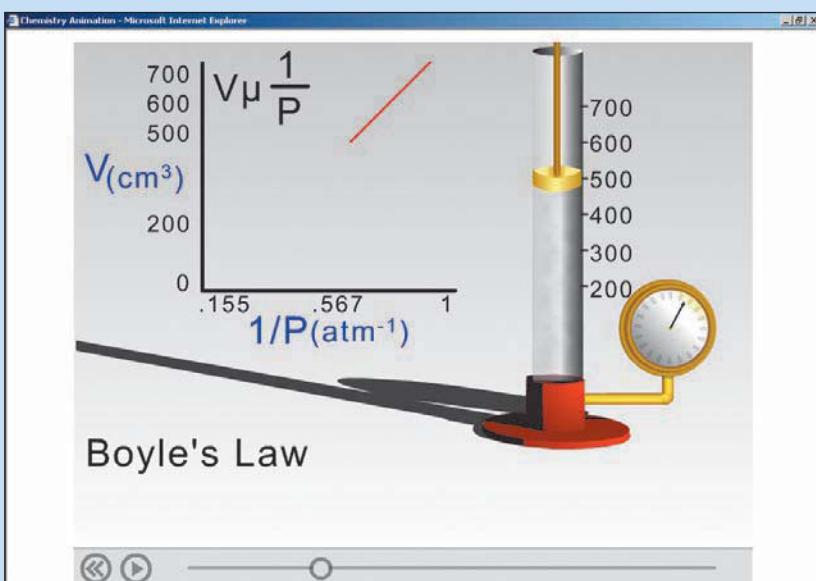


Technological Resources for Students



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ACE Practice Test
Chemistry
Chapter 1-1 : Chapter 1: Chemical Foundations

1. The central principle of modern chemistry states that all substances are ultimately composed of:

- A. atoms
- B. quarks
- C. cells
- D. electrons
- E. ions

2. Atomic theory, which forms the basis of modern chemistry, was first proposed by which of the following scientists?

- A. Darwin
- B. Mendeleev
- C. Thompson
- D. Ebbing
- E. Dalton

3. A concise statement or summary of observations of natural phenomena is called:

- A. a law

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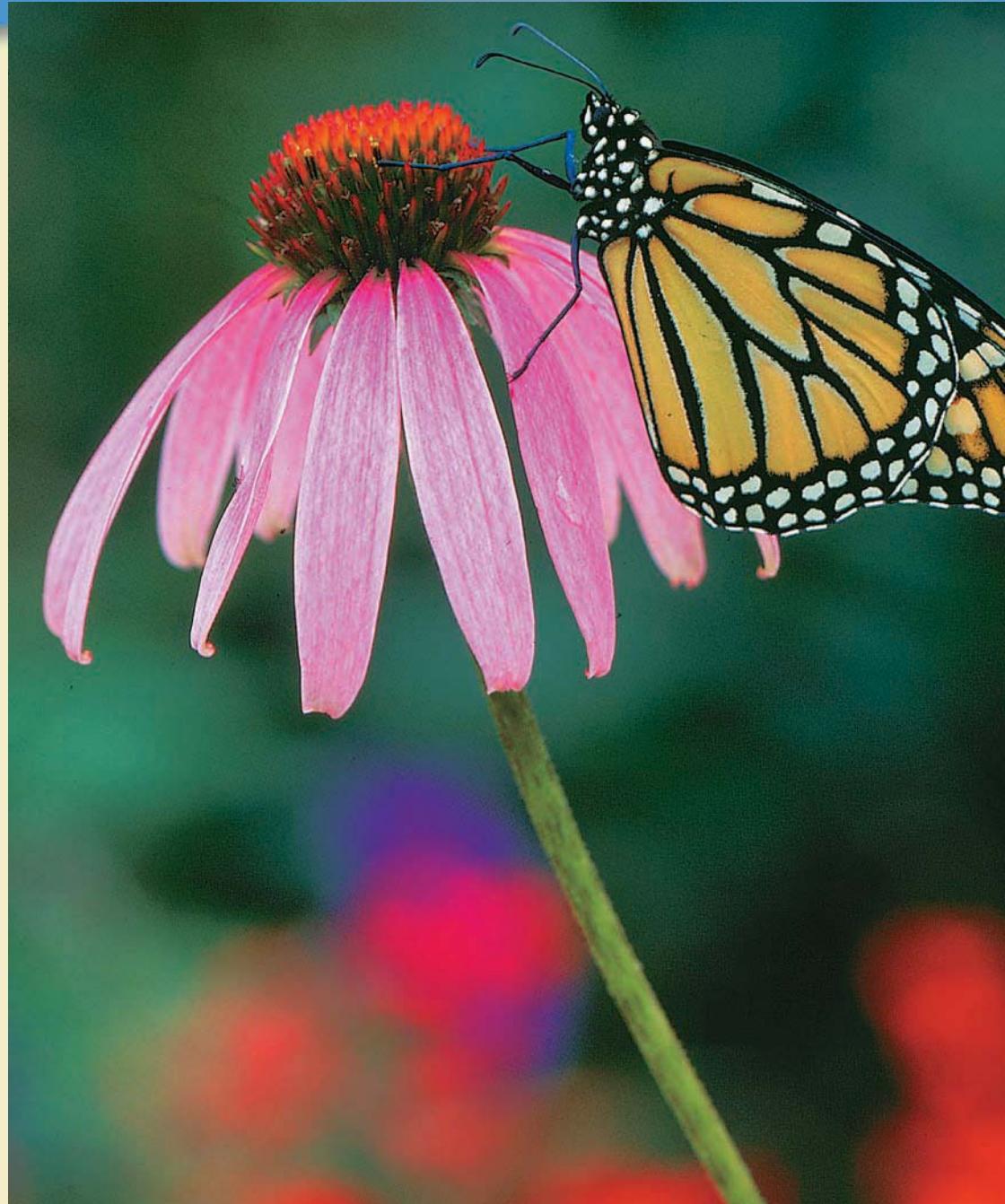
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1 Chemical Foundations

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Male Monarch butterflies use the pheromones produced by a gland on their wings to make themselves attractive to females.



W

hen you start your car, do you think about chemistry? Probably not, but you should. The power to start your car is furnished by a lead storage battery. How does this battery work, and what does it contain? When a battery goes dead, what does that mean? If you use a friend's car to "jump start" your car, did you know that your battery could explode? How can you avoid such an unpleasant possibility? What is in the gasoline that you put in your tank, and how does it furnish the energy to drive to school? What is the vapor that comes out of the exhaust pipe, and why does it cause air pollution? Your car's air conditioner might have a substance in it that is leading to the destruction of the ozone layer in the upper atmosphere. What are we doing about that? And why is the ozone layer important anyway?

All these questions can be answered by understanding some chemistry. In fact, we'll consider the answers to all these questions in this text.

Chemistry is around you all the time. You are able to read and understand this sentence because chemical reactions are occurring in your brain. The food you ate for breakfast or lunch is now furnishing energy through chemical reactions. Trees and grass grow because of chemical changes.

Chemistry also crops up in some unexpected places. When archaeologist Luis Alvarez was studying in college, he probably didn't realize that the chemical elements iridium and niobium would make him very famous when they helped him solve the problem of the disappearing dinosaurs. For decades scientists had wrestled with the mystery of why the dinosaurs, after ruling the earth for millions of years, suddenly became extinct 65 million years ago. In studying core samples of rocks dating back to that period, Alvarez and his coworkers recognized unusual levels of iridium and niobium in these samples—levels much more characteristic of extraterrestrial bodies than of the earth. Based on these observations, Alvarez hypothesized that a large meteor hit the earth 65 million years ago, changing atmospheric conditions so much that the dinosaurs' food couldn't grow, and they died—almost instantly in the geologic timeframe.

Chemistry is also important to historians. Did you realize that lead poisoning probably was a significant contributing factor to the decline of the Roman Empire? The Romans had high exposure to lead from lead-glazed pottery, lead water pipes, and a sweetening syrup called *sapa* that was prepared by boiling down grape juice in lead-lined vessels. It turns out that one reason for *sapa*'s sweetness was lead acetate ("sugar of lead") that formed as the juice was cooked down. Lead poisoning with its symptoms of lethargy and mental malfunctions certainly could have contributed to the demise of the Roman society.

Chemistry is also apparently very important in determining a person's behavior. Various studies have shown that many personality disorders can be linked directly to imbalances of trace elements in the body. For example, studies on the inmates at Stateville Prison in Illinois have linked low cobalt levels with violent behavior. Lithium salts have been shown to be very effective in controlling the effects of manic depressive disease, and you've probably at some time in your life felt a special "chemistry" for another person. Studies suggest there is literally chemistry going on between two people who are attracted to each other. "Falling in love" apparently causes changes in the chemistry of the brain; chemicals are produced that give that "high" associated with a new relationship. Unfortunately, these chemical effects seem to wear off over time, even if the relationship persists and grows.

The importance of chemistry in the interactions of people should not really surprise us, since we know that insects communicate by emitting and receiving chemical signals via molecules called *pheromones*. For example, ants have a very complicated set of chemical

signals to signify food sources, danger, and so forth. Also, various female sex attractants have been isolated and used to lure males into traps to control insect populations. It would not be surprising if humans also emitted chemical signals that we were not aware of on a conscious level. Thus chemistry is pretty interesting and pretty important. The main goal of this text is to help you understand the concepts of chemistry so that you can better appreciate the world around you and can be more effective in whatever career you choose.

1.1 Chemistry: An Overview

Since the time of the ancient Greeks, people have wondered about the answer to the question: What is matter made of? For a long time humans have believed that matter is composed of atoms, and in the previous three centuries we have collected much indirect evidence to support this belief. Very recently, something exciting has happened—for the first time we can “see” individual atoms. Of course, we cannot see atoms with the naked eye but must use a special microscope called a scanning tunneling microscope (STM). Although we will not consider the details of its operation here, the STM uses an electron current from a tiny needle to probe the surface of a substance. The STM pictures of several substances are shown in Fig. 1.1. Notice how the atoms are connected to one another by “bridges,” which, as we will see, represent the electrons that interconnect atoms.

In addition to “seeing” the atoms in solids such as salt, we have learned how to isolate and view a single atom. For example, the tiny white dot in the center of Fig. 1.2 is a single mercury atom that is held in a special trap.

So, at this point, we are fairly sure that matter consists of individual atoms. The nature of these atoms is quite complex, and the components of atoms don’t behave much like the objects we see in the world of our experience. We call this world the *macroscopic world*—the world of cars, tables, baseballs, rocks, oceans, and so forth. One of the main jobs of a scientist is to delve into the macroscopic world and discover its “parts.” For example, when you view a beach from a distance, it looks like a continuous solid substance. As you get closer, you see that the beach is really made up of individual grains of sand.

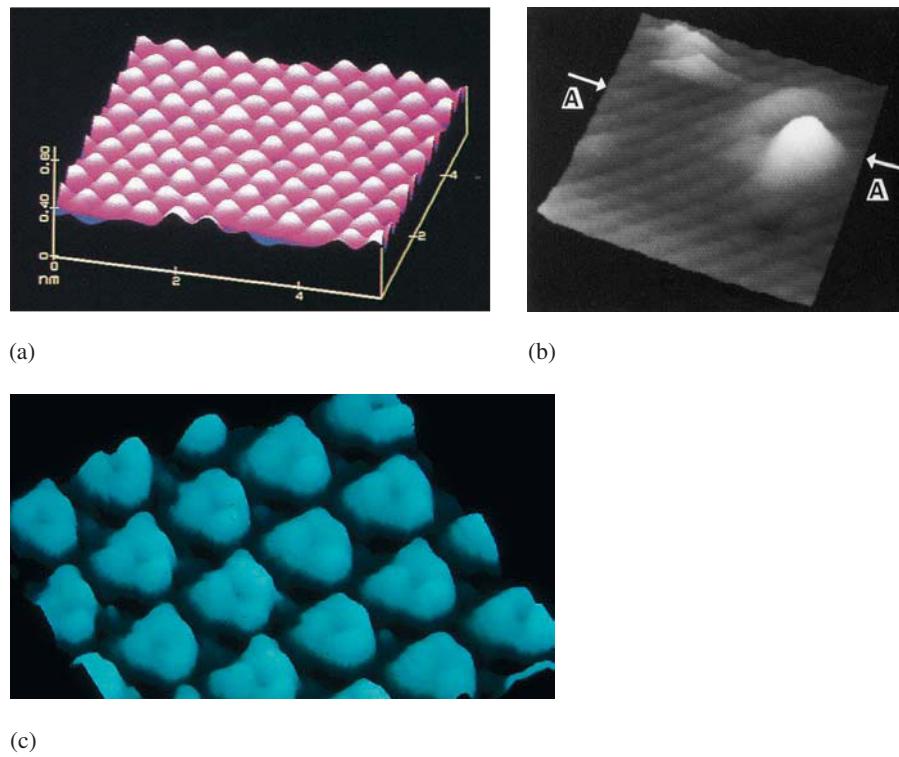
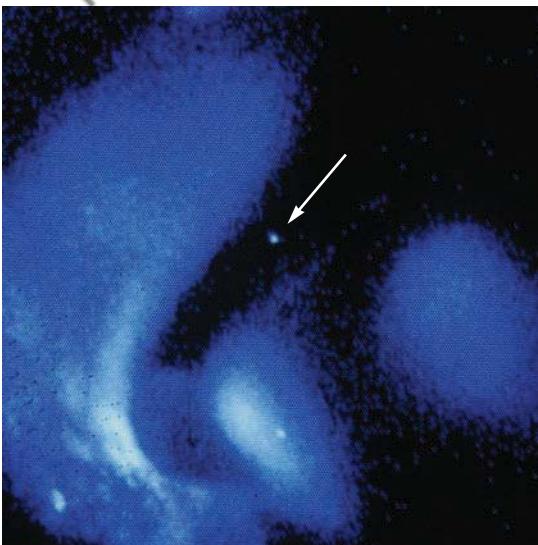


FIGURE 1.1

(a) The surface of a single grain of table salt. (b) An oxygen atom (indicated by arrow) on a gallium arsenide surface. (c) Scanning tunneling microscope image showing rows of ring-shaped clusters of benzene molecules on a rhodium surface. Each “doughnut”-shaped image represents a benzene molecule.

**FIGURE 1.2**

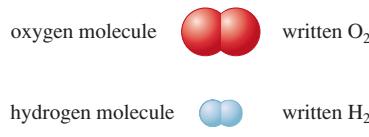
A charged mercury atom shows up as a tiny white dot (indicated by the arrow).

As we examine these grains of sand, we find they are composed of silicon and oxygen atoms connected to each other to form intricate shapes (see Fig. 1.3). One of the main challenges of chemistry is to understand the connection between the macroscopic world that we experience and the *microscopic world* of atoms and molecules. To truly understand chemistry you must learn to think on the atomic level. We will spend much time in this text helping you learn to do that.

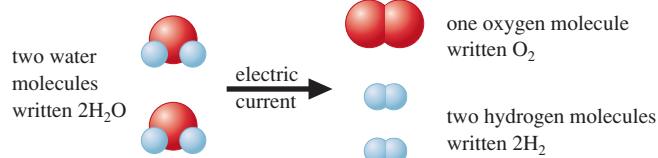
One of the amazing things about our universe is that the tremendous variety of substances we find there results from only about 100 different kinds of atoms. You can think of these approximately 100 atoms as the letters in an alphabet out of which all the “words” in the universe are made. It is the way the atoms are organized in a given substance that determines the properties of that substance. For example, water, one of the most common and important substances on earth, is composed of two types of atoms: hydrogen and oxygen. There are two hydrogen atoms and one oxygen atom bound together to form the water molecule:



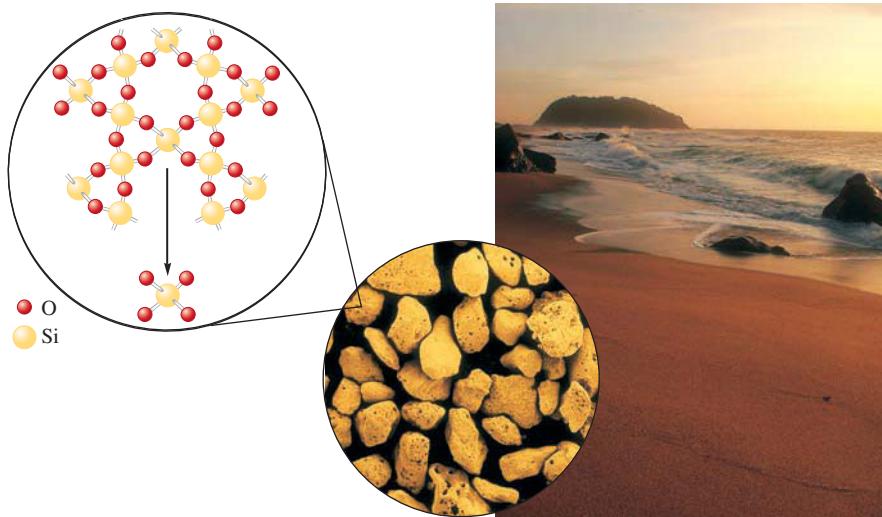
When an electric current passes through it, water is decomposed to hydrogen and oxygen. These *chemical elements* themselves exist naturally as diatomic (two-atom) molecules:



We can represent the decomposition of water to its component elements, hydrogen and oxygen, as follows:



Notice that it takes two molecules of water to furnish the right number of oxygen and hydrogen atoms to allow for the formation of the two-atom molecules. This reaction explains

**FIGURE 1.3**

Sand on a beach looks uniform from a distance, but up close the irregular sand grains are visible, and each grain is composed of tiny atoms.



CHEMICAL IMPACT

The Chemistry of Art

The importance of chemistry can show up in some unusual places. For example, a knowledge of chemistry is crucial to authenticating, preserving, and restoring art objects. The J. Paul Getty Museum in Los Angeles has a state-of-the-art chemical laboratory that costs many millions of dollars and employs many scientists. The National Gallery of Art (NGA) in Washington, D.C., also operates a highly sophisticated laboratory that employs 10 people: five chemists, a botanist, an art historian, a technician with a chemistry degree, and two fellows (interns).

One of the chemists at NGA is Barbara Berrie, who specializes in identifying paint pigments. One of her duties is to analyze a painting to see whether the paint pigments are appropriate for the time the picture was supposedly painted and consistent with the pigments known to be used by the artist given credit for the painting. This analysis is one way in which paintings can be authenticated. One of Berrie's recent projects was to analyze the 1617 oil painting *St. Cecilia and an Angel*. Her results showed the painting was the work of two artists of the time, Orazio Gentileschi and Giovanni Lanfranco. Originally the work was thought to be by Gentileschi alone.

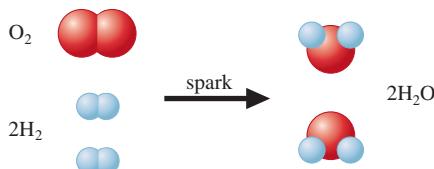
Berrie is also working to define the range of colors used by water colorist Winslow Homer (the NGA has 30 Homer paintings in its collection) and to show how his color palette changed over his career. In addition, she is exploring how acidity affects the decomposition of a particular deep green transparent pigment (called copper resinate) used by Italian Renaissance artists so that paintings using this pigment can be better preserved.

Berrie says, "The chemistry I do is not hot-dog chemistry, just good old-fashioned general chemistry."



Dr. Barbara Berrie of the National Gallery of Art is shown analyzing the glue used in the wooden supports for a 14th century altar piece.

why the battery in your car can explode if you jump start it improperly. When you hook up the jumper cables, current flows through the dead battery, which contains water (and other things), and causes hydrogen and oxygen to form by decomposition of some of the water. A spark can cause this accumulated hydrogen and oxygen to explode, forming water again.



This example illustrates two of the fundamental concepts of chemistry: (1) matter is composed of various types of atoms, and (2) one substance changes to another by reorganizing the way the atoms are attached to each other.

These are core ideas of chemistry, and we will have much more to say about them.

Science: A Process for Understanding Nature and Its Changes

How do you tackle the problems that confront you in real life? Think about your trip to school. If you live in a city, traffic is undoubtedly a problem you confront daily. How do you decide the best way to drive to school? If you are new in town, you first get a map and look at the possible ways to make the trip. Then you might collect information from people who know the area about the advantages and disadvantages of various routes. Based on this information, you probably try to predict the best route. However, you can find the best route only by trying several of them and comparing the results. After a few experiments with the various possibilities, you probably will be able to select the best way. What you are doing in solving this everyday problem is applying the same process that scientists use to study nature. The first thing you did was collect relevant data. Then you made a prediction, and then you tested it by trying it out. This process contains the fundamental elements of science.

