packaged around charged histone proteins at repeated intervals. These DNA–histone complexes, collectively called nucleosomes, are regularly spaced and include 146 nucleotides of DNA wound around eight histones like thread around a spool.

For polynucleotide synthesis to occur, the transcription machinery needs to move histones out of the way every time it encounters a nucleosome. This is accomplished by a special protein complex called **FACT**, which stands for "facilitates chromatin transcription." This complex pulls histones away from the DNA template as the polymerase moves along it. Once the pre-mRNA is synthesized, the FACT complex replaces the histones to recreate the nucleosomes.

The termination of transcription is different for the different polymerases. Unlike in prokaryotes, elongation by RNA polymerase II in eukaryotes takes place 1,000–2,000 nucleotides beyond the end of the gene being transcribed. This pre-mRNA tail is subsequently removed by cleavage during mRNA processing. On the other hand, RNA polymerases I and III require termination signals. Genes transcribed by RNA polymerase I contain a specific 18-nucleotide sequence that is recognized by a termination protein. The process of termination in RNA polymerase III involves an mRNA hairpin similar to rho-independent termination of transcription in prokaryotes.

<sup>2.</sup> H Liang et al., "Fast evolution of core promoters in primate genomes," Molecular Biology and Evolution 25 (2008): 1239–44.

## 8.4 | Ribosomes and Protein Synthesis

By the end of this section, you will be able to:

- · Describe the different steps in protein synthesis
- Discuss the role of ribosomes in protein synthesis

The synthesis of proteins consumes more of a cell's energy than any other metabolic process. In turn, proteins account for more mass than any other component of living organisms (with the exception of water), and proteins perform virtually every function of a cell. The process of translation, or protein synthesis, involves the decoding of an mRNA message into a polypeptide product. Amino acids are covalently strung together by interlinking peptide bonds in lengths ranging from approximately 50 amino acid residues to more than 1,000. Each individual amino acid has an amino group (NH<sub>2</sub>) and a carboxyl (COOH) group. Polypeptides are formed when the amino group of one amino acid forms an amide (i.e., peptide) bond with the carboxyl group of another amino acid (Figure 8.17). This reaction is catalyzed by ribosomes and generates one water molecule.



**Figure 8.17** A peptide bond links the carboxyl end of one amino acid with the amino end of another, expelling one water molecule. For simplicity in this image, only the functional groups involved in the peptide bond are shown. The R and R' designations refer to the rest of each amino acid structure.

## **The Protein Synthesis Machinery**

In addition to the mRNA template, many molecules and macromolecules contribute to the process of translation. The composition of each component may vary across species; for instance, ribosomes may consist of different numbers of rRNAs and polypeptides depending on the organism. However, the general structures and functions of the protein synthesis machinery are comparable from bacteria to human cells. Translation requires the input of an mRNA template, ribosomes, tRNAs tic factors.





Click through the steps of this **PBS** interactive (http://openstaxcollege.org/l/prokary\_protein) to see protein synthesis in action.

#### Ribosomes

Even before an mRNA is translated, a cell must invest energy to build each of its ribosomes. In *E. coli*, there are between 10,000 and 70,000 ribosomes present in each cell at any given time. A ribosome is a complex macromolecule composed of structural and catalytic rRNAs, and many distinct polypeptides. In eukaryotes, the nucleolus is completely specialized for the synthesis and assembly of rRNAs.

Ribosomes exist in the cytoplasm in prokaryotes and in the cytoplasm and rough endoplasmic reticulum in eukaryotes. Mitochondria and chloroplasts also have their own ribosomes in the matrix and stroma, which look more similar to prokaryotic ribosomes (and have similar drug sensitivities) than the ribosomes just outside their outer membranes in the cytoplasm. Ribosomes dissociate into large and small subunits when they are not synthesizing proteins and reassociate during the initiation of translation. In *E. coli*, the small subunit is described as 30S, and the large subunit is 50S, for a total of 70S (recall that Svedberg units are not additive). Mammalian ribosomes have a small 40S subunit and a large 60S subunit, for a total of 80S. The small subunit is responsible for binding the mRNA template, whereas the large subunit sequentially binds tRNAs. Each mRNA molecule is simultaneously translated by many ribosomes, all synthesizing protein in the same direction: reading the mRNA from 5' to 3' and synthesizing the polypeptide from the N terminus to the C terminus. The complete mRNA/poly-ribosome structure is called a **polysome**.

#### tRNAs

The tRNAs are structural RNA molecules that were transcribed from genes by RNA polymerase III. Depending on the species, 40 to 60 types of tRNAs exist in the cytoplasm. Serving as adaptors, specific tRNAs bind to sequences on the mRNA template and add the corresponding amino acid to the polypeptide chain. Therefore, tRNAs are the molecules that actually "translate" the language of RNA into the language of proteins.

Of the 64 possible mRNA codons—or triplet combinations of A, U, G, and C—three specify the termination of protein synthesis and 61 specify the addition of amino acids to the polypeptide chain. Of these 61, one codon (AUG) also encodes the initiation of translation. Each tRNA anticodon can base pair with one of the mRNA codons and add an amino acid or terminate translation, according to the genetic code. For instance, if the sequence CUA occurred on an mRNA template in the proper reading frame, it would bind a tRNA expressing the complementary sequence, GAU, which would be linked to the amino acid leucine.

As the adaptor molecules of translation, it is surprising that tRNAs can fit so much specificity into such a small package. Consider that tRNAs need to interact with three factors: 1) they must be recognized by the correct aminoacyl synthetase (see below); 2) they must be recognized by ribosomes; and 3) they must bind to the correct sequence in mRNA.

#### Aminoacyl tRNA Synthetases

The process of pre-tRNA synthesis by RNA polymerase III only creates the RNA portion of the adaptor molecule. The corresponding amino acid must be added later, once the tRNA is processed and exported to the cytoplasm. Through the process of tRNA "charging," each tRNA molecule is linked to its correct amino acid by a group of enzymes called **aminoacyl tRNA synthetases**. At least one type of aminoacyl tRNA synthetase exists for each of the 20 amino acids; the exact number of aminoacyl tRNA synthetases varies by species. These enzymes first bind and hydrolyze ATP to catalyze a high-energy bond between an amino acid and adenosine monophosphate (AMP); a pyrophosphate molecule is expelled in this reaction. The activated amino acid is then transferred to the tRNA, and AMP is released.

## The Mechanism of Protein Synthesis

As with mRNA synthesis, protein synthesis can be divided into three phases: initiation, elongation, and termination. The process of translation is similar in prokaryotes and eukaryotes. Here we'll explore how translation occurs in *E. coli*, a representative prokaryote, and specify any differences between prokaryotic and eukaryotic translation.

#### Initiation of Translation

Protein synthesis begins with the formation of an initiation complex. In *E. coli*, this complex involves the small 30S ribosome, the mRNA template, three initiation factors (IFs; IF-1, IF-2, and IF-3), and a special **initiator tRNA**, called tRNA<sup>Met</sup>. The initiator tRNA interacts with the **start codon** AUG (or rarely, GUG),

links to a formylated methionine called fMet, and can also bind IF-2. Formylated methionine is inserted by  $fMet - tRNA_{f}^{Met}$  at the beginning of every polypeptide chain synthesized by *E. coli*, but it is usually clipped

off after translation is complete. When an in-frame AUG is encountered during translation elongation, a non-formylated methionine is inserted by a regular Met-tRNA<sup>Met</sup>.

In *E. coli* mRNA, a sequence upstream of the first AUG codon, called the **Shine-Dalgarno sequence** (AGGAGG), interacts with the rRNA molecules that compose the ribosome. This interaction anchors the 30S ribosomal subunit at the correct location on the mRNA template. Guanosine triphosphate (GTP), which is a purine nucleotide triphosphate, acts as an energy source during translation—both at the start of elongation and

#### during the ribosome's translocation.

In eukaryotes, a similar initiation complex forms, comprising mRNA, the 40S small ribosomal subunit, IFs, and nucleoside triphosphates (GTP and ATP). The charged initiator tRNA, called Met-tRNA<sub>i</sub>, does not bind fMet in eukaryotes, but is distinct from other Met-tRNAs in that it can bind IFs.

Instead of depositing at the Shine-Dalgarno sequence, the eukaryotic initiation complex recognizes the 7-methylguanosine cap at the 5' end of the mRNA. A cap-binding protein (CBP) and several other IFs assist the movement of the ribosome to the 5' cap. Once at the cap, the initiation complex tracks along the mRNA in the 5' to 3' direction, searching for the AUG start codon. Many eukaryotic mRNAs are translated from the first AUG, but this is not always the case. According to **Kozak's rules**, the nucleotides around the AUG indicate whether it is the correct start codon. Kozak's rules state that the following consensus sequence must appear around the AUG of vertebrate genes: 5'-gccRccAUGG-3'. The R (for purine) indicates a site that can be either A or G, but cannot be C or U. Essentially, the closer the sequence is to this consensus, the higher the efficiency of translation.

Once the appropriate AUG is identified, the other proteins and CBP dissociate, and the 60S subunit binds to the complex of Met-tRNA<sub>i</sub>, mRNA, and the 40S subunit. This step completes the initiation of translation in eukaryotes.

#### Translation, Elongation, and Termination

In prokaryotes and eukaryotes, the basics of elongation are the same, so we will review elongation from the perspective of *E. coli*. The 50S ribosomal subunit of *E. coli* consists of three compartments: the A (aminoacyl) site binds incoming charged aminoacyl tRNAs. The P (peptidyl) site binds charged tRNAs carrying amino acids that have formed peptide bonds with the growing polypeptide chain but have not yet dissociated from their corresponding tRNA. The E (exit) site releases dissociated tRNAs so that they can be recharged with free amino acids. There is one exception to this assembly line of tRNAs: in *E. coli*, fMet – tRNA<sup>Met</sup> is capable of entering

the P site directly without first entering the A site. Similarly, the eukaryotic Met-tRNA<sub>i</sub>, with help from other proteins of the initiation complex, binds directly to the P site. In both cases, this creates an initiation complex with a free A site ready to accept the tRNA corresponding to the first codon after the AUG.