1. Making observations (collecting data)
2. Making a prediction (formulating a hypothesis)
3. Doing experiments to test the prediction (testing the hypothesis)

Scientists call this process the *scientific method*. We will discuss it in more detail in the next section. One of life's most important activities is solving problems—not “plug and chug” exercises, but real problems—problems that have new facets to them, that involve things you may have never confronted before. The more creative you are at solving these problems, the more effective you will be in your career and your personal life. Part of the reason for learning chemistry, therefore, is to become a better problem solver. Chemists are usually excellent problem solvers, because to master chemistry, you have to master the scientific approach. Chemical problems are frequently very complicated—there is usually no neat and tidy solution. Often it is difficult to know where to begin.

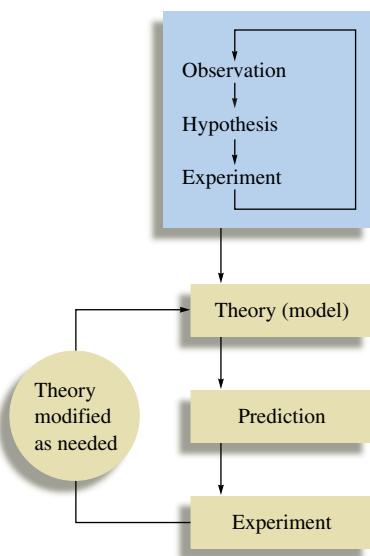


FIGURE 1.4

The fundamental steps of the scientific method.

1.2 The Scientific Method

Science is a framework for gaining and organizing knowledge. Science is not simply a set of facts but also a plan of action—a *procedure* for processing and understanding certain types of information. Scientific thinking is useful in all aspects of life, but in this text we will use it to understand how the chemical world operates. As we have said in our previous discussion, the process that lies at the center of scientific inquiry is called the **scientific method**. There are actually many scientific methods, depending on the nature of the specific problem under study and on the particular investigator involved. However, it is useful to consider the following general framework for a generic scientific method (see Fig. 1.4):

Steps in the Scientific Method

- **1** *Making observations.* Observations may be **qualitative** (the sky is blue; water is a liquid) or **quantitative** (water boils at 100°C; a certain chemistry book weighs 2 kilograms). A qualitative observation does not involve a number. A quantitative observation (called a **measurement**) involves both a number and a unit.
- **2** *Formulating hypotheses.* A hypothesis is a **possible explanation** for an observation.
- **3** *Performing experiments.* An experiment is carried out to test a hypothesis. This involves gathering new information that enables a scientist to decide whether

the hypothesis is valid—that is, whether it is supported by the new information learned from the experiment. Experiments always produce new observations, and this brings the process back to the beginning again.

To understand a given phenomenon, these steps are repeated many times, gradually accumulating the knowledge necessary to provide a possible explanation of the phenomenon.

Scientific Models

Once a set of hypotheses that agrees with the various observations is obtained, the hypotheses are assembled into a theory. A **theory**, which is often called a **model**, is a set of tested hypotheses that gives an overall explanation of some natural phenomenon.

It is very important to distinguish between observations and theories. An observation is something that is witnessed and can be recorded. A theory is an *interpretation*—a possible explanation of *why* nature behaves in a particular way. Theories inevitably change as more information becomes available. For example, the motions of the sun and stars have remained virtually the same over the thousands of years during which humans have been observing them, but our explanations—our theories—for these motions have changed greatly since ancient times. (See the Chemical Impact on Observations, Theories, and the Planets on the Web site.)

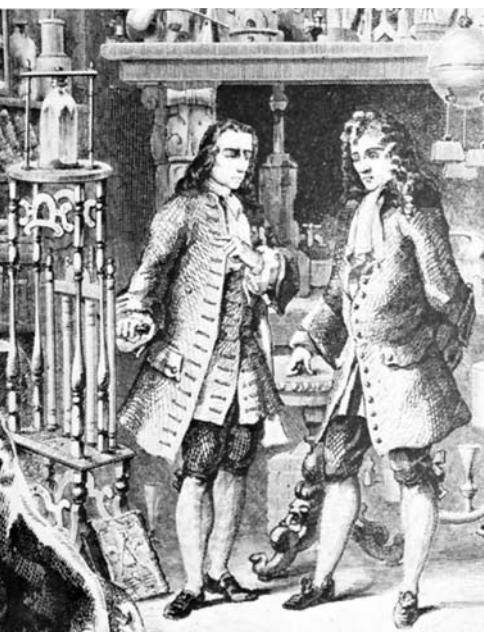
The point is that scientists do not stop asking questions just because a given theory seems to account satisfactorily for some aspect of natural behavior. They continue doing experiments to refine or replace the existing theories. This is generally done by using the currently accepted theory to make a prediction and then performing an experiment (making a new observation) to see whether the results bear out this prediction.

Always remember that theories (models) are human inventions. They represent attempts to explain observed natural behavior in terms of human experiences. A theory is actually an educated guess. We must continue to do experiments and to refine our theories (making them consistent with new knowledge) if we hope to approach a more nearly complete understanding of nature.

As scientists observe nature, they often see that the same observation applies to many different systems. For example, studies of innumerable chemical changes have shown that the total observed mass of the materials involved is the same before and after the change. Such generally observed behavior is formulated into a statement called a **natural law**. For example, the observation that the total mass of materials is not affected by a chemical change in those materials is called the **law of conservation of mass**.

Note the difference between a natural law and a theory. A natural law is a summary of observed (measurable) behavior, whereas a theory is an explanation of behavior. A *law summarizes what happens; a theory (model) is an attempt to explain why it happens*.

In this section we have described the scientific method as it might ideally be applied (see Fig. 1.5). However, it is important to remember that science does not always progress smoothly and efficiently. For one thing, hypotheses and observations are not totally independent of each other, as we have assumed in the description of the idealized scientific



Robert Boyle (1627–1691) was born in Ireland. He became especially interested in experiments involving air and developed an air pump with which he produced evacuated cylinders. He used these cylinders to show that a feather and a lump of lead fall at the same rate in the absence of air resistance and that sound cannot be produced in a vacuum. His most famous experiments involved careful measurements of the volume of a gas as a function of pressure. In his book *The Sceptical Chymist*, Boyle urged that the ancient view of elements as mystical substances should be abandoned and that an element should instead be defined as anything that cannot be broken down into simpler substances. This conception was an important step in the development of modern chemistry.



CHEMICAL IMPACT

A Note-able Achievement

Post-it Notes, a product of the 3M Corporation, revolutionized casual written communications and personal reminders. Introduced in the United States in 1980, these sticky-but-not-too-sticky notes have now found countless uses in offices, cars, and homes throughout the world.

The invention of sticky notes occurred over a period of about 10 years and involved a great deal of serendipity. The adhesive for Post-it Notes was discovered by Dr. Spencer F. Silver of 3M in 1968. Silver found that when an acrylate polymer material was made in a particular way, it formed cross-linked microspheres. When suspended in a solvent and sprayed on a sheet of paper, this substance formed a “sparse monolayer” of adhesive after the solvent evaporated. Scanning electron microscope images of the adhesive show that it has an irregular surface, a little like the surface of a gravel road. In contrast, the adhesive on cellophane tape looks smooth and uniform, like a superhighway. The bumpy surface of Silver’s adhesive caused it to be sticky but not so sticky to produce permanent adhesion, because the number of contact points between the binding surfaces was limited.

When he invented this adhesive, Silver had no specific ideas for its use, so he spread the word of his discovery to his fellow employees at 3M to see if anyone had an application for it. In addition, over the next several years development was carried out to improve the adhesive’s properties. It was not until 1974 that the idea for Post-it Notes popped up. One Sunday Art Fry, a chemical engineer for

3M, was singing in his church choir when he became annoyed that the bookmark in his hymnal kept falling out. He thought to himself that it would be nice if the bookmark were sticky enough to stay in place but not so sticky that it couldn’t be moved. Luckily, he remembered Silver’s glue—and the Post-it Note was born.

For the next three years Fry worked to overcome the manufacturing obstacles associated with the product. By 1977 enough Post-it Notes were being produced to supply 3M’s corporate headquarters, where the employees quickly became addicted to their many uses. Post-it Notes are now available in 62 colors and 25 shapes.

In the years since their introduction, 3M has heard some remarkable stories connected to the use of these notes. For example, a Post-it Note was applied to the nose of a corporate jet, where it was intended to be read by the plane’s Las Vegas ground crew. Someone forgot to remove it, however. The note was still on the nose of the plane when it landed in Minneapolis, having survived a take-off and landing and speeds of 500 miles per hour at temperatures as low as -56°F . Stories on the 3M Web site also describe how a Post-it Note on the front door of a home survived the 140 mile per hour winds of Hurricane Hugo and how a foreign official accepted Post-it Notes in lieu of cash when a small bribe was needed to cut through bureaucratic hassles.

Post-it Notes have definitely changed the way we communicate and remember things.

method. The coupling of observations and hypotheses occurs because once we begin to proceed down a given theoretical path, our hypotheses are unavoidably couched in the language of that theory. In other words, we tend to see what we expect to see and often fail to notice things that we do not expect. Thus the theory we are testing helps us because it focuses our questions. However, at the very same time, this focusing process may limit our ability to see other possible explanations.

It is also important to keep in mind that scientists are human. They have prejudices; they misinterpret data; they become emotionally attached to their theories and thus lose objectivity; and they play politics. Science is affected by profit motives, budgets, fads, wars, and religious beliefs. Galileo, for example, was forced to recant his astronomical observations in the face of strong religious resistance. Lavoisier, the father of modern chemistry, was beheaded because of his political affiliations. Great progress in the chemistry of nitrogen fertilizers resulted from the desire to produce explosives to fight wars. The progress of science is often affected more by the frailties of humans and their institutions than by the limitations of scientific measuring devices. The scientific methods are only as effective as the humans using them. They do not automatically lead to progress.



CHEMICAL IMPACT

Critical Units!

How important are conversions from one unit to another? If you ask the National Aeronautics and Space Administration (NASA), very important! In 1999 NASA lost a \$125 million Mars Climate Orbiter because of a failure to convert from English to metric units.

The problem arose because two teams working on the Mars mission were using different sets of units. NASA's scientists at the Jet Propulsion Laboratory in Pasadena, California, assumed that the thrust data for the rockets on the Orbiter they received from Lockheed Martin Astronautics in Denver, which built the spacecraft, were in metric units. In reality, the units were English. As a result the Orbiter dipped 100 kilometers lower into the Mars atmosphere than planned and the friction from the atmosphere caused the craft to burn up.

NASA's mistake refueled the controversy over whether Congress should require the United States to switch to the metric system. About 95% of the world now uses the metric system, and the United States is slowly switching from English to metric. For example, the automobile industry has adopted metric fasteners and we buy our soda in two-liter bottles.

Units can be very important. In fact, they can mean the difference between life and death on some occasions. In 1983, for example, a Canadian jetliner almost ran out of fuel when someone pumped 22,300 pounds of fuel into the aircraft instead of 22,300 kilograms. Remember to watch your units!



Artist's conception of the lost Mars Climate Orbiter.



Soda is commonly sold in 2-liter bottles—an example of the use of SI units in everyday life.

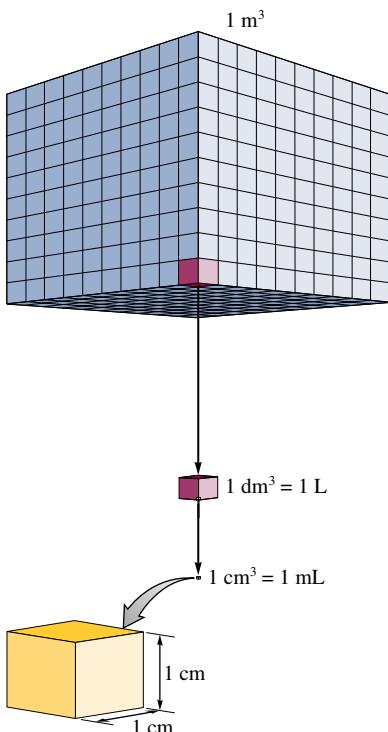
1.3 Units of Measurement

Making observations is fundamental to all science. A quantitative observation, or *measurement*, always consists of two parts: a *number* and a scale (called a *unit*). Both parts must be present for the measurement to be meaningful.

In this textbook we will use measurements of mass, length, time, temperature, electric current, and the amount of a substance, among others. Scientists recognized long ago that standard systems of units had to be adopted if measurements were to be useful. If every scientist had a different set of units, complete chaos would result. Unfortunately, different standards were adopted in different parts of the world. The two major systems are the *English system* used in the United States and the *metric system* used by most of the rest of the industrialized world. This duality causes a good deal of trouble; for example, parts as simple as bolts are not interchangeable between machines built using the two systems. As a result, the United States has begun to adopt the metric system.

Most scientists in all countries have for many years used the metric system. In 1960, an international agreement set up a system of units called the *International System (le Système International in French)*, or the **SI system**. This system is based on the metric system and units derived from the metric system. The fundamental SI units are listed in Table 1.1. We will discuss how to manipulate these units later in this chapter.

Because the fundamental units are not always convenient (expressing the mass of a pin in kilograms is awkward), prefixes are used to change the size of the unit. These are listed in Table 1.2. Some common objects and their measurements in SI units are listed in Table 1.3.

**FIGURE 1.6**

The largest cube has sides 1 m in length and a volume of 1 m^3 . The middle-sized cube has sides 1 dm in length and a volume of 1 dm^3 , or 1 L. The smallest cube has sides 1 cm in length and a volume of 1 cm^3 , or 1 mL.

TABLE 1.1 The Fundamental SI Units

Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Amount of substance	mole	mol
Luminous intensity	candela	cd

One physical quantity that is very important in chemistry is *volume*, which is not a fundamental SI unit but is derived from length. A cube that measures 1 meter (m) on each edge is represented in Fig. 1.6. This cube has a volume of $(1 \text{ m})^3 = 1 \text{ m}^3$. Recognizing that there are 10 decimeters (dm) in a meter, the volume of this cube is $(1 \text{ m})^3 = (10 \text{ dm})^3 = 1000 \text{ dm}^3$. A cubic decimeter, that is $(1 \text{ dm})^3$, is commonly called a *liter* (L), which is a unit of volume slightly larger than a quart. As shown in Fig. 1.6, 1000 liters are contained in a cube with a volume of 1 cubic meter. Similarly, since 1 decimeter equals 10 centimeters (cm), the liter can be divided into 1000 cubes each with a volume of 1 cubic centimeter:

$$1 \text{ liter} = (1 \text{ dm})^3 = (10 \text{ cm})^3 = 1000 \text{ cm}^3$$

Also, since $1 \text{ cm}^3 = 1 \text{ milliliter (mL)}$,

$$1 \text{ liter} = 1000 \text{ cm}^3 = 1000 \text{ mL}$$

Thus 1 liter contains 1000 cubic centimeters, or 1000 milliliters.

Chemical laboratory work frequently requires measurement of the volumes of liquids. Several devices for the accurate determination of liquid volume are shown in Fig. 1.7.

An important point concerning measurements is the relationship between mass and weight. Although these terms are sometimes used interchangeably, they are *not* the same.

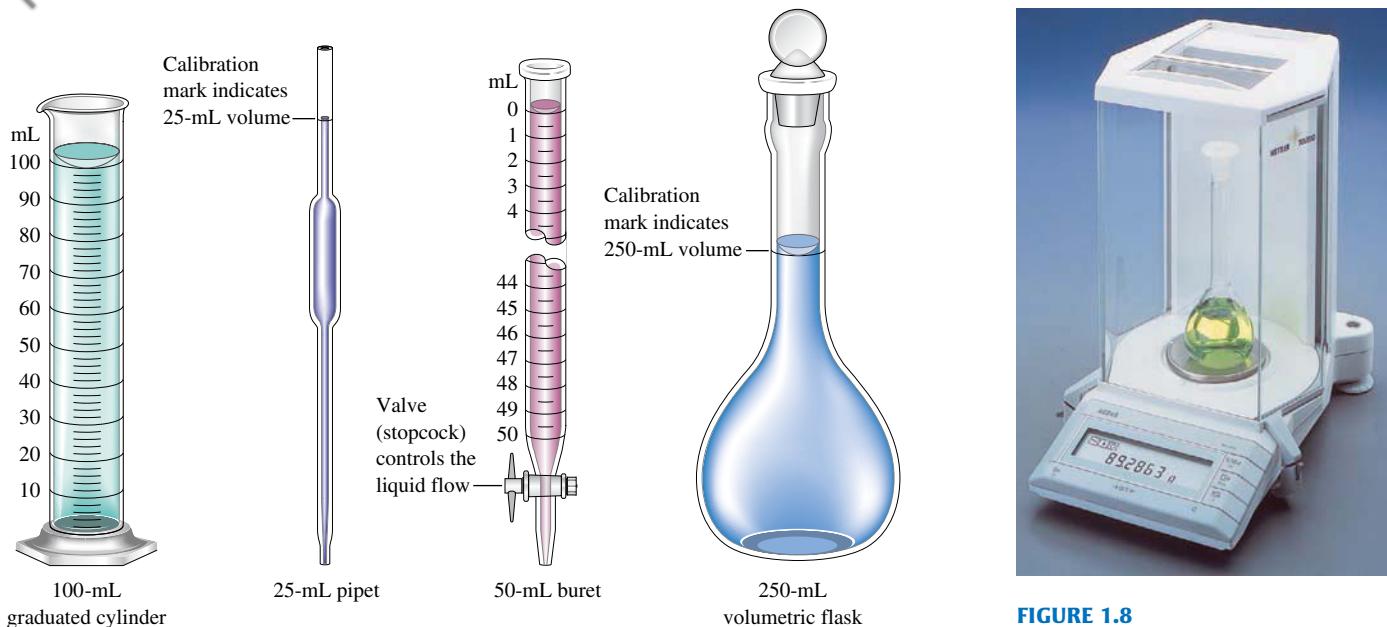
TABLE 1.2 The Prefixes Used in the SI System (Those most commonly encountered are shown in blue.)

Prefix	Symbol	Meaning	Exponential Notation*
exa	E	$1,000,000,000,000,000,000$	10^{18}
peta	P	$1,000,000,000,000,000$	10^{15}
tera	T	$1,000,000,000,000$	10^{12}
giga	G	$1,000,000,000$	10^9
mega	M	$1,000,000$	10^6
kilo	k	1,000	10^3
hecto	h	100	10^2
deka	da	10	10^1
—	—	1	10^0
deci	d	0.1	10^{-1}
centi	c	0.01	10^{-2}
milli	m	0.001	10^{-3}
micro	μ	0.000001	10^{-6}
nano	n	0.000000001	10^{-9}
pico	p	0.0000000000001	10^{-12}
femto	f	0.0000000000000001	10^{-15}
atto	a	0.0000000000000000001	10^{-18}

*See Appendix 1.1 if you need a review of exponential notation.

TABLE 1.3 Some Examples of Commonly Used Units

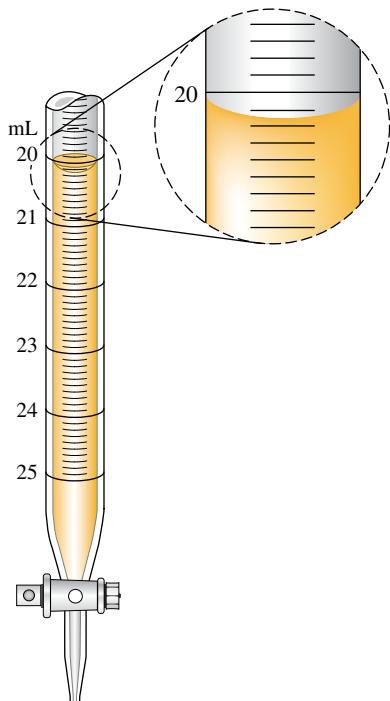
Length	A dime is 1 mm thick. A quarter is 2.5 cm in diameter. The average height of an adult man is 1.8 m.
Mass	A nickel has a mass of about 5 g. A 120-lb person has a mass of about 55 kg.
Volume	A 12-oz can of soda has a volume of about 360 mL.

**FIGURE 1.7**

Common types of laboratory equipment used to measure liquid volume.

Mass is a measure of the resistance of an object to a change in its state of motion. Mass is measured by the force necessary to give an object a certain acceleration. On earth we use the force that gravity exerts on an object to measure its mass. We call this force the object's **weight**. Since weight is the response of mass to gravity, it varies with the strength of the gravitational field. Therefore, your body mass is the same on the earth or on the moon, but your weight would be much less on the moon than on earth because of the moon's smaller gravitational field.

Because weighing something on a chemical balance (see Fig. 1.8) involves comparing the mass of that object to a standard mass, the terms *weight* and *mass* are sometimes used interchangeably, although this is incorrect.

**FIGURE 1.9**

Measurement of volume using a buret. The volume is read at the bottom of the liquid curve (called the meniscus).

**FIGURE 1.8**

An electronic analytical balance.

1.4 Uncertainty in Measurement

The number associated with a measurement is obtained using some measuring device. For example, consider the measurement of the volume of a liquid using a buret (shown in Fig. 1.9 with the scale greatly magnified). Notice that the meniscus of the liquid occurs at about 20.15 milliliters. This means that about 20.15 mL of liquid has been delivered from the buret (if the initial position of the liquid meniscus was 0.00 mL). Note that we must estimate the last number of the volume reading by interpolating between the 0.1-mL marks. Since the last number is estimated, its value may be different if another person makes the same measurement. If five different people read the same volume, the results might be as follows:

Person	Results of Measurement
1	20.15 mL
2	20.14 mL
3	20.16 mL
4	20.17 mL
5	20.16 mL

These results show that the first three numbers (20.1) remain the same regardless of who makes the measurement; these are called *certain* digits. However, the digit to the right of the 1 must be estimated and therefore varies; it is called an *uncertain* digit. We customarily report a measurement by recording all the certain digits plus the *first* uncertain digit. In our example it would not make any sense to try to record the volume of thousandths of a milliliter because the value for hundredths of a milliliter must be estimated when using the buret.

It is very important to realize that a *measurement always has some degree of uncertainty*. The uncertainty of a measurement depends on the precision of the measuring device. For example, using a bathroom scale, you might estimate the mass of a grapefruit to be approximately 1.5 pounds. Weighing the same grapefruit on a highly precise balance might produce a result of 1.476 pounds. In the first case, the uncertainty occurs in the tenths of a pound place; in the second case, the uncertainty occurs in the thousandths of a pound place. Suppose we weigh two similar grapefruits on the two devices and obtain the following results:

	Bathroom Scale	Balance
Grapefruit 1	1.5 lb	1.476 lb
Grapefruit 2	1.5 lb	1.518 lb

A measurement always has some degree of uncertainty.

Uncertainty in measurement is discussed in more detail in Appendix 1.5.

Do the two grapefruits have the same mass? The answer depends on which set of results you consider. Thus a conclusion based on a series of measurements depends on the certainty of those measurements. For this reason, it is important to indicate the uncertainty in any measurement. This is done by always recording the certain digits and the first uncertain digit (the estimated number). These numbers are called the **significant figures** of a measurement.

The convention of significant figures automatically indicates something about the uncertainty in a measurement. The uncertainty in the last number (the estimated number) is usually assumed to be ± 1 unless otherwise indicated. For example, the measurement 1.86 kilograms can be taken to mean 1.86 ± 0.01 kilograms.

Sample Exercise 1.1

Uncertainty in Measurement

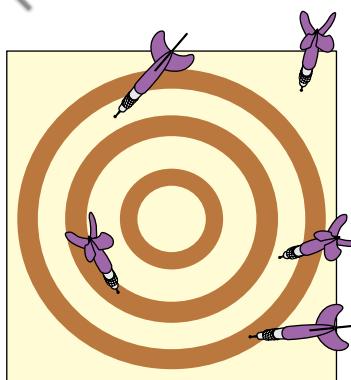
In analyzing a sample of polluted water, a chemist measured out a 25.00-mL water sample with a pipet (see Fig. 1.7). At another point in the analysis, the chemist used a graduated cylinder (see Fig. 1.7) to measure 25 mL of a solution. What is the difference between the measurements 25.00 mL and 25 mL?

Solution

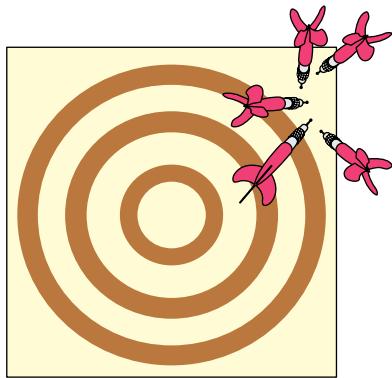
Even though the two volume measurements appear to be equal, they really convey different information. The quantity 25 mL means that the volume is between 24 mL and 26 mL, whereas the quantity 25.00 mL means that the volume is between 24.99 mL and 25.01 mL. The pipet measures volume with much greater precision than does the graduated cylinder.

See Question 1.8.

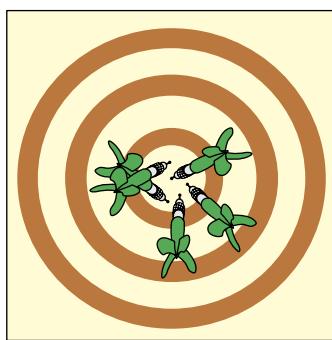
When making a measurement, it is important to record the results to the appropriate number of significant figures. For example, if a certain buret can be read to ± 0.01 mL,



(a)



(b)



(c)

FIGURE 1.10

The results of several dart throws show the difference between precise and accurate.
 (a) Neither accurate nor precise (large random errors).
 (b) Precise but not accurate (small random errors, large systematic error).
 (c) Bull's-eye! Both precise and accurate (small random errors, no systematic error).

you should record a reading of twenty-five milliliters as 25.00 mL, not 25 mL. This way at some later time when you are using your results to do calculations, the uncertainty in the measurement will be known to you.

Precision and Accuracy

Two terms often used to describe the reliability of measurements are *precision* and *accuracy*. Although these words are frequently used interchangeably in everyday life, they have different meanings in the scientific context. **Accuracy** refers to the agreement of a particular value with the true value. **Precision** refers to the degree of agreement among several measurements of the same quantity. Precision reflects the *reproducibility* of a given type of measurement. The difference between these terms is illustrated by the results of three different dart throws shown in Fig. 1.10.

Two different types of errors are illustrated in Fig. 1.10. A **random error** (also called an *indeterminate error*) means that a measurement has an equal probability of being high or low. This type of error occurs in estimating the value of the last digit of a measurement. The second type of error is called **systematic error** (or *determinate error*). This type of error occurs in the same direction each time; it is either always high or always low. Figure 1.10(a) indicates large random errors (poor technique). Figure 1.10(b) indicates small random errors but a large systematic error, and Figure 1.10(c) indicates small random errors and no systematic error.

In quantitative work, precision is often used as an indication of accuracy; we assume that the *average* of a series of precise measurements (which should “average out” the random errors because of their equal probability of being high or low) is accurate, or close to the “true” value. However, this assumption is valid only if systematic errors are absent. Suppose we weigh a piece of brass five times on a very precise balance and obtain the following results:

Weighing	Result
1	2.486 g
2	2.487 g
3	2.485 g
4	2.484 g
5	2.488 g

Normally, we would assume that the true mass of the piece of brass is very close to 2.486 grams, which is the average of the five results:

$$\frac{2.486 \text{ g} + 2.487 \text{ g} + 2.485 \text{ g} + 2.484 \text{ g} + 2.488 \text{ g}}{5} = 2.486 \text{ g}$$

However, if the balance has a defect causing it to give a result that is consistently 1.000 gram too high (a systematic error of +1.000 gram), then the measured value of 2.486 grams would be seriously in error. The point here is that high precision among several measurements is an indication of accuracy *only* if systematic errors are absent.

Precision and Accuracy

To check the accuracy of a graduated cylinder, a student filled the cylinder to the 25-mL mark using water delivered from a buret (see Fig. 1.7) and then read the volume delivered. Following are the results of five trials:

Sample Exercise 1.2

Trial	Volume Shown by Graduated Cylinder	Volume Shown by the Buret
1	25 mL	26.54 mL
2	25 mL	26.51 mL
3	25 mL	26.60 mL
4	25 mL	26.49 mL
5	25 mL	26.57 mL
Average	25 mL	26.54 mL

Is the graduated cylinder accurate?

Solution

Precision is an indication of accuracy only if there are no systematic errors.

The results of the trials show very good precision (for a graduated cylinder). The student has good technique. However, note that the average value measured using the buret is significantly different from 25 mL. Thus this graduated cylinder is not very accurate. It produces a systematic error (in this case, the indicated result is low for each measurement).

See Question 1.11.

1.5 Significant Figures and Calculations

Calculating the final result for an experiment usually involves adding, subtracting, multiplying, or dividing the results of various types of measurements. Since it is very important that the uncertainty in the final result is known correctly, we have developed rules for counting the significant figures in each number and for determining the correct number of significant figures in the final result.

Rules for Counting Significant Figures

1. *Nonzero integers.* Nonzero integers always count as significant figures.
2. *Zeros.* There are three classes of zeros:
 - a. *Leading zeros* are zeros that precede all the nonzero digits. These do not count as significant figures. In the number 0.0025, the three zeros simply indicate the position of the decimal point. This number has only two significant figures.
 - b. *Captive zeros* are zeros between nonzero digits. These always count as significant figures. The number 1.008 has four significant figures.
 - c. *Trailing zeros* are zeros at the right end of the number. They are significant only if the number contains a decimal point. The number 100 has only one significant figure, whereas the number 1.00×10^2 has three significant figures. The number one hundred written as 100. also has three significant figures.
3. *Exact numbers.* Many times calculations involve numbers that were not obtained using measuring devices but were determined by counting: 10 experiments, 3 apples, 8 molecules. Such numbers are called *exact numbers*. They can be assumed to have an infinite number of significant figures. Other examples of exact numbers are the 2 in $2\pi r$ (the circumference of a circle) and the 4 and the 3 in $\frac{4}{3}\pi r^3$ (the volume of a sphere). Exact numbers also can arise from definitions. For example, one inch is defined as exactly 2.54 centimeters. Thus, in the statement 1 in = 2.54 cm, neither the 2.54 nor the 1 limits the number of significant figures when used in a calculation.

Leading zeros are never significant figures.

Captive zeros are always significant figures.

Trailing zeros are sometimes significant figures.

Exact numbers never limit the number of significant figures in a calculation.

Exponential notation is reviewed in Appendix 1.1.

Note that the number 1.00×10^2 above is written in **exponential notation**. This type of notation has at least two advantages: the number of significant figures can be easily

indicated, and fewer zeros are needed to write a very large or very small number. For example, the number 0.000060 is much more conveniently represented as 6.0×10^{-5} . (The number has two significant figures.)

Sample Exercise 1.3**Significant Figures**

Give the number of significant figures for each of the following results.

- A student's extraction procedure on tea yields 0.0105 g of caffeine.
- A chemist records a mass of 0.050080 g in an analysis.
- In an experiment a span of time is determined to be 8.050×10^{-3} s.

Solution

- The number contains three significant figures. The zeros to the left of the 1 are leading zeros and are not significant, but the remaining zero (a captive zero) is significant.
- The number contains five significant figures. The leading zeros (to the left of the 5) are not significant. The captive zeros between the 5 and the 8 are significant, and the trailing zero to the right of the 8 is significant because the number contains a decimal point.
- This number has four significant figures. Both zeros are significant.

See Exercises 1.25 through 1.28.

To this point we have learned to count the significant figures in a given number. Next, we must consider how uncertainty accumulates as calculations are carried out. The detailed analysis of the accumulation of uncertainties depends on the type of calculation involved and can be complex. However, in this textbook we will employ the following simple rules that have been developed for determining the appropriate number of significant figures in the result of a calculation.

Rules for Significant Figures in Mathematical Operations*

- For multiplication or division*, the number of significant figures in the result is the same as the number in the least precise measurement used in the calculation. For example, consider the calculation

$$4.56 \times 1.4 = 6.38 \xrightarrow{\text{Corrected}} \begin{array}{r} 6.4 \\ \uparrow \\ \text{Limiting term has} \\ \text{two significant} \\ \text{figures} \end{array} \quad \begin{array}{r} 6.4 \\ \uparrow \\ \text{Two significant} \\ \text{figures} \end{array}$$

The product should have only two significant figures, since 1.4 has two significant figures.

- For addition or subtraction*, the result has the same number of decimal places as the least precise measurement used in the calculation. For example, consider the sum

$$\begin{array}{r} 12.11 \\ 18.0 \quad \leftarrow \text{Limiting term has one decimal place} \\ \hline 1.013 \\ \hline 31.123 \xrightarrow{\text{Corrected}} 31.1 \\ \uparrow \\ \text{One decimal place} \end{array}$$

The correct result is 31.1, since 18.0 has only one decimal place.

*Although these simple rules work well for most cases, they can give misleading results in certain cases. For more information, see L. M. Schwartz, "Propagation of Significant Figures," *J. Chem. Ed.* **62** (1985): 693; and H. Bradford Thompson, "Is 8°C equal to 50°F?" *J. Chem. Ed.* **68** (1991): 400.

Note that for multiplication and division, significant figures are counted. For addition and subtraction, the decimal places are counted.

In most calculations you will need to round numbers to obtain the correct number of significant figures. The following rules should be applied when rounding.

Rules for Rounding

1. In a series of calculations, carry the extra digits through to the final result, *then* round.
2. If the digit to be removed
 - a. is less than 5, the preceding digit stays the same. For example, 1.33 rounds to 1.3.
 - b. is equal to or greater than 5, the preceding digit is increased by 1. For example, 1.36 rounds to 1.4.

Rule 2 is consistent with the operation of electronic calculators.

Although rounding is generally straightforward, one point requires special emphasis. As an illustration, suppose that the number 4.348 needs to be rounded to two significant figures. In doing this, we look *only* at the *first number* to the right of the 3:

4.348
↑
Look at this number to
round to two significant figures.

Do not round sequentially. The number 6.8347 rounded to three significant figures is 6.83, not 6.84.

The number is rounded to 4.3 because 4 is less than 5. It is incorrect to round sequentially. For example, do *not* round the 4 to 5 to give 4.35 and then round the 3 to 4 to give 4.4.

When rounding, *use only the first number to the right of the last significant figure.*

It is important to note that Rule 1 above usually will not be followed in the Sample Exercises in this text because we want to show the correct number of significant figures in *each step* of a problem. This same practice is followed for the detailed solutions given in the *Solutions Guide*. However, as stated in Rule 1, the best procedure is to carry extra digits throughout a series of calculations and round to the correct number of significant figures only at the end. This is the practice you should follow. The fact that your rounding procedures are different from those used in this text must be taken into account when you check your answer with the one given at the end of the book or in the *Solutions Guide*. Your answer (based on rounding only at the end of a calculation) may differ in the last place from that given here as the “correct” answer because we have rounded after each step. To help you understand the difference between these rounding procedures, we will consider them further in Sample Exercise 1.4.

Sample Exercise 1.4

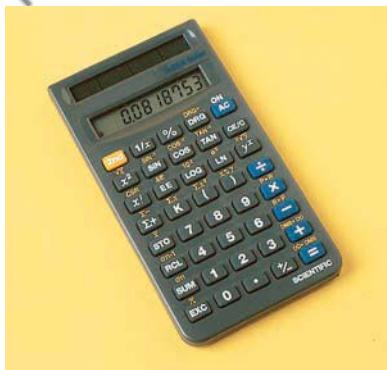
Significant Figures in Mathematical Operations

Carry out the following mathematical operations, and give each result with the correct number of significant figures.

- a. $1.05 \times 10^{-3} \div 6.135$
- b. $21 - 13.8$
- c. As part of a lab assignment to determine the value of the gas constant (R), a student measured the pressure (P), volume (V), and temperature (T) for a sample of gas, where

$$R = \frac{PV}{T}$$

The following values were obtained: $P = 2.560$, $T = 275.15$, and $V = 8.8$. (Gases will be discussed in detail in Chapter 5; we will not be concerned at this time about the units for these quantities.) Calculate R to the correct number of significant figures.



This number must be rounded to two significant figures.

Solution

- The result is 1.71×10^{-4} , which has three significant figures because the term with the least precision (1.05×10^{-3}) has three significant figures.
- The result is 7 with no decimal point because the number with the least number of decimal places (21) has none.

c.
$$R = \frac{PV}{T} = \frac{(2.560)(8.8)}{275.15}$$

The correct procedure for obtaining the final result can be represented as follows:

$$\begin{aligned} \frac{(2.560)(8.8)}{275.15} &= \frac{22.528}{275.15} = 0.0818753 \\ &= 0.082 = 8.2 \times 10^{-2} = R \end{aligned}$$

The final result must be rounded to two significant figures because 8.8 (the least precise measurement) has two significant figures. To show the effects of rounding at intermediate steps, we will carry out the calculation as follows:

$$\begin{array}{c} \text{Rounded to two} \\ \text{significant figures} \\ \downarrow \\ \frac{(2.560)(8.8)}{275.15} = \frac{22.528}{275.15} = \frac{23}{275.15} \end{array}$$

Now we proceed with the next calculation:

$$\frac{23}{275.15} = 0.0835908$$

Rounded to two significant figures, this result is

$$0.084 = 8.4 \times 10^{-2}$$

Note that intermediate rounding gives a significantly different result than was obtained by rounding only at the end. Again, we must reemphasize that in *your* calculations you should round *only at the end*. However, because rounding is carried out at intermediate steps in this text (to always show the correct number of significant figures), the final answer given in the text may differ slightly from the one you obtain (rounding only at the end).

See Exercises 1.31 through 1.34.

There is a useful lesson to be learned from part c of Sample Exercise 1.4. The student measured the pressure and temperature to greater precision than the volume. A more precise value of R (one with more significant figures) could have been obtained if a more precise measurement of V had been made. As it is, the efforts expended to measure P and T very precisely were wasted. Remember that a series of measurements to obtain some final result should all be done to about the same precision.

TABLE 1.4 English–Metric Equivalents

Length	1 m = 1.094 yd 2.54 cm = 1 in
Mass	1 kg = 2.205 lb 453.6 g = 1 lb
Volume	1 L = 1.06 qt 1 ft ³ = 28.32 L

1.6 Dimensional Analysis

It is often necessary to convert a given result from one system of units to another. The best way to do this is by a method called the **unit factor method**, or more commonly **dimensional analysis**. To illustrate the use of this method, we will consider several unit conversions. Some equivalents in the English and metric systems are listed in Table 1.4. A more complete list of conversion factors given to more significant figures appears in Appendix 6.

Consider a pin measuring 2.85 centimeters in length. What is its length in inches? To accomplish this conversion, we must use the equivalence statement

$$2.54 \text{ cm} = 1 \text{ in}$$

If we divide both sides of this equation by 2.54 centimeters, we get

$$1 = \frac{1 \text{ in}}{2.54 \text{ cm}}$$

This expression is called a *unit factor*. Since 1 inch and 2.54 centimeters are exactly equivalent, multiplying any expression by this unit factor will not change its *value*.

The pin has a length of 2.85 centimeters. Multiplying this length by the appropriate unit factor gives

$$2.85 \text{ cm} \times \frac{1 \text{ in}}{2.54 \text{ cm}} = \frac{2.85}{2.54} \text{ in} = 1.12 \text{ in}$$

Note that the centimeter units cancel to give inches for the result. This is exactly what we wanted to accomplish. Note also that the result has three significant figures, as required by the number 2.85. Recall that the 1 and 2.54 in the conversion factor are exact numbers by definition.

Sample Exercise 1.5

Unit Conversions I

A pencil is 7.00 in long. What is its length in centimeters?

Solution

In this case we want to convert from inches to centimeters. Therefore, we must use the reciprocal of the unit factor used above to do the opposite conversion:

$$7.00 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = (7.00)(2.54) \text{ cm} = 17.8 \text{ cm}$$

Here the inch units cancel, leaving centimeters, as requested.

See Exercises 1.37 and 1.38.

Note that two unit factors can be derived from each equivalence statement. For example, from the equivalence statement $2.54 \text{ cm} = 1 \text{ in}$, the two unit factors are

$$\frac{2.54 \text{ cm}}{1 \text{ in}} \quad \text{and} \quad \frac{1 \text{ in}}{2.54 \text{ cm}}$$

Consider the direction of the required change to select the correct unit factor.

How do you choose which one to use in a given situation? Simply look at the *direction* of the required change. To change from inches to centimeters, the inches must cancel. Thus the factor $2.54 \text{ cm}/1 \text{ in}$ is used. To change from centimeters to inches, centimeters must cancel, and the factor $1 \text{ in}/2.54 \text{ cm}$ is appropriate.