During translation elongation, the mRNA template provides specificity. As the ribosome moves along the mRNA, each mRNA codon comes into register, and specific binding with the corresponding charged tRNA anticodon is ensured. If mRNA were not present in the elongation complex, the ribosome would bind tRNAs nonspecifically.

Elongation proceeds with charged tRNAs entering the A site and then shifting to the P site followed by the E site with each single-codon "step" of the ribosome. Ribosomal steps are induced by conformational changes that advance the ribosome by three bases in the 3' direction. The energy for each step of the ribosome is donated by an elongation factor that hydrolyzes GTP. Peptide bonds form between the amino group of the amino acid attached to the A-site tRNA and the carboxyl group of the amino acid attached to the P-site tRNA. The formation of each peptide bond is catalyzed by **peptidyl transferase**, an RNA-based enzyme that is integrated into the 50S ribosomal subunit. The energy for each peptide bond formation is derived from GTP hydrolysis, which is catalyzed by a separate elongation factor. The amino acid bound to the P-site tRNA is also linked to the growing polypeptide chain. As the ribosome steps across the mRNA, the former P-site tRNA enters the E site, detaches from the amino acid, and is expelled (Figure 8.18). Amazingly, the *E. coli* translation apparatus takes only 0.05 seconds to add each amino acid, meaning that a 200-amino acid protein can be translated in just 10 seconds.



**Figure 8.18** Translation begins when an initiator tRNA anticodon recognizes a codon on mRNA. The large ribosomal subunit joins the small subunit, and a second tRNA is recruited. As the mRNA moves relative to the ribosome, the polypeptide chain is formed. Entry of a release factor into the A site terminates translation and the components dissociate.

Many antibiotics inhibit bacterial protein synthesis. For example, tetracycline blocks the A site on the bacterial ribosome, and chloramphenicol blocks peptidyl transfer. What specific effect would you expect each of these antibiotics to have on protein synthesis?

Tetracycline would directly affect:

- a. tRNA binding to the ribosome
- b. ribosome assembly
- c. growth of the protein chain

Chloramphenicol would directly affect

- a. tRNA binding to the ribosome
- b. ribosome assembly
- c. growth of the protein chain

Termination of translation occurs when a nonsense codon (UAA, UAG, or UGA) is encountered. Upon aligning with the A site, these nonsense codons are recognized by release factors in prokaryotes and eukaryotes that instruct peptidyl transferase to add a water molecule to the carboxyl end of the P-site amino acid. This reaction forces the P-site amino acid to detach from its tRNA, and the newly made protein is released. The small and large ribosomal subunits dissociate from the mRNA and from each other; they are recruited almost immediately

into another translation initiation complex. After many ribosomes have completed translation, the mRNA is degraded so the nucleotides can be reused in another transcription reaction.

## Protein Folding, Modification, and Targeting

During and after translation, individual amino acids may be chemically modified, signal sequences may be appended, and the new protein "folds" into a distinct three-dimensional structure as a result of intramolecular interactions. A **signal sequence** is a short tail of amino acids that directs a protein to a specific cellular compartment. These sequences at the amino end or the carboxyl end of the protein can be thought of as the protein's "train ticket" to its ultimate destination. Other cellular factors recognize each signal sequence and help transport the protein from the cytoplasm to its correct compartment. For instance, a specific sequence at the amino terminus will direct a protein to the mitochondria or chloroplasts (in plants). Once the protein reaches its cellular destination, the signal sequence is usually clipped off.

Many proteins fold spontaneously, but some proteins require helper molecules, called chaperones, to prevent them from aggregating during the complicated process of folding. Even if a protein is properly specified by its corresponding mRNA, it could take on a completely dysfunctional shape if abnormal temperature or pH conditions prevent it from folding correctly.

## **KEY TERMS**

- aminoacyl tRNA synthetase enzyme that "charges" tRNA molecules by catalyzing a bond between the tRNA and a corresponding amino acid
- CAAT box (GGCCAATCT) essential eukaryotic promoter sequence involved in binding transcription factors
- Central Dogma states that genes specify the sequence of mRNAs, which in turn specify the sequence of proteins
- **codon** three consecutive nucleotides in mRNA that specify the insertion of an amino acid or the release of a polypeptide chain during translation
- colinear in terms of RNA and protein, three "units" of RNA (nucleotides) specify one "unit" of protein (amino acid) in a consecutive fashion
- **degeneracy** (of the genetic code) describes that a given amino acid can be encoded by more than one nucleotide triplet; the code is degenerate, but not ambiguous
- electrophoresis technique used to separate DNA fragments according to size
- **FACT** complex that "facilitates chromatin transcription" by disassembling nucleosomes ahead of a transcribing RNA polymerase II and reassembling them after the polymerase passes by
- **GC-rich box** (GGCG) nonessential eukaryotic promoter sequence that binds cellular factors to increase the efficiency of transcription; may be present several times in a promoter
- initiator tRNA in prokaryotes, called  $tRNA_f^{Met}$ ; in eukaryotes, called tRNA; a tRNA that interacts with a start

codon, binds directly to the ribosome P site, and links to a special methionine to begin a polypeptide chain

- Kozak's rules determines the correct initiation AUG in a eukaryotic mRNA; the following consensus sequence must appear around the AUG: 5'-GCC(purine)CCAUGG-3'; the bolded bases are most important
- nonsense codon one of the three mRNA codons that specifies termination of translation
- Octamer box (ATTTGCAT) nonessential eukaryotic promoter sequence that binds cellular factors to increase the efficiency of transcription; may be present several times in a promoter
- **peptidyl transferase** RNA-based enzyme that is integrated into the 50S ribosomal subunit and catalyzes the formation of peptide bonds
- polysome mRNA molecule simultaneously being translated by many ribosomes all going in the same direction
- preinitiation complex cluster of transcription factors and other proteins that recruit RNA polymerase II for transcription of a DNA template
- **reading frame** sequence of triplet codons in mRNA that specify a particular protein; a ribosome shift of one or two nucleotides in either direction completely abolishes synthesis of that protein
- Shine-Dalgarno sequence (AGGAGG); initiates prokaryotic translation by interacting with rRNA molecules comprising the 30S ribosome
- signal sequence short tail of amino acids that directs a protein to a specific cellular compartment
- small nuclear RNA molecules synthesized by RNA polymerase III that have a variety of functions, including splicing pre-mRNAs and regulating transcription factors

start codon AUG (or rarely, GUG) on an mRNA from which translation begins; always specifies methionine

## **CHAPTER SUMMARY**

#### 8.1 DNA Structure and Sequencing

The currently accepted model of the double-helix structure of DNA was proposed by Watson and Crick. Some of the salient features are that the two strands that make up the double helix are complementary and antiparallel in nature. Deoxyribose sugars and phosphates form the backbone of the structure, and the nitrogenous bases are stacked inside. The diameter of the double helix, 2 nm, is uniform throughout. A purine always pairs with a pyrimidine; A pairs with T, and G pairs with C. One turn of the helix has ten base pairs. During cell division, each daughter cell receives a copy of the DNA by a process known as DNA replication. Prokaryotes are much simpler than eukaryotes in many of their features. Most prokaryotes contain a single, circular chromosome. In general, eukaryotic chromosomes contain a linear DNA molecule packaged into nucleosomes, and have two distinct regions that can be distinguished by staining, reflecting different states of packaging and compaction.

#### 8.3 The Genetic Code

The genetic code refers to the DNA alphabet (A, T, C, G), the RNA alphabet (A, U, C, G), and the polypeptide alphabet (20 amino acids). The Central Dogma describes the flow of genetic information in the cell from genes to mRNA to proteins. Genes are used to make mRNA by the process of transcription; mRNA is used to synthesize proteins by the process of translation. The genetic code is degenerate because 64 triplet codons in mRNA specify only 20 amino acids and three nonsense codons. Almost every species on the planet uses the same genetic code.

#### 8.4 Eukaryotic Transcription

Transcription in eukaryotes involves one of three types of polymerases, depending on the gene being transcribed. RNA polymerase II transcribes all of the protein-coding genes, whereas RNA polymerase I transcribes rRNA genes, and RNA polymerase III transcribes rRNA, tRNA, and small nuclear RNA genes. The initiation of transcription in eukaryotes involves the binding of several transcription factors to complex promoter sequences that are usually located upstream of the gene being copied. The mRNA is synthesized in the 5' to 3' direction, and the FACT complex moves and reassembles nucleosomes as the polymerase passes by. Whereas RNA polymerases I and III terminate transcription by protein- or RNA hairpin-dependent methods, RNA polymerase II transcribes for 1,000 or more nucleotides beyond the gene template and cleaves the excess during pre-mRNA processing.

#### 8.5 Ribosomes and Protein Synthesis

The players in translation include the mRNA template, ribosomes, tRNAs, and various enzymatic factors. The small ribosomal subunit forms on the mRNA template either at the Shine-Dalgarno sequence (prokaryotes) or the 5' cap (eukaryotes). Translation begins at the initiating AUG on the mRNA, specifying methionine. The formation of peptide bonds occurs between sequential amino acids specified by the mRNA template according to the genetic code. Charged tRNAs enter the ribosomal A site, and their amino acid bonds with the amino acid at the P site. The entire mRNA is translated in three-nucleotide "steps" of the ribosome. When a nonsense codon is encountered, a release factor binds and dissociates the components and frees the new protein. Folding of the protein occurs during and after translation.

## **ART CONNECTION QUESTIONS**

**1. Figure 8.8** In eukaryotic cells, DNA and RNA synthesis occur in a separate compartment from protein synthesis. In prokaryotic cells, both processes occur together. What advantages might there be to separating the processes? What advantages might there be to having them occur together?