Converting from One Unit to Another

- To convert from one unit to another, use the equivalence statement that relates the two units.
- Derive the appropriate unit factor by looking at the direction of the required change (to cancel the unwanted units).
- Multiply the quantity to be converted by the unit factor to give the quantity with the desired units.

Sample Exercise 1.6**Unit Conversions II**

You want to order a bicycle with a 25.5-in frame, but the sizes in the catalog are given only in centimeters. What size should you order?

Solution

You need to go from inches to centimeters, so $2.54 \text{ cm} = 1 \text{ in}$ is appropriate:

$$25.5 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = 64.8 \text{ cm}$$

See Exercises 1.37 and 1.38.

To ensure that the conversion procedure is clear, a multistep problem is considered in Sample Exercise 1.7.

Sample Exercise 1.7**Unit Conversions III**

A student has entered a 10.0-km run. How long is the run in miles?

Solution

This conversion can be accomplished in several different ways. Since we have the equivalence statement $1 \text{ m} = 1.094 \text{ yd}$, we will proceed by a path that uses this fact. Before we start any calculations, let us consider our strategy. We have kilometers, which we want to change to miles. We can do this by the following route:

kilometers \longrightarrow meters \longrightarrow yards \longrightarrow miles

To proceed in this way, we need the following equivalence statements:

$$1 \text{ km} = 1000 \text{ m}$$

$$1 \text{ m} = 1.094 \text{ yd}$$

$$1760 \text{ yd} = 1 \text{ mi}$$

To make sure the process is clear, we will proceed step by step:

Kilometers to Meters:

$$10.0 \text{ km} \times \frac{1000 \text{ m}}{1 \text{ km}} = 1.00 \times 10^4 \text{ m}$$

Meters to Yards:

$$1.00 \times 10^4 \text{ m} \times \frac{1.094 \text{ yd}}{1 \text{ m}} = 1.094 \times 10^4 \text{ yd}$$

Note that we should have only three significant figures in the result. Since this is an intermediate result, however, we will carry the extra digit. Remember, round off only the final result.

Yards to Miles:

$$1.094 \times 10^4 \text{ yd} \times \frac{1 \text{ mi}}{1760 \text{ yd}} = 6.216 \text{ mi}$$

Note in this case that $1 \text{ mi} = 1760 \text{ yd}$ by designation. Thus 1760 is an exact number.

Since the distance was originally given as 10.0 km, the result can have only three significant figures and should be rounded to 6.22 mi. Thus

$$10.0 \text{ km} = 6.22 \text{ mi}$$

Sample Exercise 1.6**Unit Conversions II**

You want to order a bicycle with a 25.5-in frame, but the sizes in the catalog are given only in centimeters. What size should you order?

Solution

You need to go from inches to centimeters, so $2.54 \text{ cm} = 1 \text{ in}$ is appropriate:

$$25.5 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = 64.8 \text{ cm}$$

See Exercises 1.37 and 1.38.

To ensure that the conversion procedure is clear, a multistep problem is considered in Sample Exercise 1.7.

Sample Exercise 1.7**Unit Conversions III**

A student has entered a 10.0-km run. How long is the run in miles?

Solution

This conversion can be accomplished in several different ways. Since we have the equivalence statement $1 \text{ m} = 1.094 \text{ yd}$, we will proceed by a path that uses this fact. Before we start any calculations, let us consider our strategy. We have kilometers, which we want to change to miles. We can do this by the following route:

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To proceed in this way, we need the following equivalence statements:

$$1 \text{ km} = 1000 \text{ m}$$

$$1 \text{ m} = 1.094 \text{ yd}$$

$$1760 \text{ yd} = 1 \text{ mi}$$

To make sure the process is clear, we will proceed step by step:

Kilometers to Meters:

$$10.0 \text{ km} \times \frac{1000 \text{ m}}{1 \text{ km}} = 1.00 \times 10^4 \text{ m}$$

Meters to Yards:

$$1.00 \times 10^4 \text{ m} \times \frac{1.094 \text{ yd}}{1 \text{ m}} = 1.094 \times 10^4 \text{ yd}$$

Note that we should have only three significant figures in the result. Since this is an intermediate result, however, we will carry the extra digit. Remember, round off only the final result.

Yards to Miles:

$$1.094 \times 10^4 \text{ yd} \times \frac{1 \text{ mi}}{1760 \text{ yd}} = 6.216 \text{ mi}$$

Note in this case that $1 \text{ mi} = 1760 \text{ yd}$ by designation. Thus 1760 is an exact number.

Since the distance was originally given as 10.0 km, the result can have only three significant figures and should be rounded to 6.22 mi. Thus

$$10.0 \text{ km} = 6.22 \text{ mi}$$

Sample Exercise 1.6**Unit Conversions II**

You want to order a bicycle with a 25.5-in frame, but the sizes in the catalog are given only in centimeters. What size should you order?

Solution

You need to go from inches to centimeters, so $2.54 \text{ cm} = 1 \text{ in}$ is appropriate:

$$25.5 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = 64.8 \text{ cm}$$

See Exercises 1.37 and 1.38.

To ensure that the conversion procedure is clear, a multistep problem is considered in Sample Exercise 1.7.

Sample Exercise 1.7**Unit Conversions III**

A student has entered a 10.0-km run. How long is the run in miles?

Solution

This conversion can be accomplished in several different ways. Since we have the equivalence statement $1 \text{ m} = 1.094 \text{ yd}$, we will proceed by a path that uses this fact. Before we start any calculations, let us consider our strategy. We have kilometers, which we want to change to miles. We can do this by the following route:

kilometers \longrightarrow meters \longrightarrow yards \longrightarrow miles

To proceed in this way, we need the following equivalence statements:

$$1 \text{ km} = 1000 \text{ m}$$

$$1 \text{ m} = 1.094 \text{ yd}$$

$$1760 \text{ yd} = 1 \text{ mi}$$

To make sure the process is clear, we will proceed step by step:

Kilometers to Meters:

$$10.0 \text{ km} \times \frac{1000 \text{ m}}{1 \text{ km}} = 1.00 \times 10^4 \text{ m}$$

Meters to Yards:

$$1.00 \times 10^4 \text{ m} \times \frac{1.094 \text{ yd}}{1 \text{ m}} = 1.094 \times 10^4 \text{ yd}$$

Note that we should have only three significant figures in the result. Since this is an intermediate result, however, we will carry the extra digit. Remember, round off only the final result.

Yards to Miles:

$$1.094 \times 10^4 \text{ yd} \times \frac{1 \text{ mi}}{1760 \text{ yd}} = 6.216 \text{ mi}$$

Note in this case that $1 \text{ mi} = 1760 \text{ yd}$ by designation. Thus 1760 is an exact number.

Since the distance was originally given as 10.0 km, the result can have only three significant figures and should be rounded to 6.22 mi. Thus

$$10.0 \text{ km} = 6.22 \text{ mi}$$

Alternatively, we can combine the steps:

$$10.0 \text{ km} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1.094 \text{ yd}}{1 \text{ m}} \times \frac{1 \text{ mi}}{1760 \text{ yd}} = 6.22 \text{ mi}$$

See Exercises 1.37 and 1.38.

In using dimensional analysis, your verification that everything has been done correctly is that you end up with the correct units. *In doing chemistry problems, you should always include the units for the quantities used.* Always check to see that the units cancel to give the correct units for the final result. This provides a very valuable check, especially for complicated problems.

Study the procedures for unit conversions in the following Sample Exercises.

Sample Exercise 1.8

Unit Conversion IV

The speed limit on many highways in the United States is 55 mi/h. What number would be posted in kilometers per hour?

Solution

Result obtained by rounding only at the end of the calculation

$$\frac{55 \text{ mi}}{\text{h}} \times \frac{1760 \text{ yd}}{1 \text{ mi}} \times \frac{1 \text{ m}}{1.094 \text{ yd}} \times \frac{1 \text{ km}}{1000 \text{ m}} = 88 \text{ km/h}$$

Note that all units cancel except the desired kilometers per hour.

See Exercises 1.43 through 1.45.

Sample Exercise 1.9

Unit Conversions V

A Japanese car is advertised as having a gas mileage of 15 km/L. Convert this rating to miles per gallon.

Solution

Result obtained by rounding only at the end of the calculation

$$\frac{15 \text{ km}}{\text{L}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1.094 \text{ yd}}{1 \text{ m}} \times \frac{1 \text{ mi}}{1760 \text{ yd}} \times \frac{1 \text{ L}}{1.06 \text{ qt}} \times \frac{4 \text{ qt}}{1 \text{ gal}} = 35 \text{ mi/gal}$$

See Exercise 1.46.

1.7 Temperature

Three systems for measuring temperature are widely used: the Celsius scale, the Kelvin scale, and the Fahrenheit scale. The first two temperature systems are used in the physical sciences, and the third is used in many of the engineering sciences. Our purpose here is to define the three temperature scales and show how conversions from one scale to another can be performed. Although these conversions can be carried out routinely on most calculators, we will consider the process in some detail here to illustrate methods of problem solving.

The three temperature scales are defined and compared in Fig. 1.11. Note that the size of the temperature unit (the *degree*) is the same for the Kelvin and Celsius scales.

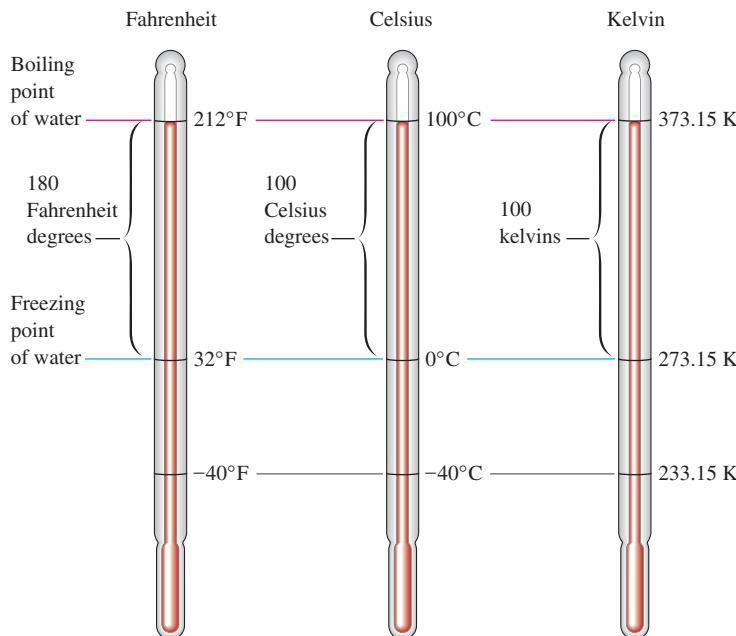


FIGURE 1.11
The three major temperature scales.

The fundamental difference between these two temperature scales is in their zero points. Conversion between these two scales simply requires an adjustment for the different zero points.

$$T_K = T_C + 273.15$$

$$\text{Temperature (Kelvin)} = \text{temperature (Celsius)} + 273.15$$

or

$$T_C = T_K - 273.15$$

$$\text{Temperature (Celsius)} = \text{temperature (Kelvin)} - 273.15$$

For example, to convert 300.00 K to the Celsius scale, we do the following calculation:

$$300.00 - 273.15 = 26.85^\circ\text{C}$$

Note that in expressing temperature in Celsius units, the designation ${}^\circ\text{C}$ is used. The degree symbol is not used when writing temperature in terms of the Kelvin scale. The unit of temperature on this scale is called a *kelvin* and is symbolized by the letter K.

Converting between the Fahrenheit and Celsius scales is somewhat more complicated because both the degree sizes and the zero points are different. Thus we need to consider two adjustments: one for degree size and one for the zero point. First, we must account for the difference in degree size. This can be done by reconsidering Fig. 1.11. Notice that since $212^\circ\text{F} = 100^\circ\text{C}$ and $32^\circ\text{F} = 0^\circ\text{C}$,

$$212 - 32 = 180 \text{ Fahrenheit degrees} = 100 - 0 = 100 \text{ Celsius degrees}$$

Thus 180° on the Fahrenheit scale is equivalent to 100° on the Celsius scale, and the unit factor is

$$\frac{180^\circ\text{F}}{100^\circ\text{C}} \quad \text{or} \quad \frac{9^\circ\text{F}}{5^\circ\text{C}}$$

or the reciprocal, depending on the direction in which we need to go.

Next, we must consider the different zero points. Since $32^\circ\text{F} = 0^\circ\text{C}$, we obtain the corresponding Celsius temperature by first subtracting 32 from the Fahrenheit temperature

to account for the different zero points. Then the unit factor is applied to adjust for the difference in the degree size. This process is summarized by the equation

$$(T_F - 32^\circ\text{F}) \frac{5^\circ\text{C}}{9^\circ\text{F}} = T_C \quad (1.1)$$

where T_F and T_C represent a given temperature on the Fahrenheit and Celsius scales, respectively. In the opposite conversion, we first correct for degree size and then correct for the different zero point. This process can be summarized in the following general equation:

$$T_F = T_C \times \frac{9^\circ\text{F}}{5^\circ\text{C}} + 32^\circ\text{F} \quad (1.2)$$

Equations (1.1) and (1.2) are really the same equation in different forms. See if you can obtain Equation (1.2) by starting with Equation (1.1) and rearranging.

At this point it is worthwhile to weigh the two alternatives for learning to do temperature conversions: You can simply memorize the equations, or you can take the time to learn the differences between the temperature scales and to understand the processes involved in converting from one scale to another. The latter approach may take a little more effort, but the understanding you gain will stick with you much longer than the memorized formulas. This choice also will apply to many of the other chemical concepts. Try to think things through!

Sample Exercise 1.10

Temperature Conversions I

Normal body temperature is 98.6°F . Convert this temperature to the Celsius and Kelvin scales.

Solution

Rather than simply using the formulas to solve this problem, we will proceed by thinking it through. The situation is diagramed in Fig. 1.12. First, we want to convert 98.6°F to the Celsius scale. The number of Fahrenheit degrees between 32.0°F and 98.6°F is 66.6°F . We must convert this difference to Celsius degrees:

$$66.6^\circ\text{F} \times \frac{5^\circ\text{C}}{9^\circ\text{F}} = 37.0^\circ\text{C}$$



A physician taking the temperature of a patient.

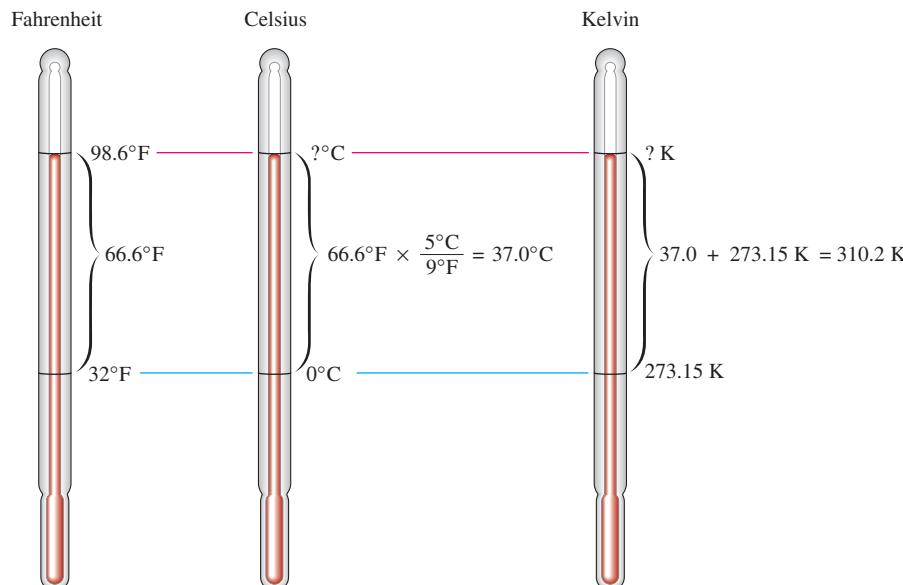


FIGURE 1.12

Normal body temperature on the Fahrenheit, Celsius, and Kelvin scales.



CHEMICAL IMPACT

Faux Snow

Skiing is challenging and fun, but it is also big business. Both skiers and ski operators want the season to last as long as possible. The major factor in maximizing the length of the ski season and in salvaging dry periods during the winter is the ability to “make snow.” Machine-made snow is now a required part of maintaining ideal conditions at major ski areas such as Aspen, Breckenridge, and Taos.

Snow is relatively easy to make if the air is cold enough. To manufacture snow, water is cooled to just above 0°C and then pumped at high pressure through a “gun” that produces a fine mist of water droplets that freeze before dropping to the ground. As might be expected, atmospheric conditions are critical when making snow. With an air temperature of -8°C (18°F) or less, untreated water can be used in the snow guns. However, the ideal type of snow for skiing is “powder”—fluffy snow made up of small, individual crystals. To achieve powdery snow requires sufficient nucleation

sites—that is, sites where crystal growth is initiated. This condition can be achieved by “doping” the water with ions such as calcium or magnesium or with fine particles of clay. Also, when the air temperature is between 0°C and -8°C , materials such as silver iodide, detergents, and organic materials may be added to the water to seed the snow.

A discovery at the University of Wisconsin in the 1970s led to the additive most commonly used for snow making. The Wisconsin scientists found that a bacterium (*Pseudomonas syringae*) commonly found in nature makes a protein that acts as a very effective nucleation site for ice formation. In fact, this discovery helped to explain why ice forms at 0°C on the blossoms of fruit trees instead of the water supercooling below 0°C , as pure water does when the temperature is lowered slowly below the freezing point. To help protect fruit blossoms from freeze damage, this bacterium has been genetically modified to remove the ice nucleation protein. As a result, fruit blossoms can survive

Thus 98.6°F corresponds to 37.0°C .

Now we can convert to the Kelvin scale:

$$T_{\text{K}} = T_{\text{C}} + 273.15 = 37.0 + 273.15 = 310.2 \text{ K}$$

Note that the final answer has only one decimal place (37.0 is limiting).

See Exercises 1.49, 1.51, and 1.52.

Sample Exercise 1.11

Temperature Conversions II

One interesting feature of the Celsius and Fahrenheit scales is that -40°C and -40°F represent the same temperature, as shown in Fig. 1.11. Verify that this is true.

Solution

The difference between 32°F and -40°F is 72°F . The difference between 0°C and -40°C is 40°C . The ratio of these is

$$\frac{72^{\circ}\text{F}}{40^{\circ}\text{C}} = \frac{8 \times 9^{\circ}\text{F}}{8 \times 5^{\circ}\text{C}} = \frac{9^{\circ}\text{F}}{5^{\circ}\text{C}}$$

as required. Thus -40°C is equivalent to -40°F .

See Challenge Problem 1.86.

Since, as shown in Sample Exercise 1.11, -40° on both the Fahrenheit and Celsius scales represents the same temperature, this point can be used as a reference point (like 0°C and 32°F) for a relationship between the two scales:

$$\frac{\text{Number of Fahrenheit degrees}}{\text{Number of Celsius degrees}} = \frac{T_{\text{F}} - (-40)}{T_{\text{C}} - (-40)} = \frac{9^{\circ}\text{F}}{5^{\circ}\text{C}}$$

intact even if the temperature briefly falls below 0°C. (See the Chemical Impact on Organisms and Ice Formation on page 516.) For snow-making purposes, this protein forms the basis for Snowmax (prepared and sold by York Snow of Victor, New York), which is the most popular additive for snow making.

Obviously, snow cannot be made in the summer, so what is a skiing fanatic to do during the warm months? The answer is “dryslope” skiing. Although materials for dryslopes can be manufactured in a variety of ways, polymers are most commonly used for this application. One company that makes a multilayer polymer for artificial ski slopes is Briton Engineering Developments (Yorkshire, England), the producer of Snowflex. Snowflex consists of a slippery polymer fiber placed on top of a shock-absorbing base and lubricated by misting water through holes in its surface. Of course, this virtual skiing is not much like the real thing but it does provide some relief for summer ski withdrawal.

As artificial and synthetic snow amply demonstrate, chemistry makes life more fun.



A freestyle ski area at Sheffield Ski Village, in England, uses Snowflex “virtual snow” for year-round fun.

$$\text{or} \quad \frac{T_F + 40}{T_C + 40} = \frac{9^\circ\text{F}}{5^\circ\text{C}} \quad (1.3)$$

where T_F and T_C represent the same temperature (but not the same number). This equation can be used to convert Fahrenheit temperatures to Celsius, and vice versa, and may be easier to remember than Equations (1.1) and (1.2).