**2. Figure 8.16** A scientist splices a eukaryotic promoter in front of a bacterial gene and inserts the gene in a bacterial chromosome. Would you expect the bacteria to transcribe the gene?

**3. Figure 8.18** Many antibiotics inhibit bacterial protein synthesis. For example, tetracycline blocks the A site on the bacterial ribosome, and chloramphenicol blocks peptidyl transfer. What specific effect would you expect each of these antibiotics to have on protein synthesis?

Tetracycline would directly affect:
- a. tRNA binding to the ribosome
- b. ribosome assembly
- c. growth of the protein chain

Chloramphenicol would directly affect

# **REVIEW QUESTIONS**

**4.** DNA double helix does not have which of the following?

- a. antiparallel configuration
- b. complementary base pairing
- c. major and minor grooves
- d. uracil

5. In eukaryotes, what is the DNA wrapped around?

- a. single-stranded binding proteins
- b. sliding clamp
- c. polymerase
- d. histones

**6.** The AUC and AUA codons in mRNA both specify isoleucine. What feature of the genetic code explains this?

- a. complementarity
- b. nonsense codons
- c. universality
- d. degeneracy

7. How many nucleotides are in 12 mRNA codons?

- a. 12
- b. 24
- c. 36
- d. 48

# **CRITICAL THINKING QUESTIONS**

**12.** Provide a brief summary of the Sanger sequencing method.

**13.** Describe the structure and complementary base pairing of DNA.

**14.** Imagine if there were 200 commonly occurring amino acids instead of 20. Given what you know about the genetic code, what would be the shortest possible codon length? Explain.

# CHAPTER SUMMARY

#### 8.1 DNA Structure and Sequencing

a. tRNA binding to the ribosome

- b. ribosome assembly
- c. growth of the protein chain

**8.** Which feature of promoters can be found in both prokaryotes and eukaryotes?

- a. GC box
- b. TATA box
- c. octamer box
- d. -10 and -35 sequences

**9.** What transcripts will be most affected by low levels of  $\alpha$ -amanitin?

- a. 18S and 28S rRNAs
- b. pre-mRNAs
- c. 5S rRNAs and tRNAs
- d. other small nuclear RNAs

10. The RNA components of ribosomes are

- synthesized in the \_\_\_\_\_
  - a. cytoplasm
  - b. nucleus
  - c. nucleolus
  - d. endoplasmic reticulum

**11.** In any given species, there are at least how many types of aminoacyl tRNA synthetases?

- a. 20
- b. 40
- c. 100
- d. 200

**15.** Discuss how degeneracy of the genetic code makes cells more robust to mutations.

**16.** Transcribe and translate the following DNA sequence (nontemplate strand): 5'-ATGGCCGGTTATTAAGCA-3'

**17.** Explain how single nucleotide changes can have vastly different effects on protein function.

The currently accepted model of the double-helix structure of DNA was proposed by Watson and Crick. Some of the salient features are that the two strands that make up the double helix are complementary and antiparallel in nature. Deoxyribose sugars and phosphates form the backbone of the structure, and the nitrogenous bases are stacked inside. The diameter of the double helix, 2 nm, is uniform throughout. A purine always pairs with a pyrimidine; A pairs with T, and G pairs with C. One turn of the helix has ten base pairs. During cell division, each daughter cell receives a copy of the DNA by a process known as DNA replication. Prokaryotes are much simpler than eukaryotes in many of their features. Most prokaryotes contain a single, circular chromosome. In general, eukaryotic chromosomes contain a linear DNA molecule packaged into nucleosomes, and have two distinct regions that can be distinguished by staining, reflecting different states of packaging and compaction.

#### 8.3 The Genetic Code

The genetic code refers to the DNA alphabet (A, T, C, G), the RNA alphabet (A, U, C, G), and the polypeptide alphabet (20 amino acids). The Central Dogma describes the flow of genetic information in the cell from genes to mRNA to proteins. Genes are used to make mRNA by the process of transcription; mRNA is used to synthesize proteins by the process of translation. The genetic code is degenerate because 64 triplet codons in mRNA specify only 20 amino acids and three nonsense codons. Almost every species on the planet uses the same genetic code.

#### 8.4 Eukaryotic Transcription

Transcription in eukaryotes involves one of three types of polymerases, depending on the gene being transcribed. RNA polymerase II transcribes all of the protein-coding genes, whereas RNA polymerase I transcribes rRNA genes, and RNA polymerase III transcribes rRNA, tRNA, and small nuclear RNA genes. The initiation of transcription in eukaryotes involves the binding of several transcription factors to complex promoter sequences that are usually located upstream of the gene being copied. The mRNA is synthesized in the 5' to 3' direction, and the FACT complex moves and reassembles nucleosomes as the polymerase passes by. Whereas RNA polymerases I and III terminate transcription by protein- or RNA hairpin-dependent methods, RNA polymerase II transcribes for 1,000 or more nucleotides beyond the gene template and cleaves the excess during pre-mRNA processing.