Sample Exercise 1.12

Temperature Conversions III

Liquid nitrogen, which is often used as a coolant for low-temperature experiments, has a boiling point of 77 K. What is this temperature on the Fahrenheit scale?

Solution

We will first convert 77 K to the Celsius scale:

$$T_C = T_K - 273.15 = 77 - 273.15 = -196^\circ\text{C}$$

To convert to the Fahrenheit scale, we will use Equation (1.3):

$$\begin{aligned} \frac{T_F + 40}{T_C + 40} &= \frac{9^\circ\text{F}}{5^\circ\text{C}} \\ \frac{T_F + 40}{-196^\circ\text{C} + 40} &= \frac{T_F + 40}{-156^\circ\text{C}} = \frac{9^\circ\text{F}}{5^\circ\text{C}} \\ T_F + 40 &= \frac{9^\circ\text{F}}{5^\circ\text{C}}(-156^\circ\text{C}) = -281^\circ\text{F} \\ T_F &= -281^\circ\text{F} - 40 = -321^\circ\text{F} \end{aligned}$$



Liquid nitrogen is so cold that water condenses out of the surrounding air, forming a cloud as the nitrogen is poured.

See Exercises 1.49, 1.51, and 1.52.

1.8 Density

A property of matter that is often used by chemists as an “identification tag” for a substance is **density**, the mass of substance per unit volume of the substance:

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

The density of a liquid can be determined easily by weighing an accurately known volume of liquid. This procedure is illustrated in Sample Exercise 1.13.

Sample Exercise 1.13

Determining Density

A chemist, trying to identify the main component of a compact disc cleaning fluid, finds that 25.00 cm^3 of the substance has a mass of 19.625 g at 20°C . The following are the names and densities of the compounds that might be the main component:

Compound	Density in g/cm^3 at 20°C
Chloroform	1.492
Diethyl ether	0.714
Ethanol	0.789
Isopropyl alcohol	0.785
Toluene	0.867

Which of these compounds is the most likely to be the main component of the compact disc cleaner?

Solution

To identify the unknown substance, we must determine its density. This can be done by using the definition of density:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{19.625\text{ g}}{25.00\text{ cm}^3} = 0.7850\text{ g}/\text{cm}^3$$

This density corresponds exactly to that of isopropyl alcohol, which is therefore the most likely main component of the cleaner. However, note that the density of ethanol is also very close. To be sure that the compound is isopropyl alcohol, we should run several more density experiments. (In the modern laboratory, many other types of tests could be done to distinguish between these two liquids.)

See Exercises 1.55 and 1.56.

Besides being a tool for the identification of substances, density has many other uses. For example, the liquid in your car’s lead storage battery (a solution of sulfuric acid) changes density because the sulfuric acid is consumed as the battery discharges. In a fully charged battery, the density of the solution is about $1.30\text{ g}/\text{cm}^3$. If the density falls below $1.20\text{ g}/\text{cm}^3$, the battery will have to be recharged. Density measurement is also used to determine the amount of antifreeze, and thus the level of protection against freezing, in the cooling system of a car.

The densities of various common substances are given in Table 1.5.

TABLE 1.5 Densities of Various Common Substances* at 20°C

Substance	Physical State	Density (g/cm ³)
Oxygen	Gas	0.00133
Hydrogen	Gas	0.000084
Ethanol	Liquid	0.789
Benzene	Liquid	0.880
Water	Liquid	0.9982
Magnesium	Solid	1.74
Salt (sodium chloride)	Solid	2.16
Aluminum	Solid	2.70
Iron	Solid	7.87
Copper	Solid	8.96
Silver	Solid	10.5
Lead	Solid	11.34
Mercury	Liquid	13.6
Gold	Solid	19.32

*At 1 atmosphere pressure

1.9 Classification of Matter

Before we can hope to understand the changes we see going on around us—the growth of plants, the rusting of steel, the aging of people, rain becoming more acidic—we must find out how matter is organized. **Matter**, best defined as anything occupying space and having mass, is the material of the universe. Matter is complex and has many levels of organization. In this section we introduce basic ideas about the structure of matter and its behavior.

We will start by considering the definitions of the fundamental properties of matter. Matter exists in three **states**: solid, liquid, and gas. A *solid* is rigid; it has a fixed volume and shape. A *liquid* has a definite volume but no specific shape; it assumes the shape of its container. A *gas* has no fixed volume or shape; it takes on the shape and volume of its container. In contrast to liquids and solids, which are only slightly compressible, gases are highly compressible; it is relatively easy to decrease the volume of a gas. Molecular-level pictures of the three states of water are given in Fig. 1.13. The different properties of ice, liquid water, and steam are determined by the different arrangements of the molecules in these substances. Table 1.5 gives the states of some common substances at 20°C and 1 atmosphere of pressure.

Most of the matter around us consists of **mixtures** of pure substances. Wood, gasoline, wine, soil, and air are all mixtures. The main characteristic of a mixture is that it has *variable composition*. For example, wood is a mixture of many substances, the proportions of which vary depending on the type of wood and where it grows. Mixtures can be classified as **homogeneous** (having visibly indistinguishable parts) or **heterogeneous** (having visibly distinguishable parts).

A homogeneous mixture is called a **solution**. Air is a solution consisting of a mixture of gases. Wine is a complex liquid solution. Brass is a solid solution of copper and zinc. Sand in water and iced tea with ice cubes are examples of heterogeneous mixtures. Heterogeneous mixtures usually can be separated into two or more homogeneous mixtures or pure substances (for example, the ice cubes can be separated from the tea).

Mixtures can be separated into pure substances by physical methods. A **pure substance** is one with constant composition. Water is a good illustration of these ideas. As we will discuss in detail later, pure water is composed solely of H₂O molecules,



Visualizations:
Structure of a Gas
Structure of a Liquid
Structure of a Solid



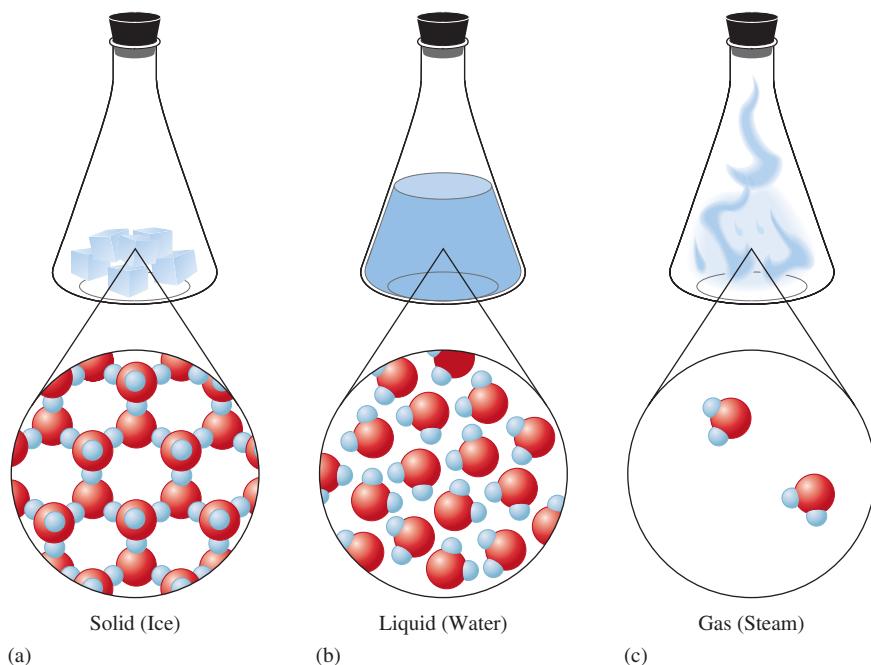
Visualization: Comparison of a Compound and a Mixture



Visualization: Comparison of a Solution and a Mixture



Visualization: Homogeneous Mixtures: Air and Brass

**FIGURE 1.13**

The three states of water (where red spheres represent oxygen atoms and blue spheres represent hydrogen atoms). (a) Solid: the water molecules are locked into rigid positions and are close together. (b) Liquid: the water molecules are still close together but can move around to some extent. (c) Gas: the water molecules are far apart and move randomly.

but the water found in nature (groundwater or the water in a lake or ocean) is really a mixture. Seawater, for example, contains large amounts of dissolved minerals. Boiling seawater produces steam, which can be condensed to pure water, leaving the minerals behind as solids. The dissolved minerals in seawater also can be separated out by freezing the mixture, since pure water freezes out. The processes of boiling and freezing are **physical changes**: When water freezes or boils, it changes its state but remains water; it is still composed of H_2O molecules. A physical change is a change in the form of a substance, not in its chemical composition. A physical change can be used to separate a mixture into pure compounds, but it will not break compounds into elements.

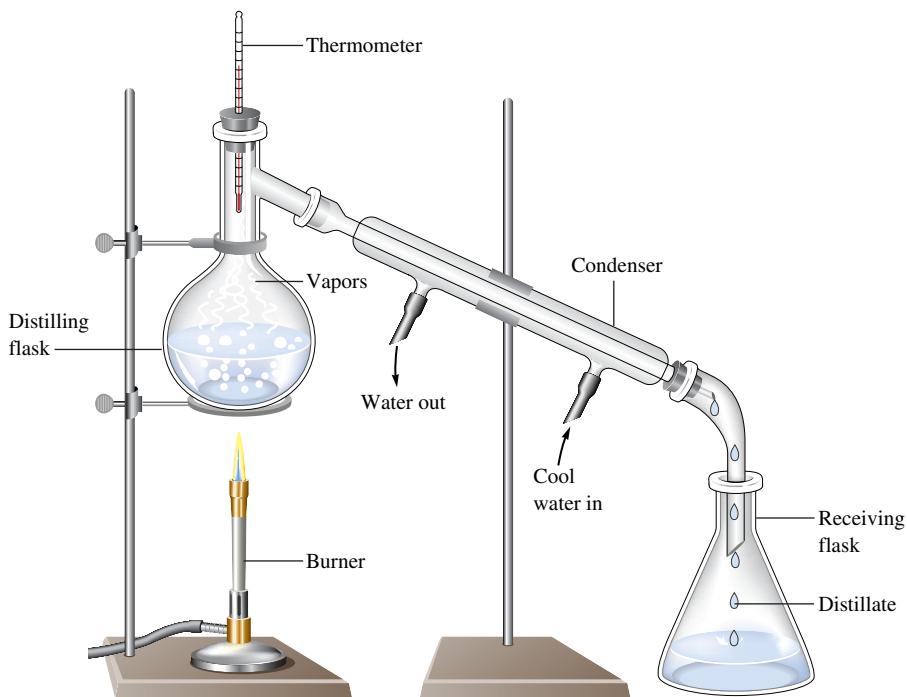
One of the most important methods for separating the components of a mixture is **distillation**, a process that depends on differences in the volatility (how readily substances become gases) of the components. In simple distillation, a mixture is heated in a device such as that shown in Fig. 1.14. The most volatile component vaporizes at the lowest temperature, and the vapor passes through a cooled tube (a condenser), where it condenses back into its liquid state.

The simple, one-stage distillation apparatus shown in Fig. 1.14 works very well when only one component of the mixture is volatile. For example, a mixture of water and sand is easily separated by boiling off the water. Water containing dissolved minerals behaves in much the same way. As the water is boiled off, the minerals remain behind as nonvolatile solids. Simple distillation of seawater using the sun as the heat source is an excellent way to desalinate (remove the minerals from) seawater.

However, when a mixture contains several volatile components, the one-step distillation does not give a pure substance in the receiving flask, and more elaborate methods are required.

Another method of separation is simple **filtration**, which is used when a mixture consists of a solid and a liquid. The mixture is poured onto a mesh, such as filter paper, which passes the liquid and leaves the solid behind.

The term **volatile** refers to the ease with which a substance can be changed to its vapor.

**FIGURE 1.14**

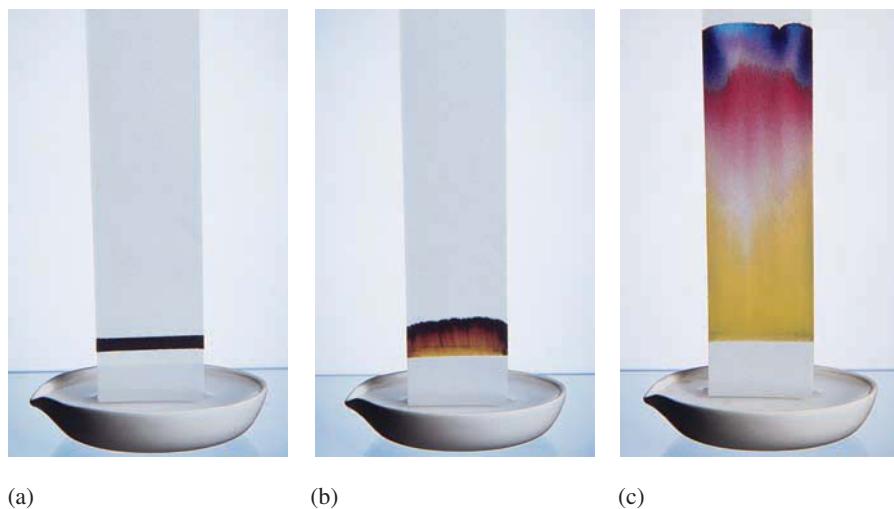
Simple laboratory distillation apparatus. Cool water circulates through the outer portion of the condenser, causing vapors from the distilling flask to condense into a liquid. The nonvolatile component of the mixture remains in the distilling flask.

A third method of separation is called **chromatography**. Chromatography is the general name applied to a series of methods that employ a system with two *phases* (states) of matter: a mobile phase and a stationary phase. The *stationary phase* is a solid, and the *mobile phase* is either a liquid or a gas. The separation process occurs because the components of the mixture have different affinities for the two phases and thus move through the system at different rates. A component with a high affinity for the mobile phase moves relatively quickly through the chromatographic system, whereas one with a high affinity for the solid phase moves more slowly.

One simple type of chromatography, **paper chromatography**, employs a strip of porous paper, such as filter paper, for the stationary phase. A drop of the mixture to be separated is placed on the paper, which is then dipped into a liquid (the mobile phase) that travels up the paper as though it were a wick (see Fig. 1.15). This method of separating a mixture is often used by biochemists, who study the chemistry of living systems.

It should be noted that when a mixture is separated, the absolute purity of the separated components is an ideal. Because water, for example, inevitably comes into contact with other materials when it is synthesized or separated from a mixture, it is never absolutely pure. With great care, however, substances can be obtained in very nearly pure form.

Pure substances contain compounds (combinations of elements) or free elements. A **compound** is a substance with *constant composition* that can be broken down into elements by chemical processes. An example of a chemical process is the electrolysis of water, in which an electric current is passed through water to break it down into the free elements hydrogen and oxygen. This process produces a chemical change because the water molecules have been broken down. The water is gone, and in its place we have the free elements hydrogen and oxygen. A **chemical change** is one in which a given substance becomes a new substance or substances with different properties and different

**FIGURE 1.15**

Paper chromatography of ink. (a) A line of the mixture to be separated is placed at one end of a sheet of porous paper. (b) The paper acts as a wick to draw up the liquid. (c) The component with the weakest attraction for the paper travels faster than the components that cling to the paper.



The element mercury (top left) combines with the element iodine (top right) to form the compound mercuric iodide (bottom). This is an example of a chemical change.

composition. **Elements** are substances that cannot be decomposed into simpler substances by chemical or physical means.

We have seen that the matter around us has various levels of organization. The most fundamental substances we have discussed so far are elements. As we will see in later chapters, elements also have structure: They are composed of atoms, which in turn are composed of nuclei and electrons. Even the nucleus has structure: It is composed of protons and neutrons. And even these can be broken down further, into elementary particles called *quarks*. However, we need not concern ourselves with such details at this point. Figure 1.16 summarizes our discussion of the organization of matter.

FIGURE 1.16

The organization of matter.

Key Terms

Section 1.2

scientific method
measurement
hypothesis
theory
model
natural law
law of conservation of mass

Section 1.3

SI system
mass
weight

Section 1.4

uncertainty
significant figures
accuracy
precision
random error
systematic error

Section 1.5

exponential notation

Section 1.6

unit factor method
dimensional analysis

Section 1.8

density

Section 1.9

matter
states (of matter)
homogeneous mixture
heterogeneous mixture
solution
pure substance
physical change
distillation
filtration
chromatography
paper chromatography
compound
chemical change
element

For Review

Scientific method

- Make observations
- Formulate hypotheses
- Perform experiments

Models (theories) are explanation of why nature behaves in a particular way.

- They are subject to modification over time and sometimes fail.

Quantitative observations are called measurements.

- Consist of a number and a unit
- Involve some uncertainty
- Uncertainty is indicated by using significant figures
 - Rules to determine significant figures
 - Calculations using significant figures
- Preferred system is SI

Temperature conversions

- $T_K = T_C + 273$
- $T_C = (T_F - 32^\circ\text{F}) \left(\frac{5^\circ\text{C}}{9^\circ\text{F}} \right)$
- $T_F = T_C \left(\frac{5^\circ\text{F}}{9^\circ\text{C}} \right) + 32^\circ\text{F}$

Density

- Density = $\frac{\text{mass}}{\text{volume}}$

Matter can exist in three states:

- Solid
- Liquid
- Gas

Mixtures can be separated by methods involving only physical changes:

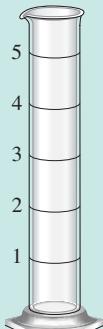
- Distillation
- Filtration
- Chromatography

Compounds can be decomposed to elements only through chemical changes.

REVIEW QUESTIONS

1. Define and explain the differences between the following terms.
 - a. law and theory
 - b. theory and experiment
 - c. qualitative and quantitative
 - d. hypothesis and theory
2. Is the scientific method suitable for solving problems only in the sciences? Explain.
3. Which of the following statements (hypotheses) could be tested by quantitative measurement?
 - a. Ty Cobb was a better hitter than Pete Rose.
 - b. Ivory soap is $99\frac{44}{100}\%$ pure.
 - c. Rolaids consumes 47 times its weight in excess stomach acid.

4. For each of the following pieces of glassware, provide a sample measurement and discuss the number of significant figures and uncertainty.



a.



b.



c.

5. A student performed an analysis of a sample for its calcium content and got the following results:

14.92% 14.91% 14.88% 14.91%

The actual amount of calcium in the sample is 15.70%. What conclusions can you draw about the accuracy and precision of these results?

6. Compare and contrast the multiplication/division significant figure rule to the significant figure rule applied for addition/subtraction mathematical operations.
7. Explain how density can be used as a conversion factor to convert the volume of an object to the mass of the object, and vice versa.
8. On which temperature scale ($^{\circ}\text{F}$, $^{\circ}\text{C}$, or K) does 1 degree represent the smallest change in temperature?
9. Distinguish between physical changes and chemical changes.
10. Why is the separation of mixtures into pure or relatively pure substances so important when performing a chemical analysis?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

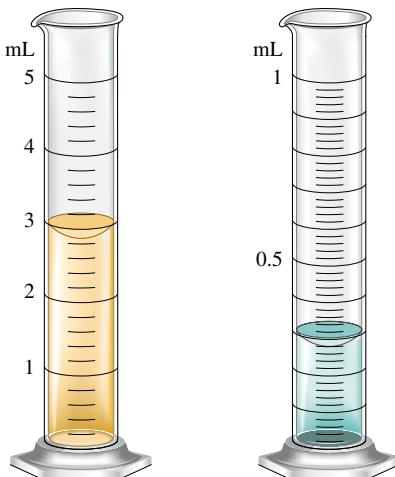
1. a. There are 365 days per year, 24 hours per day, 12 months per year, and 60 minutes per hour. Use these data to determine how many minutes are in a month.
b. Now use the following data to calculate the number of minutes in a month: 24 hours per day, 60 minutes per hour, 7 days per week, and 4 weeks per month.
c. Why are these answers different? Which (if any) is more correct? Why?
2. You go to a convenience store to buy candy and find the owner to be rather odd. He allows you to buy pieces in multiples of four, and to buy four, you need \$0.23. He only allows you to do this by using 3 pennies and 2 dimes. You have a bunch of pennies and dimes, and instead of counting them, you decide to weigh them.

You have 636.3 g of pennies, and each penny weighs 3.03 g. Each dime weighs 2.29 g. Each piece of candy weighs 10.23 g.

- a. How many pennies do you have?
- b. How many dimes do you need to buy as much candy as possible?
- c. How much should all these dimes weigh?
- d. How many pieces of candy could you buy? (number of dimes from part b)
- e. How much would this candy weigh?
- f. How many pieces of candy could you buy with twice as many dimes?
3. When a marble is dropped into a beaker of water, it sinks to the bottom. Which of the following is the best explanation?
 - a. The surface area of the marble is not large enough to be held up by the surface tension of the water.
 - b. The mass of the marble is greater than that of the water.
 - c. The marble weighs more than an equivalent volume of the water.
 - d. The force from dropping the marble breaks the surface tension of the water.
 - e. The marble has greater mass and volume than the water.

Justify your choice, and for choices you did not pick, explain what is wrong about them.

4. You have two beakers, one filled to the 100-mL mark with sugar (the sugar has a mass of 180.0 g) and the other filled to the 100-mL mark with water (the water has a mass of 100.0 g). You pour all the sugar and all the water together in a bigger beaker and stir until the sugar is completely dissolved.
 - a. Which of the following is true about the mass of the solution? Explain.
 - i. It is much greater than 280.0 g.
 - ii. It is somewhat greater than 280.0 g.
 - iii. It is exactly 280.0 g.
 - iv. It is somewhat less than 280.0 g.
 - v. It is much less than 280.0 g.
 - b. Which of the following is true about the volume of the solution? Explain.
 - i. It is much greater than 200.0 mL.
 - ii. It is somewhat greater than 200.0 mL.
 - iii. It is exactly 200.0 mL.
 - iv. It is somewhat less than 200.0 mL.
 - v. It is much less than 200.0 mL.
5. You may have noticed that when water boils, you can see bubbles that rise to the surface of the water.
 - a. What is inside these bubbles?
 - i. air
 - ii. hydrogen and oxygen gas
 - iii. oxygen gas
 - iv. water vapor
 - v. carbon dioxide gas
 - b. Is the boiling of water a chemical or physical change? Explain.
6. If you place a glass rod over a burning candle, the glass appears to turn black. What is happening to each of the following (physical change, chemical change, both, or neither) as the candle burns? Explain each answer.
 - a. the wax
 - b. the wick
 - c. the glass rod
7. Which characteristics of a solid, a liquid, and a gas are exhibited by each of the following substances? How would you classify each substance?
 - a. a bowl of pudding
 - b. a bucketful of sand
8. You have water in each graduated cylinder shown:



You then add both samples to a beaker. How would you write the number describing the total volume? What limits the precision of this number?

9. Paracelsus, a sixteenth-century alchemist and healer, adopted as his slogan: "The patients are your textbook, the sickbed is your study." Is this view consistent with using the scientific method?
10. What is wrong with the following statement?
"The results of the experiment do not agree with the theory. Something must be wrong with the experiment."
11. Why is it incorrect to say that the results of a measurement were accurate but not precise?
12. What data would you need to estimate the money you would spend on gasoline to drive your car from New York to Chicago? Provide estimates of values and a sample calculation.
13. Sketch two pieces of glassware: one that can measure volume to the thousandths place and one that can measure volume only to the ones place.
14. You have a 1.0-cm³ sample of lead and a 1.0-cm³ sample of glass. You drop each in separate beakers of water. How do the volumes of water displaced by each sample compare? Explain.
15. Sketch a magnified view (showing atoms/molecules) of each of the following and explain:
 - a. a heterogeneous mixture of two different compounds
 - b. a homogeneous mixture of an element and a compound
16. You are driving 65 mi/h and take your eyes off the road for "just a second." What distance (in feet) do you travel in this time?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

17. The difference between a *law* and a *theory* is the difference between *what* and *why*. Explain.
18. Explain the fundamental steps of the scientific method.
19. A measurement is a quantitative observation involving both a number and a unit. What is a qualitative observation? What are the SI units for mass, length, and volume? What is the assumed uncertainty in a number (unless stated otherwise)? The uncertainty of a measurement depends on the precision of the measuring device. Explain.
20. To determine the volume of a cube, a student measured one of the dimensions of the cube several times. If the true dimension of the cube is 10.62 cm, give an example of four sets of measurements that would illustrate the following.
 - a. imprecise and inaccurate data
 - b. precise but inaccurate data
 - c. precise and accurate data
 Give a possible explanation as to why data can be imprecise or inaccurate. What is wrong with saying a set of measurements is imprecise but accurate?
21. What are significant figures? Show how to indicate the number one thousand to 1 significant figure, 2 significant figures, 3 significant figures, and 4 significant figures. Why is the answer, to

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the correct number of significant figures, not 1.0 for the following calculation?

$$\frac{1.5 - 1.0}{0.50} =$$

- 22.** What is the volume per unit mass equal to? What unit conversion would the volume per unit mass be useful for?
- 23.** When the temperature in degrees Fahrenheit (T_F) is plotted versus the temperature in degrees Celsius (T_C), a straight line plot results. A straight line plot also results when T_C is plotted versus T_K (the temperature in degrees Kelvin). Reference Appendix A1.3 and determine the slope and y-intercept of each of these two plots.
- 24.** Give four examples illustrating each of the following terms.
- a. homogeneous mixture
 - b. heterogeneous mixture
 - c. compound
 - d. element
 - e. physical change
 - f. chemical change

Exercises

In this section similar exercises are paired.

Significant Figures and Unit Conversions

- 25.** Which of the following are exact numbers?

- a. There are 100 cm in 1 m.
- b. One meter equals 1.094 yard.
- c. We can use the equation

$$^{\circ}\text{F} = \frac{9}{5}^{\circ}\text{C} + 32$$

to convert from Celsius to Fahrenheit temperature. Are the numbers $\frac{9}{5}$ and 32 exact or inexact?

d. $\pi = 3.1415927$.

- 26.** Indicate the number of significant figures in each of the following:
- a. This book contains more than 1000 pages.
 - b. A mile is about 5300 ft.
 - c. A liter is equivalent to 1.059 qt.
 - d. The population of the United States is approaching 3.0×10^2 million.
 - e. A kilogram is 1000 g.
 - f. The Boeing 747 cruises at around 600 mi/h.

- 27.** How many significant figures are there in each of the following values?

- a. 6.07×10^{-15}
- b. 0.003840
- c. 17.00
- d. 8×10^8
- e. 463.8052
- f. 300
- g. 301
- h. 300.

- 28.** How many significant figures are in each of the following?

- a. 100
- b. 1.0×10^2
- c. 1.00×10^3
- d. 100.
- e. 0.0048
- f. 0.00480
- g. 4.80×10^{-3}
- h. 4.800×10^{-3}

- 29.** Round off each of the following numbers to the indicated number of significant digits and write the answer in standard scientific notation.

- a. 0.00034159 to three digits
- b. 103.351×10^2 to four digits
- c. 17.9915 to five digits
- d. 3.365×10^5 to three digits

- 30.** Use exponential notation to express the number 480 to

- a. one significant figure
- b. two significant figures
- c. three significant figures
- d. four significant figures

- 31.** Evaluate each of the following and write the answer to the appropriate number of significant figures.

- a. $212.2 + 26.7 + 402.09$
- b. $1.0028 + 0.221 + 0.10337$
- c. $52.331 + 26.01 - 0.9981$
- d. $2.01 \times 10^2 + 3.014 \times 10^3$
- e. $7.255 - 6.8350$

- 32.** Perform the following mathematical operations, and express each result to the correct number of significant figures.

- a. $\frac{1.012 \times 0.0821 \times 273}{1.01}$
- b. $0.14 \times 6.022 \times 10^{23}$
- c. $4.0 \times 10^4 \times 5.021 \times 10^{-3} \times 7.34993 \times 10^2$
- d. $\frac{2.00 \times 10^6}{3.00 \times 10^{-7}}$

- 33.** Perform the following mathematical operations and express the result to the correct number of significant figures.

- a. $\frac{2.526}{3.1} + \frac{0.470}{0.623} + \frac{80.705}{0.4326}$
- b. $(6.404 \times 2.91)/(18.7 - 17.1)$
- c. $6.071 \times 10^{-5} - 8.2 \times 10^{-6} - 0.521 \times 10^{-4}$
- d. $(3.8 \times 10^{-12} + 4.0 \times 10^{-13})/(4 \times 10^{12} + 6.3 \times 10^{13})$
- e. $\frac{9.5 + 4.1 + 2.8 + 3.175}{4}$

(Assume that this operation is taking the average of four numbers. Thus 4 in the denominator is exact.)

- f. $\frac{8.925 - 8.905}{8.925} \times 100$

(This type of calculation is done many times in calculating a percentage error. Assume that this example is such a calculation; thus 100 can be considered to be an exact number.)

- 34.** Perform the following mathematical operations, and express the result to the correct number of significant figures.

- a. $6.022 \times 10^{23} \times 1.05 \times 10^2$
- b. $\frac{6.6262 \times 10^{-34} \times 2.998 \times 10^8}{2.54 \times 10^{-9}}$
- c. $1.285 \times 10^{-2} + 1.24 \times 10^{-3} + 1.879 \times 10^{-1}$
- d. $1.285 \times 10^{-2} - 1.24 \times 10^{-3}$
- e. $\frac{(1.00866 - 1.00728)}{6.02205 \times 10^{23}}$
- f. $\frac{9.875 \times 10^2 - 9.795 \times 10^2}{9.875 \times 10^2} \times 100$ (100 is exact)
- g. $\frac{9.42 \times 10^2 + 8.234 \times 10^2 + 1.625 \times 10^3}{3}$ (3 is exact)

- 35.** Perform each of the following conversions.

- a. 8.43 cm to millimeters
- b. 2.41×10^2 cm to meters
- c. 294.5 nm to centimeters
- d. 1.445×10^4 m to kilometers

- e. 235.3 m to millimeters
f. 903.3 nm to micrometers

- 36.** a. How many kilograms are in one teragram?
b. How many nanometers are in 6.50×10^2 terameters?
c. How many kilograms are in 25 femtograms?
d. How many liters are in 8.0 cubic decimeters?
e. How many microliters are in one milliliter?
f. How many picograms are in one microgram?

- 37.** Perform the following unit conversions.

- a. Congratulations! You and your spouse are the proud parents of a new baby, born while you are studying in a country that uses the metric system. The nurse has informed you that the baby weighs 3.91 kg and measures 51.4 cm. Convert your baby's weight to pounds and ounces and her length to inches (rounded to the nearest quarter inch).
b. The circumference of the earth is 25,000 mi at the equator. What is the circumference in kilometers? in meters?
c. A rectangular solid measures 1.0 m by 5.6 cm by 2.1 dm. Express its volume in cubic meters, liters, cubic inches, and cubic feet.

- 38.** Perform the following unit conversions.

- a. 908 oz to kilograms
b. 12.8 L to gallons
c. 125 mL to quarts
d. 2.89 gal to milliliters
e. 4.48 lb to grams
f. 550 mL to quarts

- 39.** Use the following exact conversion factors to perform the stated calculations:

$$\begin{aligned} 5\frac{1}{2} \text{ yards} &= 1 \text{ rod} \\ 40 \text{ rods} &= 1 \text{ furlong} \\ 8 \text{ furlongs} &= 1 \text{ mile} \end{aligned}$$

- a. The Kentucky Derby race is 1.25 miles. How long is the race in rods, furlongs, meters, and kilometers?
b. A marathon race is 26 miles, 385 yards. What is this distance in rods, furlongs, meters, and kilometers?
40. Although the preferred SI unit of area is the square meter, land is often measured in the metric system in hectares (ha). One hectare is equal to $10,000 \text{ m}^2$. In the English system, land is often measured in acres ($1 \text{ acre} = 160 \text{ rod}^2$). Use the exact conversions and those given in Exercise 39 to calculate the following.
a. $1 \text{ ha} = \underline{\hspace{2cm}}$ km^2 .
b. The area of a 5.5-acre plot of land in hectares, square meters, and square kilometers.
c. A lot with dimensions 120 ft by 75 ft is to be sold for \$6500. What is the price per acre? What is the price per hectare?

- 41.** Precious metals and gems are measured in troy weights in the English system:

$$\begin{aligned} 24 \text{ grains} &= 1 \text{ pennyweight (exact)} \\ 20 \text{ pennyweight} &= 1 \text{ troy ounce (exact)} \\ 12 \text{ troy ounces} &= 1 \text{ troy pound (exact)} \\ 1 \text{ grain} &= 0.0648 \text{ gram} \\ 1 \text{ carat} &= 0.200 \text{ gram} \end{aligned}$$

- a. The most common English unit of mass is the pound avoirdupois. What is one troy pound in kilograms and in pounds?

- b. What is the mass of a troy ounce of gold in grams and in carats?
c. The density of gold is 19.3 g/cm^3 . What is the volume of a troy pound of gold?

- 42.** Apothecaries (druggists) use the following set of measures in the English system:

$$\begin{aligned} 20 \text{ grains ap} &= 1 \text{ scruple (exact)} \\ 3 \text{ scruples} &= 1 \text{ dram ap (exact)} \\ 8 \text{ dram ap} &= 1 \text{ oz ap (exact)} \\ 1 \text{ dram ap} &= 3.888 \text{ g} \end{aligned}$$

- a. Is an apothecary grain the same as a troy grain? (See Exercise 41.)
b. $1 \text{ oz ap} = \underline{\hspace{2cm}} \text{ oz troy}$.
c. An aspirin tablet contains 5.00×10^2 mg of active ingredient. What mass in grains ap of active ingredient does it contain? What mass in scruples?
d. What is the mass of 1 scruple in grams?

- 43.** Science fiction often uses nautical analogies to describe space travel. If the starship *U.S.S. Enterprise* is traveling at warp factor 1.71, what is its speed in knots and in miles per hour? (Warp 1.71 = 5.00 times the speed of light; speed of light = $3.00 \times 10^8 \text{ m/s}$; 1 knot = 2000 yd/h, exactly.)

- 44.** The world record for the hundred meter dash is 9.77 s. What is the corresponding average speed in units of m/s, km/h, ft/s, and mi/h? At this speed, how long would it take to run 1.00×10^2 yards?

- 45.** Would a car traveling at a constant speed of 65 km/h violate a 40. mi/h speed limit?

- 46.** You pass a road sign saying "New York 112 km." If you drive at a constant speed of 65 mi/h, how long should it take you to reach New York? If your car gets 28 miles to the gallon, how many liters of gasoline are necessary to travel 112 km?

- 47.** If you put 8.21 gallons of gas in your car and it cost you a total of \$17.25, what is the cost of gas per liter in Canadian dollars? Assume 0.82 dollar U.S. = 1.00 dollar Canadian.

- 48.** A children's pain relief elixir contains 80. mg acetaminophen per 0.50 teaspoon. The dosage recommended for a child who weighs between 24 and 35 lb is 1.5 teaspoons. What is the range of acetaminophen dosages, expressed in mg acetaminophen/kg body weight, for children who weigh between 24 and 35 lb?

Temperature

- 49.** Convert the following Fahrenheit temperatures to the Celsius and Kelvin scales.

- a. -459°F , an extremely low temperature
b. -40°F , the answer to a trivia question
c. 68°F , room temperature
d. $7 \times 10^7^\circ\text{F}$, temperature required to initiate fusion reactions in the sun

- 50.** A thermometer gives a reading of $96.1^\circ\text{F} \pm 0.2^\circ\text{F}$. What is the temperature in $^\circ\text{C}$? What is the uncertainty?

- 51.** Convert the following Celsius temperatures to Kelvin and to Fahrenheit degrees.

- a. the temperature of someone with a fever, 39.2°C
b. a cold wintery day, -25°C
c. the lowest possible temperature, -273°C
d. the melting-point temperature of sodium chloride, 801°C

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52. Convert the following Kelvin temperatures to Celsius and Fahrenheit degrees.

- the temperature that registers the same value on both the Fahrenheit and Celsius scales, 233 K
- the boiling point of helium, 4 K
- the temperature at which many chemical quantities are determined, 298 K
- the melting point of tungsten, 3680 K

Density

53. A material will float on the surface of a liquid if the material has a density less than that of the liquid. Given that the density of water is approximately 1.0 g/mL, will a block of material having a volume of 1.2×10^4 in³ and weighing 350 lb float or sink when placed in a reservoir of water?

54. For a material to float on the surface of water, the material must have a density less than that of water (1.0 g/mL) and must not react with the water or dissolve in it. A spherical ball has a radius of 0.50 cm and weighs 2.0 g. Will this ball float or sink when placed in water? (Note: Volume of a sphere = $\frac{4}{3}\pi r^3$.)

55. A star is estimated to have a mass of 2×10^{36} kg. Assuming it to be a sphere of average radius 7.0×10^5 km, calculate the average density of the star in units of grams per cubic centimeter.

56. A rectangular block has dimensions 2.9 cm × 3.5 cm × 10.0 cm. The mass of the block is 615.0 g. What are the volume and density of the block?

57. Diamonds are measured in carats, and 1 carat = 0.200 g. The density of diamond is 3.51 g/cm³. What is the volume of a 5.0-carat diamond?

58. The volume of a diamond is found to be 2.8 mL. What is the mass of the diamond in carats? (See Exercise 57.)

59. A sample containing 33.42 g of metal pellets is poured into a graduated cylinder initially containing 12.7 mL of water, causing the water level in the cylinder to rise to 21.6 mL. Calculate the density of the metal.

60. The density of pure silver is 10.5 g/cm³ at 20°C. If 5.25 g of pure silver pellets is added to a graduated cylinder containing 11.2 mL of water, to what volume level will the water in the cylinder rise?

61. In each of the following pairs, which has the greater mass? (See Table 1.5.)

- 1.0 kg of feathers or 1.0 kg of lead
- 1.0 mL of mercury or 1.0 mL of water
- 19.3 mL of water or 1.00 mL of gold
- 75 mL of copper or 1.0 L of benzene

62. Mercury poisoning is a debilitating disease that is often fatal. In the human body, mercury reacts with essential enzymes leading to irreversible inactivity of these enzymes. If the amount of mercury in a polluted lake is 0.4 µg Hg/mL, what is the total mass in kilograms of mercury in the lake? (The lake has a surface area of 100 mi² and an average depth of 20 ft.)

63. In each of the following pairs, which has the greater volume?

- 1.0 kg of feathers or 1.0 kg of lead
- 100 g of gold or 100 g of water
- 1.0 L of copper or 1.0 L of mercury

64. Using Table 1.5, calculate the volume of 25.0 g of each of the following substances at 1 atm.

- hydrogen gas
- water
- iron

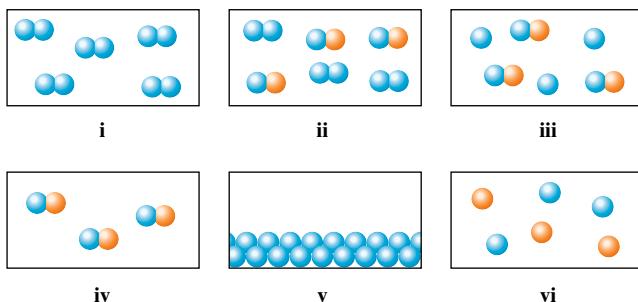
Chapter 5 discusses the properties of gases. One property unique to gases is that they contain mostly empty space. Explain using the results of your calculations.

65. The density of osmium (the densest metal) is 22.57 g/cm³. If a 1.00-kg rectangular block of osmium has two dimensions of 4.00 cm × 4.00 cm, calculate the third dimension of the block.

66. A copper wire (density = 8.96 g/cm³) has a diameter of 0.25 mm. If a sample of this copper wire has a mass of 22 g, how long is the wire?

Classification and Separation of Matter

67. Match each description below with the following microscopic pictures. More than one picture may fit each description. A picture may be used more than once or not used at all.



- a gaseous compound
- a mixture of two gaseous elements
- a solid element
- a mixture of a gaseous element and a gaseous compound

68. Define the following terms: solid, liquid, gas, pure substance, element, compound, homogeneous mixture, heterogeneous mixture, solution, chemical change, physical change.

69. What is the difference between homogeneous and heterogeneous matter? Classify each of the following as homogeneous or heterogeneous.

- a door
- the air you breathe
- a cup of coffee (black)
- the water you drink
- salsa
- your lab partner

70. Classify each of the following as a mixture or a pure substance.

- | | |
|---------------|----------------------|
| a. water | f. uranium |
| b. blood | g. wine |
| c. the oceans | h. leather |
| d. iron | i. table salt (NaCl) |
| e. brass | |

Of the pure substances, which are elements and which are compounds?