#### 8.5 Ribosomes and Protein Synthesis

The players in translation include the mRNA template, ribosomes, tRNAs, and various enzymatic factors. The small ribosomal subunit forms on the mRNA template either at the Shine-Dalgarno sequence (prokaryotes) or the 5' cap (eukaryotes). Translation begins at the initiating AUG on the mRNA, specifying methionine. The formation of peptide bonds occurs between sequential amino acids specified by the mRNA template according to the genetic code. Charged tRNAs enter the ribosomal A site, and their amino acid bonds with the amino acid at the P site. The entire mRNA is translated in three-nucleotide "steps" of the ribosome. When a nonsense codon is encountered, a release factor binds and dissociates the components and frees the new protein. Folding of the protein occurs during and after translation.

# **ART CONNECTION QUESTIONS**

**18. Figure 8.8** In eukaryotic cells, DNA and RNA synthesis occur in a separate compartment from protein synthesis. In prokaryotic cells, both processes occur together. What advantages might there be to separating the processes? What advantages might there be to having them occur together?

**19. Figure 8.16** A scientist splices a eukaryotic promoter in front of a bacterial gene and inserts the gene in a bacterial chromosome. Would you expect the bacteria to transcribe the gene?

**20. Figure 8.18** Many antibiotics inhibit bacterial protein synthesis. For example, tetracycline blocks the A site on the bacterial ribosome, and chloramphenicol blocks peptidyl transfer. What

# **REVIEW QUESTIONS**

**21.** DNA double helix does not have which of the following?

specific effect would you expect each of these antibiotics to have on protein synthesis?

Tetracycline would directly affect:

- a. tRNA binding to the ribosome
- b. ribosome assembly
- c. growth of the protein chain

Chloramphenicol would directly affect

- a. tRNA binding to the ribosome
- b. ribosome assembly
- c. growth of the protein chain
- a. antiparallel configuration
- b. complementary base pairing
- c. major and minor grooves
- d. uracil

22. In eukaryotes, what is the DNA wrapped around?

- a. single-stranded binding proteins
- b. sliding clamp
- c. polymerase
- d. histones

**23.** The AUC and AUA codons in mRNA both specify isoleucine. What feature of the genetic code explains this?

- a. complementarity
- b. nonsense codons
- c. universality
- d. degeneracy

24. How many nucleotides are in 12 mRNA codons?

- a. 12
- b. 24
- c. 36
- d. 48

**25.** Which feature of promoters can be found in both prokaryotes and eukaryotes?

# **CRITICAL THINKING QUESTIONS**

**29.** Provide a brief summary of the Sanger sequencing method.

**30.** Describe the structure and complementary base pairing of DNA.

**31.** Imagine if there were 200 commonly occurring amino acids instead of 20. Given what you know about the genetic code, what would be the shortest possible codon length? Explain.

- a. GC box
- b. TATA box
- c. octamer box
- d. -10 and -35 sequences

**26.** What transcripts will be most affected by low levels of  $\alpha$ -amanitin?

- a. 18S and 28S rRNAs
- b. pre-mRNAs
- c. 5S rRNAs and tRNAs
- d. other small nuclear RNAs

27. The RNA components of ribosomes are

- synthesized in the \_
  - a. cytoplasm
  - b. nucleus
  - c. nucleolus
  - d. endoplasmic reticulum

**28.** In any given species, there are at least how many types of aminoacyl tRNA synthetases?

- a. 20
- b. 40
- c. 100
- d. 200

**32.** Discuss how degeneracy of the genetic code makes cells more robust to mutations.

**33.** Transcribe and translate the following DNA sequence (nontemplate strand): 5'-ATGGCCGGTTATTAAGCA-3'

**34.** Explain how single nucleotide changes can have vastly different effects on protein function.

# APPENDIX A | THE PERIODIC TABLE OF ELEMENTS



Figure A1

# APPENDIX B | MEASUREMENTS AND THE METRIC SYSTEM

Magguramant	Linit	Abbroviation	Metric	Approximate Standard
Measurement	Unit	Appreviation	Equivalent	Equivalent
Length	nanometer	nm	1 nm = 10 <sup>-9</sup> m	1 mm = 0.039 inch 1 cm = 0.394 inch 1 m = 39.37 inches 1 m = 3.28 feet 1 m = 1.093 yards 1 km = 0.621 miles
	micrometer	μm	1 μm = 10 <sup>-6</sup> m	
	millimeter	mm	1 mm = 0.001 m	
	centimeter	cm	1 cm = 0.01 m	
	meter	m	1 m = 100 cm	
			1 m = 1000 mm	
	kilometer	km	1 km = 1000 m	
Mass	microgram	μg	$1 \mu g = 10^{-6}  g$	1 g = 0.035 ounce 1 kg = 2.205 pounds
	milligram	mg	$1 \text{ mg} = 10^{-3} \text{ g}$	
	gram	g	1 g = 1000 mg	
	kilogram	kg	1 kg = 1000 g	
Volume	microliter	μΙ	1 μl = 10 <sup>-6</sup> l	1 ml = 0.034 fluid ounce 1 l = 1.057 quarts 1 kl = 264.172 gallons
	milliliter	ml	$1 \text{ ml} = 10^{-3} \text{ l}$	
	liter	1	1 l = 1000 ml	
	kiloliter	kl	1 kl = 1000 l	
Area	square centimeter	cm <sup>2</sup>	$1 \text{ cm}^2 = 100 \text{ mm}^2$	$1 \text{ cm}^2 = 0.155 \text{ square inch}$ $1 \text{ m}^2 = 10.764 \text{ square feet}$ $1 \text{ m}^2 = 1.196 \text{ square yards}$ 1  ha = 2.471  acres
	square meter	m <sup>2</sup>	$1 m^2 = 10,000$ cm <sup>2</sup>	
	hectare	ha	1 ha = 10,000 m <sup>2</sup>	
Temperature	Celsius	°C	—	1 °C = 5/9 × (°F − 32)