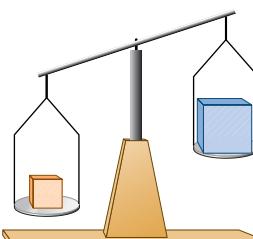
- 71.** Classify following as physical or chemical changes.
- Moth balls gradually vaporize in a closet.
 - Hydrofluoric acid attacks glass, and is used to etch calibration marks on glass laboratory utensils.
 - A French chef making a sauce with brandy is able to burn off the alcohol from the brandy, leaving just the brandy flavoring.
 - Chemistry majors sometimes get holes in the cotton jeans they wear to lab because of acid spills.
- 72.** The properties of a mixture are typically averages of the properties of its components. The properties of a compound may differ dramatically from the properties of the elements that combine to produce the compound. For each process described below, state whether the material being discussed is most likely a mixture or a compound, and state whether the process is a chemical change or a physical change.
- An orange liquid is distilled, resulting in the collection of a yellow liquid and a red solid.
 - A colorless, crystalline solid is decomposed, yielding a pale yellow-green gas and a soft, shiny metal.
 - A cup of tea becomes sweeter as sugar is added to it.

Additional Exercises

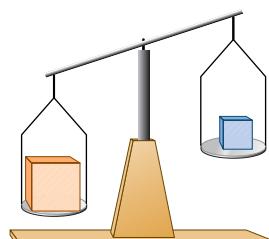
- 73.** For a pharmacist dispensing pills or capsules, it is often easier to weigh the medication to be dispensed rather than to count the individual pills. If a single antibiotic capsule weighs 0.65 g, and a pharmacist weighs out 15.6 g of capsules, how many capsules have been dispensed?
- 74.** In Shakespeare's *Richard III*, the First Murderer says:
- "Take that, and that! [Stabs Clarence]
If that is not enough, I'll drown you in a malmsey butt within!"
- Given that 1 butt = 126 gal, in how many liters of malmsey (a foul brew similar to mead) was the unfortunate Clarence about to be drowned?
- 75.** The contents of one 40. lb bag of topsoil will cover 10. square feet of ground to a depth of 1.0 inch. What number of bags are needed to cover a plot that measures 200. by 300. m to a depth of 4.0 cm?
- 76.** In the opening scenes of the movie *Raiders of the Lost Ark*, Indiana Jones tries to remove a gold idol from a booby-trapped pedestal. He replaces the idol with a bag of sand of approximately equal volume. (Density of gold = 19.32 g/cm³; density of sand ≈ 2 g/cm³.)
- Did he have a reasonable chance of not activating the mass-sensitive booby trap?
 - In a later scene he and an unscrupulous guide play catch with the idol. Assume that the volume of the idol is about 1.0 L. If it were solid gold, what mass would the idol have? Is playing catch with it plausible?
- 77.** A column of liquid is found to expand linearly on heating 5.25 cm for a 10.0°F rise in temperature. If the initial temperature of the liquid is 98.6°F, what will the final temperature be in °C if the liquid has expanded by 18.5 cm?
- 78.** A 25.00-g sample of a solid is placed in a graduated cylinder and then the cylinder is filled to the 50.0 mL mark with benzene. The mass of benzene and solid together is 58.80 g. Assuming that the

solid is insoluble in benzene and that the density of benzene is 0.880 g/cm³, calculate the density of the solid.

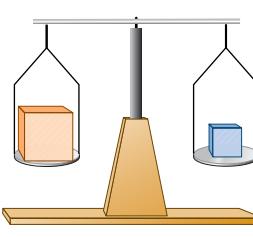
- 79.** For each of the following, decide which block is more dense: the orange block, the blue block, or it cannot be determined. Explain your answers.



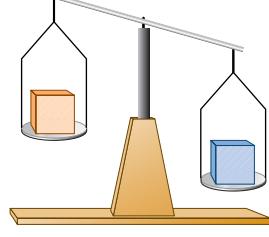
a.



b.



c.



d.

- 80.** According to the *Official Rules of Baseball*, a baseball must have a circumference not more than 9.25 in or less than 9.00 in and a mass not more than 5.25 oz or less than 5.00 oz. What range of densities can a baseball be expected to have? Express this range as a single number with an accompanying uncertainty limit.
- 81.** The density of an irregularly shaped object was determined as follows. The mass of the object was found to be 28.90 g ± 0.03 g. A graduated cylinder was partially filled with water. The reading of the level of the water was 6.4 cm³ ± 0.1 cm³. The object was dropped in the cylinder, and the level of the water rose to 9.8 cm³ ± 0.1 cm³. What is the density of the object with appropriate error limits? (See Appendix 1.5.)
- Challenge Problems**
- 82.** Draw a picture showing the markings (graduations) on glassware that would allow you to make each of the following volume measurements of water and explain your answers (the numbers given are as precise as possible).
- 128.7 mL
 - 18 mL
 - 23.45 mL
- If you made the measurements of three samples of water and then poured all of the water together in one container, what total volume of water should you report? Support your answer.
- 83.** Many times errors are expressed in terms of percentage. The percent error is the absolute value of the difference of the true value and the experimental value, divided by the true value, and multiplied by 100.

$$\text{Percent error} = \frac{|\text{true value} - \text{experimental value}|}{\text{true value}} \times 100$$

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- Calculate the percent error for the following measurements.
- The density of an aluminum block determined in an experiment was 2.64 g/cm^3 . (True value 2.70 g/cm^3 .)
 - The experimental determination of iron in iron ore was 16.48%. (True value 16.12%).
 - A balance measured the mass of a 1.000-g standard as 0.9981 g.
- 84.** A person weighed 15 pennies on a balance and recorded the following masses:

3.112 g	3.109 g	3.059 g
2.467 g	3.079 g	2.518 g
3.129 g	2.545 g	3.050 g
3.053 g	3.054 g	3.072 g
3.081 g	3.131 g	3.064 g

Curious about the results, he looked at the dates on each penny. Two of the light pennies were minted in 1983 and one in 1982. The dates on the 12 heavier pennies ranged from 1970 to 1982. Two of the 12 heavier pennies were minted in 1982.

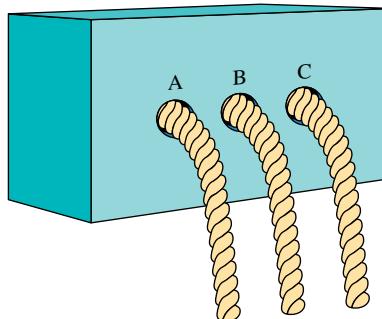
- Do you think the Bureau of the Mint changed the way it made pennies? Explain.
 - The person calculated the average mass of the 12 heavy pennies. He expressed this average as $3.0828 \text{ g} \pm 0.0482 \text{ g}$. What is wrong with the numbers in this result, and how should the value be expressed?
- 85.** On October 21, 1982, the Bureau of the Mint changed the composition of pennies (see Exercise 84). Instead of an alloy of 95% Cu and 5% Zn by mass, a core of 99.2% Zn and 0.8% Cu with a thin shell of copper was adopted. The overall composition of the new penny was 97.6% Zn and 2.4% Cu by mass. Does this account for the difference in mass among the pennies in Exercise 84? Assume the volume of the individual metals that make up each penny can be added together to give the overall volume of the penny, and assume each penny is the same size. (Density of Cu = 8.96 g/cm^3 ; density of Zn = 7.14 g/cm^3 .)
- 86.** Ethylene glycol is the main component in automobile antifreeze. To monitor the temperature of an auto cooling system, you intend to use a meter that reads from 0 to 100. You devise a new temperature scale based on the approximate melting and boiling points of a typical antifreeze solution (-45°C and 115°C). You wish these points to correspond to 0°A and 100°A , respectively.
- Derive an expression for converting between ${}^\circ\text{A}$ and ${}^\circ\text{C}$.
 - Derive an expression for converting between ${}^\circ\text{F}$ and ${}^\circ\text{A}$.
 - At what temperature would your thermometer and a Celsius thermometer give the same numerical reading?
 - Your thermometer reads 86°A . What is the temperature in ${}^\circ\text{C}$ and in ${}^\circ\text{F}$?
 - What is a temperature of 45°C in ${}^\circ\text{A}$?
- 87.** Sterling silver is a solid solution of silver and copper. If a piece of a sterling silver necklace has a mass of 105.0 g and a volume of 10.12 mL, calculate the mass percent of copper in the piece of necklace. Assume that the volume of silver present plus the volume of copper present equals the total volume. Refer to Table 1.5.

$$\text{Mass percent of copper} = \frac{\text{mass of copper}}{\text{total mass}} \times 100$$

- 88.** Use molecular-level (microscopic) drawings for each of the following.

- Show the differences between a gaseous mixture that is a homogeneous mixture of two different compounds, and a gaseous mixture that is a homogeneous mixture of a compound and an element.
- Show the differences among a gaseous element, a liquid element, and a solid element.

- 89.** Confronted with the box shown in the diagram, you wish to discover something about its internal workings. You have no tools and cannot open the box. You pull on rope B, and it moves rather freely. When you pull on rope A, rope C appears to be pulled slightly into the box. When you pull on rope C, rope A almost disappears into the box.*



- Based on these observations, construct a model for the interior mechanism of the box.
- What further experiments could you do to refine your model?

- 90.** An experiment was performed in which an empty 100-mL graduated cylinder was weighed. It was weighed once again after it had been filled to the 10.0-mL mark with dry sand. A 10-mL pipet was used to transfer 10.00 mL of methanol to the cylinder. The sand–methanol mixture was stirred until bubbles no longer emerged from the mixture and the sand looked uniformly wet. The cylinder was then weighed again. Use the data obtained from this experiment (and displayed at the end of this problem) to find the density of the dry sand, the density of methanol, and the density of sand particles. Does the bubbling that occurs when the methanol is added to the dry sand indicate that the sand and methanol are reacting?

Mass of cylinder plus wet sand	45.2613 g
Mass of cylinder plus dry sand	37.3488 g
Mass of empty cylinder	22.8317 g
Volume of dry sand	10.0 mL
Volume of sand + methanol	17.6 mL
Volume of methanol	10.00 mL

*From Yoder, Suydam, and Snavely, *Chemistry* (New York: Harcourt Brace Jovanovich, 1975), pp. 9–11.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

91. The U.S. trade deficit at the beginning of 2005 was \$475,000,000. If the wealthiest 1.00 percent of the U.S. population (297,000,000) contributed an equal amount of money to bring the trade deficit to \$0, how many dollars would each person contribute? If one of these people were to pay their share in nickels only, how many nickels are needed? Another person living abroad at the time decides to pay in pounds sterling (£). How many pounds sterling does this person contribute (assume a conversion rate of 1 £ = \$ 1.869)?
92. The density of osmium is reported by one source to be 22610 kg/m³. What is this density in g/cm³? What is the mass of a block of osmium measuring 10.0 cm × 8.0 cm × 9.0 cm?
93. At the Amundsen-Scott South Pole base station in Antarctica, when the temperature is −100.0°F, researchers who live there can join the “300 Club” by stepping into a sauna heated to 200.0°F then quickly running outside and around the pole that marks the South Pole. What are these temperatures in °C? What are these temperatures in K? If you measured the temperatures only in °C and K, can you become a member of the “300 Club” (that is, is there a 300.-degree difference between the temperature extremes when measured in °C and K?)

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

94. A cylindrical bar of gold that is 1.5 in high and 0.25 in in diameter has a mass of 23.1984 g, as determined on an analytical balance. An empty graduated cylinder is weighed on a triple-beam balance and has a mass of 73.47 g. After pouring a small amount of a liquid into the graduated cylinder, the mass is 79.16 g. When the gold cylinder is placed in the graduated cylinder (the liquid covers the top of the gold cylinder), the volume indicated on the graduated cylinder is 8.5 mL. Assume that the temperature of the gold bar and the liquid are 86°F. If the density of the liquid decreases by 1.0% for each 10.°C rise in temperature (over the range 0 to 50°C), determine
 - a. the density of the gold at 86°F.
 - b. the density of the liquid at 40.°F.

Note: Parts a and b can be answered independently.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

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2 Atoms, Molecules, and Ions

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- 2.6 Molecules and Ions
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 - Formulas from Names
 - Binary Ionic Compounds (Type II)
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 - Binary Covalent Compounds (Type III)
 - Acids



A worker in Thailand piles up salt crystals.



W

here does one start in learning chemistry? Clearly we must consider some essential vocabulary and something about the origins of the science before we can proceed very far. Thus, while Chapter 1 provided background on the fundamental ideas and procedures of science in general, Chapter 2 covers the specific chemical background necessary for understanding the material in the next few chapters. The coverage of these topics is necessarily brief at this point. We will develop these ideas more fully as it becomes appropriate to do so. A major goal of this chapter is to present the systems for naming chemical compounds to provide you with the vocabulary necessary to understand this book and to pursue your laboratory studies.

Because chemistry is concerned first and foremost with chemical changes, we will proceed as quickly as possible to a study of chemical reactions (Chapters 3 and 4). However, before we can discuss reactions, we must consider some fundamental ideas about atoms and how they combine.

2.1 The Early History of Chemistry

Chemistry has been important since ancient times. The processing of natural ores to produce metals for ornaments and weapons and the use of embalming fluids are just two applications of chemical phenomena that were utilized prior to 1000 B.C.

The Greeks were the first to try to explain why chemical changes occur. By about 400 B.C. they had proposed that all matter was composed of four fundamental substances: fire, earth, water, and air. The Greeks also considered the question of whether matter is continuous, and thus infinitely divisible into smaller pieces, or composed of small, indivisible particles. Supporters of the latter position were Demokritos* of Abdera (c. 460–c. 370 B.C.) and Leucippos, who used the term *atomos* (which later became *atoms*) to describe these ultimate particles. However, because the Greeks had no experiments to test their ideas, no definitive conclusion could be reached about the divisibility of matter.

The next 2000 years of chemical history were dominated by a pseudoscience called *alchemy*. Some alchemists were mystics and fakes who were obsessed with the idea of turning cheap metals into gold. However, many alchemists were serious scientists, and this period saw important advances: The alchemists discovered several elements and learned to prepare the mineral acids.

The foundations of modern chemistry were laid in the sixteenth century with the development of systematic metallurgy (extraction of metals from ores) by a German, Georg Bauer (1494–1555), and the medicinal application of minerals by a Swiss alchemist/physician known as Paracelsus (full name: Philippus Theophrastus Bombastus von Hohenheim [1493–1541]).

The first “chemist” to perform truly quantitative experiments was Robert Boyle (1627–1691), who carefully measured the relationship between the pressure and volume of air. When Boyle published his book *The Skeptical Chymist* in 1661, the quantitative sciences of physics and chemistry were born. In addition to his results on the quantitative behavior of gases, Boyle’s other major contribution to chemistry consisted of his ideas about the chemical elements. Boyle held no preconceived notion about the number of elements. In his view, a substance was an element unless it could be broken down into two or more simpler substances. As Boyle’s experimental definition of an element became generally accepted, the list of known elements began to grow, and the Greek system of

*Democritus is an alternate spelling.



CHEMICAL IMPACT

There's Gold in Them There Plants!

Gold has always held a strong allure. For example, the alchemists were obsessed with finding a way to transform cheap metals into gold. Also, when gold was discovered in California in 1849, a frantic rush occurred to that area and other areas in the west. Although gold is still valuable, most of the high-grade gold ores have been exhausted. This leaves the low-grade ores—ores with low concentrations of gold that are expensive to process relative to the amount of gold finally obtained.

Now two scientists have come across a novel way to concentrate the gold from low-grade ores. Christopher Anderson and Robert Brooks of Massey University in Palmerston North, New Zealand, have found plants that accumulate gold atoms as they grow in soil containing gold ore [*Nature* 395 (1998): 553]. The plants brassica (of the mustard family) and chicory seem especially effective as botanical “gold miners.” When these plants are dried and burned (after having grown in gold-rich soil), the resulting ash contains approximately 150 ppm (parts per million) of gold. (1 ppm gold represents 1 g of gold in 10^6 g of sample.)

The New Zealand scientists were able to double the amount of gold taken from the soil by the plants by treating

the soil with ammonium thiocyanate (NH_4SCN). The thiocyanate, which reacts with the gold, making it more available to the plants, subsequently breaks down in the soil and therefore poses no environmental hazard.

Thus plants seem to hold great promise as gold miners. They are efficient and reliable and will never go on strike.



This plant from the mustard family is a newly discovered source of gold.

four elements finally died. Although Boyle was an excellent scientist, he was not always right. For example, he clung to the alchemists’ views that metals were not true elements and that a way would eventually be found to change one metal into another.

The phenomenon of combustion evoked intense interest in the seventeenth and eighteenth centuries. The German chemist Georg Stahl (1660–1734) suggested that a substance he called “phlogiston” flowed out of the burning material. Stahl postulated that a substance burning in a closed container eventually stopped burning because the air in the container became saturated with phlogiston. Oxygen gas, discovered by Joseph Priestley (1733–1804),* an English clergyman and scientist (Fig. 2.1), was found to support vigorous combustion and was thus supposed to be low in phlogiston. In fact, oxygen was originally called “dephlogisticated air.”

FIGURE 2.1

The Priestley Medal is the highest honor given by the American Chemical Society. It is named for Joseph Priestley, who was born in England on March 13, 1733. He performed many important scientific experiments, among them the discovery that a gas later identified as carbon dioxide could be dissolved in water to produce *seltzer*. Also, as a result of meeting Benjamin Franklin in London in 1766, Priestley became interested in electricity and was the first to observe that graphite was an electrical conductor. However, his greatest discovery occurred in 1774 when he isolated oxygen by heating mercuric oxide.

Because of his nonconformist political views, Priestley was forced to leave England. He died in the United States in 1804.



*Oxygen gas was actually first observed by the Swedish chemist Karl W. Scheele (1742–1786), but because his results were published after Priestley’s, the latter is commonly credited with the discovery of oxygen.

2.2 Fundamental Chemical Laws

By the late eighteenth century, combustion had been studied extensively; the gases carbon dioxide, nitrogen, hydrogen, and oxygen had been discovered; and the list of elements continued to grow. However, it was Antoine Lavoisier (1743–1794), a French chemist (Fig. 2.2), who finally explained the true nature of combustion, thus clearing the way for the tremendous progress that was made near the end of the eighteenth century. Lavoisier, like Boyle, regarded measurement as the essential operation of chemistry. His experiments, in which he carefully weighed the reactants and products of various reactions, suggested that *mass is neither created nor destroyed*. Lavoisier's verification of this **law of conservation of mass** was the basis for the developments in chemistry in the nineteenth century.

Oxygen is from the French *oxygène*, meaning “generator of acid,” because it was initially considered to be an integral part of all acids.

Lavoisier's quantitative experiments showed that combustion involved oxygen (which Lavoisier named), not phlogiston. He also discovered that life was supported by a process that also involved oxygen and was similar in many ways to combustion. In 1789 Lavoisier published the first modern chemistry textbook, *Elementary Treatise on Chemistry*, in which he presented a unified picture of the chemical knowledge assembled up to that time. Unfortunately, in the same year the text was published, the French Revolution broke out. Lavoisier, who had been associated with collecting taxes for the government, was executed on the guillotine as an enemy of the people in 1794.

After 1800, chemistry was dominated by scientists who, following Lavoisier's lead, performed careful weighing experiments to study the course of chemical reactions and to determine the composition of various chemical compounds. One of these chemists, a Frenchman, Joseph Proust (1754–1826), showed that *a given compound always contains exactly the same proportion of elements by mass*. For example, Proust found that the substance copper carbonate is always 5.3 parts copper to 4 parts oxygen to 1 part carbon (by mass). The principle of the constant composition of compounds, originally called “Proust's law,” is now known as the **law of definite proportion**.

Proust's discovery stimulated John Dalton (1766–1844), an English schoolteacher (Fig. 2.3), to think about atoms as the particles that might compose elements. Dalton reasoned that if elements were composed of tiny individual particles, a given compound should always contain the same combination of these atoms. This concept explained why the same relative masses of elements were always found in a given compound.

But Dalton discovered another principle that convinced him even more of the existence of atoms. He noted, for example, that carbon and oxygen form two different compounds that contain different relative amounts of carbon and oxygen, as shown by the following data:

Mass of Oxygen That Combines with 1 g of Carbon	
Compound I	1.33 g
Compound II	2.66 g

Dalton noted that compound II contains twice as much oxygen per gram of carbon as compound I, a fact that could easily be explained in terms of atoms. Compound I might be CO, and compound II might be CO₂.^{*} This principle, which was found to apply to compounds of other elements as well, became known as the **law of multiple proportions**: *When two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers.*

To make sure the significance of this observation is clear, in Sample Exercise 2.1 we will consider data for a series of compounds consisting of nitrogen and oxygen.