#### Measurements and the Metric System

Table B1

# ANSWER KEY

### Chapter 1

**27** Figure 1.15 Carbon-12 has six neutrons. Carbon-13 has seven neutrons. **29** A **31** C **33** lonic bonds are created between ions. The electrons are not shared between the atoms, but rather are associated more with one ion than the other. Ionic bonds are strong bonds, but are weaker than covalent bonds, meaning it takes less energy to break an ionic bond compared with a covalent one.

#### **Chapter 2**

#### **Chapter 3**

#### **Chapter 4**

1 Figure 4.5 Glucose and galactose are aldoses. Fructose is a ketose. 3 Figure 4.33 Adenine is larger than cytosine and will not be able to base pair properly with the guanine on the opposing strand. This will cause the DNA to bulge. DNA repair enzymes may recognize the bulge and replace the incorrect nucleotide. 4 C 6 D 8 B 10 D 12 C 14 C 16 Biological macromolecules are organic because they contain carbon. 18 Glycogen and starch are polysaccharides. They are the storage form of glucose. Glycogen is stored in animals in the liver and in muscle cells, whereas starch is stored in the roots, seeds, and leaves of plants. Starch has two different forms, one unbranched (amylose) and one branched (amylopectin), whereas glycogen is a single type of a highly branched molecule. 20 Fat serves as a valuable way for animals to store energy. It can also provide insulation. Waxes can protect plant leaves and mammalian fur from getting wet. Phospholipids and steroids are important components of animal cell membranes, as well as plant, fungal, and bacterial membranes. 22 A change in gene sequence can lead to a different amino acid being added to a polypeptide chain instead of the normal one. This causes a change in protein structure and function. For example, in sickle cell anemia, the hemoglobin  $\beta$  chain has a single amino acid substitution—the amino acid glutamic acid in position six is substituted by valine. Because of this change, hemoglobin molecules form aggregates, and the disc-shaped red blood cells assume a crescent shape, which results in serious health problems. 24 DNA has a double-helix structure. The sugar and the phosphate are on the outside of the helix and the nitrogenous bases are in the interior. The monomers of DNA are nucleotides containing deoxyribose, one of the four nitrogenous bases (A. T, G and C), and a phosphate group. RNA is usually single-stranded and is made of ribonucleotides that are linked by phosphodiester linkages. A ribonucleotide contains ribose (the pentose sugar), one of the four nitrogenous bases (A,U, G, and C), and the phosphate group.

#### **Chapter 5**

**1** Figure 5.5 Free ribosomes and rough endoplasmic reticulum (which contains ribosomes) would not be able to form. **2** C **4** D **6** A **8** A light microscope would be ideal when viewing a small living organism, especially when the cell has been stained to reveal details. **10** A transmission electron microscope would be ideal for viewing the cell's internal structures, because many of the internal structures have membranes that are not visible by the light microscope. **12** Ribosomes are abundant in muscle cells as well because muscle cells are constructed of the proteins made by the ribosomes.

#### **Chapter 6**

**1** Figure 6.12 No, it must have been hypotonic as a hypotonic solution would cause water to enter the cells, thereby making them burst. **3** Figure 6.19 A decrease in pH means an increase in positively charged H<sup>+</sup> ions, and an increase in the electrical gradient across the membrane. The transport of amino acids into the cell will increase. **4** A **6** A **8** C **10** D **12** D **13** The fluid characteristic of the cell membrane allows greater flexibility to the cell than it would if the membrane were rigid. It also allows the motion of membrane components, required for some types of membrane transport. **15** Heavy molecules move more slowly than lighter ones. It takes more energy in the medium to move them along. Increasing or decreasing temperature increases or decreases the energy in the medium, affecting molecular movement. The denser a solution is, the harder it is for molecules to move through it, causing diffusion to slow down due to friction. Living cells require a steady supply of nutrients and a steady rate of waste removal. If the distance these substances need to travel is too great, diffusion cannot move nutrients and waste materials efficiently to sustain life. **17** Injection of isotonic solutions ensures that there will be no perturbation of the osmotic balance, and no water taken from tissues or added to them from the blood. **19** The sodium-potassium pump forces out three (positive) Na<sup>+</sup>

ions for every two (positive)  $K^+$  ions it pumps in, thus the cell loses a positive charge at every cycle of the pump.

## Chapter 7

23 Figure 7.8 C 25 Figure 7.17 No. We can store chemical energy because of the need to overcome the barrier to its breakdown. 27 Figure 7.24 Levels of carbon dioxide (a necessary photosynthetic substrate) will immediately fall. As a result, the rate of photosynthesis will be inhibited. 28 A 30 A 32 A 34 C 36 C 38 B 40 A 42 C 44 B 46 C 48 Essential nutrients are those nutrients that must be obtained from the diet because they cannot be produced by the body. Vitamins and minerals are examples of essential nutrients. 50 In the United States, obesity, particularly childhood obesity, is a growing concern. Some of the contributors to this situation include sedentary lifestyles and consuming more processed foods and less fruits and vegetables. As a result, even young children who are obese can face health concerns. 52 Lipids add flavor to food and promote a sense of satiety or fullness. Fatty foods are sources of high energy; one gram of lipid contains nine calories. Lipids are also required in the diet to aid the absorption of lipid-soluble vitamins and for the production of lipid-soluble hormones. 54 Energy is required for cellular motion, through beating of cilia or flagella, as well as human motion, produced by muscle contraction. Cells also need energy to perform digestion, as humans require energy to digest food. 56 The transition state is always higher in energy than the reactants and the products of a reaction (therefore, above), regardless of whether the reaction is endergonic or exergonic. 58 The outcome of light reactions in photosynthesis is the conversion of solar energy into chemical energy that the chloroplasts can use to do work (mostly anabolic production of carbohydrates from carbon dioxide). 60 The energy carriers that move from the light-dependent reaction to the light-independent one are "full" because they bring energy. After the energy is released, the "empty" energy carriers return to the light-dependent reaction to obtain more energy. There is not much actual movement involved. Both ATP and NADPH are produced in the stroma where they are also used and reconverted into ADP, Pi, and NADP<sup>+</sup>. 62 Feedback inhibition allows cells to control the amounts of metabolic products produced. If there is too much of a particular product relative to what the cell's needs, feedback inhibition effectively causes the cell to decrease production of that particular product. In general, this reduces the production of superfluous products and conserves energy, maximizing energy efficiency. 23 Figure 7.8 C 25 Figure 7.17 No. We can store chemical energy because of the need to overcome the barrier to its breakdown. 27 Figure 7.24 Levels of carbon dioxide (a necessary photosynthetic substrate) will immediately fall. 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#### **Chapter 8**

**1** Figure 8.7 Compartmentalization enables a eukaryotic cell to divide processes into discrete steps so it can build more complex protein and RNA products. But there is an advantage to having a single compartment as well: RNA and protein synthesis occurs much more quickly in a prokaryotic cell. **3** Figure 8.18 Tetracycline: a; Chloramphenicol: c. **4** D **6** D **8** B **10** C **12** The template DNA strand is mixed with a DNA polymerase, a primer, the 4 deoxynucleotides, and a limiting concentration of 4 dideoxynucleotides. DNA polymerase synthesizes a strand complementary to the template. Incorporation of ddNTPs at different locations results in DNA fragments that have terminated at every possible base in the template. These fragments are separated by gel electrophoresis and visualized by a laser detector to determine the sequence of bases. **14** For 200 commonly occurring amino acids, codons consisting of four types of nucleotides would have to be at least four nucleotides long, because  $4^4 = 256$ . There would be much less degeneracy in this case. **16** The mRNA would be: 5'-AUGGCCGGUUAUUAAGCA-3'. The protein would be: MAGY. Even though there are six codons, the fifth codon corresponds to a stop, so the sixth codon would not be translated. **1** Figure 8.7

Compartmentalization enables a eukaryotic cell to divide processes into discrete steps so it can build more complex protein and RNA products. But there is an advantage to having a single compartment as well: RNA and protein synthesis occurs much more quickly in a prokaryotic cell. **3 Figure 8.18** Tetracycline: a; Chloramphenicol: c. **4** D **6** D **8** B **10** C **12** The template DNA strand is mixed with a DNA polymerase, a primer, the 4 deoxynucleotides, and a limiting concentration of 4 dideoxynucleotides. DNA polymerase synthesizes a strand complementary to the template. Incorporation of ddNTPs at different locations results in DNA fragments that have terminated at every possible base in the template. These fragments are separated by gel electrophoresis and visualized by a laser detector to determine the sequence of bases. **14** For 200 commonly occurring amino acids, codons consisting of four types of nucleotides would have to be at least four nucleotides long, because  $4^4 = 256$ . There would be much less degeneracy in this case. **16** The mRNA would be: 5'-AUGGCCGGUUAUUAAGCA-3'. The protein would be: MAGY. Even though there are six codons, the fifth codon corresponds to a stop, so the sixth codon would not be translated.

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# Symbols

 $\alpha$ -helix, **254**  $\beta$ -pleated sheet, **254** 

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