Sample Exercise 2.1

Illustrating the Law of Multiple Proportions

The following data were collected for several compounds of nitrogen and oxygen:

Mass of Nitrogen That Combines with 1 g of Oxygen	
Compound A	1.750 g
Compound B	0.8750 g
Compound C	0.4375 g

Show how these data illustrate the law of multiple proportions.

Solution

For the law of multiple proportions to hold, the ratios of the masses of nitrogen combining with 1 gram of oxygen in each pair of compounds should be small whole numbers. We therefore compute the ratios as follows:

$$\begin{aligned} \frac{A}{B} &= \frac{1.750}{0.875} = \frac{2}{1} \\ \frac{B}{C} &= \frac{0.875}{0.4375} = \frac{2}{1} \\ \frac{A}{C} &= \frac{1.750}{0.4375} = \frac{4}{1} \end{aligned}$$

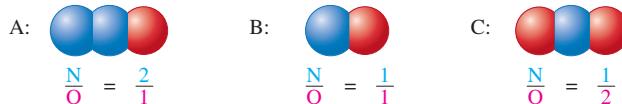
These results support the law of multiple proportions.

See Exercises 2.27 and 2.28.

^{*}Subscripts are used to show the numbers of atoms present. The number 1 is understood (not written). The symbols for the elements and the writing of chemical formulas will be illustrated further in Sections 2.6 and 2.7.

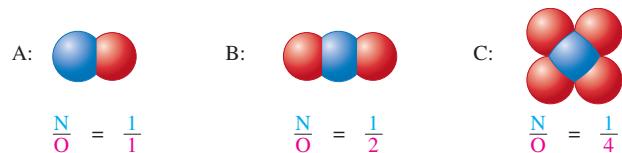
The significance of the data in Sample Exercise 2.1 is that compound A contains twice as much nitrogen (N) per gram of oxygen (O) as does compound B and that compound B contains twice as much nitrogen per gram of oxygen as does compound C.

These data can be explained readily if the substances are composed of molecules made up of nitrogen atoms and oxygen atoms. For example, one set of possibilities for compounds A, B, and C is



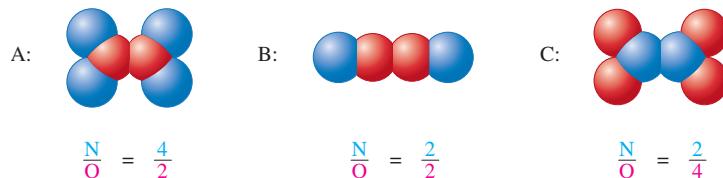
Now we can see that compound A contains two atoms of N for every atom of O, whereas compound B contains one atom of N per atom of O. That is, compound A contains twice as much nitrogen per given amount of oxygen as does compound B. Similarly, since compound B contains one N per O and compound C contains one N per *two* O's, the nitrogen content of compound C per given amount of oxygen is half that of compound B.

Another set of compounds that fits the data in Sample Exercise 2.1 is



Verify for yourself that these compounds satisfy the requirements.

Still another set that works is



See if you can come up with still another set of compounds that satisfies the data in Sample Exercise 2.1. How many more possibilities are there?

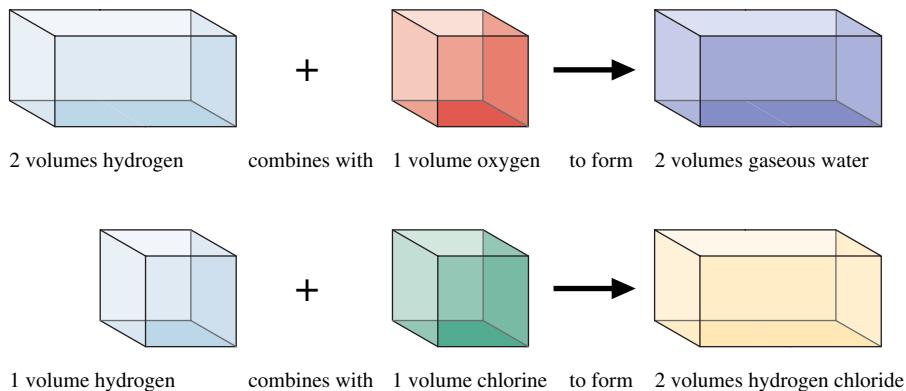
In fact, an infinite number of other possibilities exists. Dalton could not deduce absolute formulas from the available data on relative masses. However, the data on the composition of compounds in terms of the relative masses of the elements supported his hypothesis that each element consisted of a certain type of atom and that compounds were formed from specific combinations of atoms.

2.3 Dalton's Atomic Theory

In 1808 Dalton published *A New System of Chemical Philosophy*, in which he presented his theory of atoms:

1. Each element is made up of tiny particles called atoms.
2. The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways.
3. Chemical compounds are formed when atoms of different elements combine with each other. A given compound always has the same relative numbers and types of atoms.
4. Chemical reactions involve reorganization of the atoms—changes in the way they are bound together. The atoms themselves are not changed in a chemical reaction.

These statements are a modern paraphrase of Dalton's ideas.

**FIGURE 2.4**

A representation of some of Gay-Lussac's experimental results on combining gas volumes.



Joseph Louis Gay-Lussac, a French physicist and chemist, was remarkably versatile. Although he is now known primarily for his studies on the combining of volumes of gases, Gay-Lussac was instrumental in the studies of many of the other properties of gases. Some of Gay-Lussac's motivation to learn about gases arose from his passion for ballooning. In fact, he made ascents to heights of over 4 miles to collect air samples, setting altitude records that stood for about 50 years. Gay-Lussac also was the codiscoverer of boron and the developer of a process for manufacturing sulfuric acid. As chief assayer of the French mint, Gay-Lussac developed many techniques for chemical analysis and invented many types of glassware now used routinely in labs. Gay-Lussac spent his last 20 years as a lawmaker in the French government.

It is instructive to consider Dalton's reasoning on the relative masses of the atoms of the various elements. In Dalton's time water was known to be composed of the elements hydrogen and oxygen, with 8 grams of oxygen present for every 1 gram of hydrogen. If the formula for water were OH, an oxygen atom would have to have 8 times the mass of a hydrogen atom. However, if the formula for water were H₂O (two atoms of hydrogen for every oxygen atom), this would mean that each atom of oxygen is 16 times as massive as *each* atom of hydrogen (since the ratio of the mass of one oxygen to that of *two* hydrogens is 8 to 1). Because the formula for water was not then known, Dalton could not specify the relative masses of oxygen and hydrogen unambiguously. To solve the problem, Dalton made a fundamental assumption: He decided that nature would be as simple as possible. This assumption led him to conclude that the formula for water should be OH. He thus assigned hydrogen a mass of 1 and oxygen a mass of 8.

Using similar reasoning for other compounds, Dalton prepared the first table of **atomic masses** (sometimes called **atomic weights** by chemists, since mass is often determined by comparison to a standard mass—a process called *weighing*). Many of the masses were later proved to be wrong because of Dalton's incorrect assumptions about the formulas of certain compounds, but the construction of a table of masses was an important step forward.

Although not recognized as such for many years, the keys to determining absolute formulas for compounds were provided in the experimental work of the French chemist Joseph Gay-Lussac (1778–1850) and by the hypothesis of an Italian chemist named Amadeo Avogadro (1776–1856). In 1809 Gay-Lussac performed experiments in which he measured (under the same conditions of temperature and pressure) the volumes of gases that reacted with each other. For example, Gay-Lussac found that 2 volumes of hydrogen react with 1 volume of oxygen to form 2 volumes of gaseous water and that 1 volume of hydrogen reacts with 1 volume of chlorine to form 2 volumes of hydrogen chloride. These results are represented schematically in Fig. 2.4.

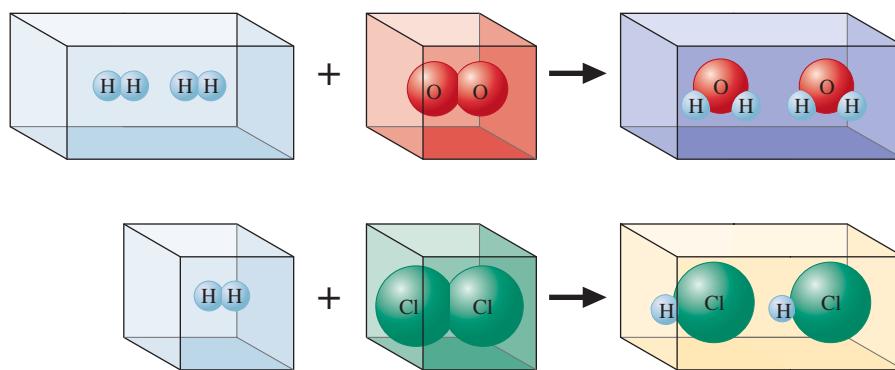
In 1811 Avogadro interpreted these results by proposing that *at the same temperature and pressure, equal volumes of different gases contain the same number of particles*. This assumption (called **Avogadro's hypothesis**) makes sense if the distances between the particles in a gas are very great compared with the sizes of the particles. Under these conditions, the volume of a gas is determined by the number of molecules present, not by the size of the individual particles.

If Avogadro's hypothesis is correct, Gay-Lussac's result,

2 volumes of hydrogen react with 1 volume of oxygen → 2 volumes of water vapor
can be expressed as follows:

2 molecules* of hydrogen react with 1 molecule of oxygen → 2 molecules of water

*A *molecule* is a collection of atoms (see Section 2.6).

**FIGURE 2.5**

A representation of combining gases at the molecular level. The spheres represent atoms in the molecules.

The Italian chemist Stanislao Cannizzaro (1826–1910) cleared up the confusion in 1860 by doing a series of molar mass determinations that convinced the scientific community that the correct atomic mass of carbon is 12. For more information, see *From Caveman to Chemist* by Hugh Salzberg (American Chemical Society, 1991), p. 223.

These observations can best be explained by assuming that gaseous hydrogen, oxygen, and chlorine are all composed of diatomic (two-atom) molecules: H₂, O₂, and Cl₂, respectively. Gay-Lussac's results can then be represented as shown in Fig. 2.5. (Note that this reasoning suggests that the formula for water is H₂O, not OH as Dalton believed.)

Unfortunately, Avogadro's interpretations were not accepted by most chemists, and a half-century of confusion followed, in which many different assumptions were made about formulas and atomic masses.

During the nineteenth century, painstaking measurements were made of the masses of various elements that combined to form compounds. From these experiments a list of relative atomic masses could be determined. One of the chemists involved in contributing to this list was a Swede named Jöns Jakob Berzelius (1779–1848), who discovered the elements cerium, selenium, silicon, and thorium and developed the modern symbols for the elements used in writing the formulas of compounds.

2.4 Early Experiments to Characterize the Atom

On the basis of the work of Dalton, Gay-Lussac, Avogadro, and others, chemistry was beginning to make sense. The concept of atoms was clearly a good idea. Inevitably, scientists began to wonder about the nature of the atom. What is an atom made of, and how do the atoms of the various elements differ?

The Electron

The first important experiments that led to an understanding of the composition of the atom were done by the English physicist J. J. Thomson (Fig. 2.6), who studied electrical discharges in partially evacuated tubes called **cathode-ray tubes** (Fig. 2.7) during the period from 1898 to 1903. Thomson found that when high voltage was applied to the tube, a “ray” he called a **cathode ray** (because it emanated from the negative electrode, or cathode) was produced. Because this ray was produced at the negative electrode and was repelled by the negative pole of an applied electric field (see Fig. 2.8), Thomson postulated that the ray was a stream of negatively charged particles, now called **electrons**. From experiments in which he measured the deflection of the beam of electrons in a magnetic field, Thomson determined the *charge-to-mass ratio* of an electron:

$$\frac{e}{m} = -1.76 \times 10^8 \text{ C/g}$$

where *e* represents the charge on the electron in coulombs (C) and *m* represents the electron mass in grams.



CHEMICAL IMPACT

Berzelius, Selenium, and Silicon

Jöns Jakob Berzelius was probably the best experimental chemist of his generation and, given the crudeness of his laboratory equipment, maybe the best of all time. Unlike Lavoisier, who could afford to buy the best laboratory equipment available, Berzelius worked with minimal equipment

in very plain surroundings. One of Berzelius's students described the Swedish chemist's workplace: "The laboratory consisted of two ordinary rooms with the very simplest arrangements; there were neither furnaces nor hoods, neither water system nor gas. Against the walls stood some closets with the chemicals, in the middle the mercury trough and the

blast lamp table. Beside this was the sink consisting of a stone water holder with a stopcock and a pot standing under it. [Next door in the kitchen] stood a small heating furnace."

In these simple facilities Berzelius performed more than 2000 experiments over a 10-year period to determine accurate atomic masses for the 50 elements then known. His success can be seen from the data in the table at left. These remarkably accurate values attest to his experimental skills and patience.

Besides his table of atomic masses, Berzelius made many other major contributions to chemistry. The most important of these was the invention of a simple set of symbols for the elements along with a system for writing the formulas of compounds to replace the awkward symbolic representations of the alchemists. Although some chemists, including Dalton, objected to the new system, it was gradually adopted and forms the basis of the system we use today.

In addition to these accomplishments, Berzelius discovered the elements cerium, thorium, selenium, and silicon. Of these elements, selenium and silicon are particularly important in today's world. Berzelius discovered selenium in 1817 in connection with his studies of sulfuric acid. For years selenium's toxicity has been known, but only recently have we become aware that it may have a positive effect on human

Comparison of Several of Berzelius's Atomic Masses with the Modern Values

Element	Atomic Mass	
	Berzelius's Value	Current Value
Chlorine	35.41	35.45
Copper	63.00	63.55
Hydrogen	1.00	1.01
Lead	207.12	207.2
Nitrogen	14.05	14.01
Oxygen	16.00	16.00
Potassium	39.19	39.10
Silver	108.12	107.87
Sulfur	32.18	32.07

One of Thomson's primary goals in his cathode-ray tube experiments was to gain an understanding of the structure of the atom. He reasoned that since electrons could be produced from electrodes made of various types of metals, *all* atoms must contain electrons. Since atoms were known to be electrically neutral, Thomson further assumed that atoms also must contain some positive charge. Thomson postulated that an atom consisted of a



Visualization: Cathode-Ray Tube

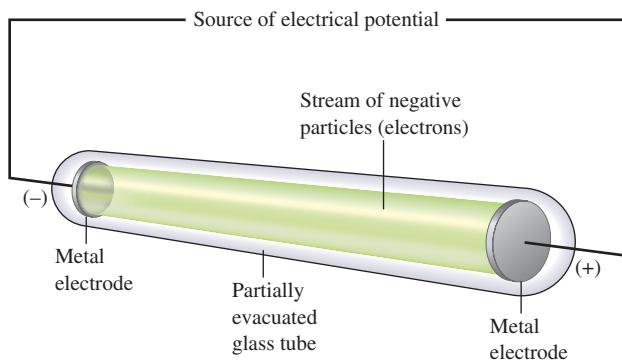


FIGURE 2.7

A cathode-ray tube. The fast-moving electrons excite the gas in the tube, causing a glow between the electrodes. The green color in the photo is due to the response of the screen (coated with zinc sulfide) to the electron beam.

The Alchemists' Symbols for Some Common Elements and Compounds	
Substance	Alchemists' Symbol
Silver	☽
Lead	☿
Tin	☿
Platinum	○○
Sulfuric acid	+○
Alcohol	▽
Sea salt	○:

the selenium content of the blood and the incidence of breast cancer in women. A study reported in 1998 used the toenail clippings of 33,737 men to show that selenium seems to protect against prostate cancer. Selenium is also found in the heart muscle and may play an important role in proper heart

health. Studies have shown that trace amounts of selenium in the diet may protect people from heart disease and cancer. One study based on data from 27 countries showed an inverse relationship between the cancer death rate and the selenium content of soil in a particular region (low cancer death rate in areas with high selenium content). Another research paper reported an inverse relationship between

function. Because of these and other studies, selenium's reputation has improved, and many scientists are now studying its function in the human body.

Silicon is the second most abundant element in the earth's crust, exceeded only by oxygen. As we will see in Chapter 10, compounds involving silicon bonded to oxygen make up most of the earth's sand, rock, and soil. Berzelius prepared silicon in its pure form in 1824 by heating silicon tetrafluoride (SiF_4) with potassium metal. Today, silicon forms the basis for the modern microelectronics industry centered near San Francisco in a place that has come to be known as "Silicon Valley." The technology of the silicon chip (see figure) with

its printed circuits has transformed computers from room-sized monsters with thousands of unreliable vacuum tubes to desktop and notebook-sized units with trouble-free "solid-state" circuitry.

A silicon chip.

See E. J. Holmyard, *Alchemy* (New York: Penguin Books, 1968).

diffuse cloud of positive charge with the negative electrons embedded randomly in it. This model, shown in Fig. 2.9, is often called the *plum pudding model* because the electrons are like raisins dispersed in a pudding (the positive charge cloud), as in plum pudding, a favorite English dessert.

In 1909 Robert Millikan (1868–1953), working at the University of Chicago, performed very clever experiments involving charged oil drops. These experiments allowed

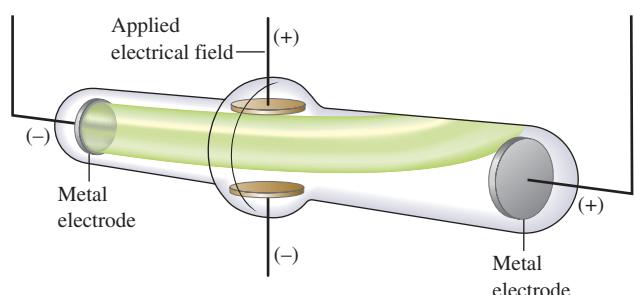


FIGURE 2.8
Deflection of cathode rays by an applied electric field.

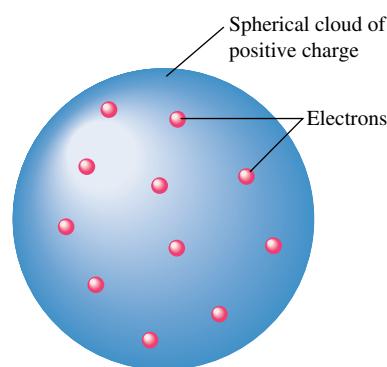


FIGURE 2.9
The plum pudding model of the atom.



Visualization: Millikan's Oil Drop Experiment



A technician using a scanner to monitor the uptake of radioactive iodine in a patient's thyroid.

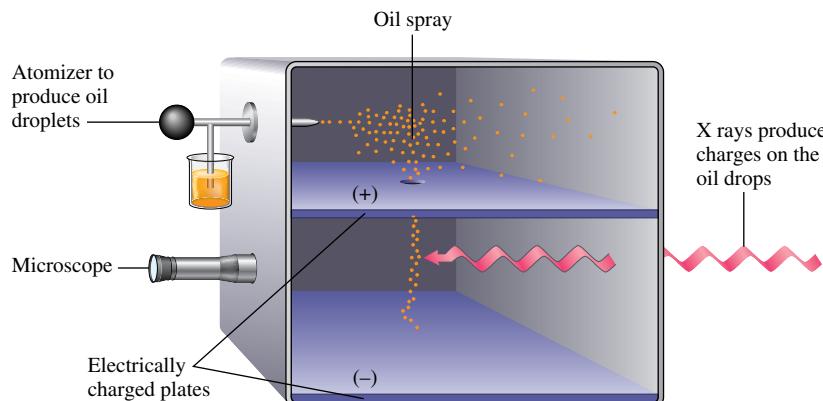


FIGURE 2.10

A schematic representation of the apparatus Millikan used to determine the charge on the electron. The fall of charged oil droplets due to gravity can be halted by adjusting the voltage across the two plates. This voltage and the mass of the oil drop can then be used to calculate the charge on the oil drop. Millikan's experiments showed that the charge on an oil drop is always a whole-number multiple of the electron charge.



FIGURE 2.11

Ernest Rutherford (1871–1937) was born on a farm in New Zealand. In 1895 he placed second in a scholarship competition to attend Cambridge University but was awarded the scholarship when the winner decided to stay home and get married. As a scientist in England, Rutherford did much of the early work on characterizing radioactivity. He named the α and β particles and the γ ray and coined the term *half-life* to describe an important attribute of radioactive elements. His experiments on the behavior of α particles striking thin metal foils led him to postulate the nuclear atom. He also invented the name *proton* for the nucleus of the hydrogen atom. He received the Nobel Prize in chemistry in 1908.

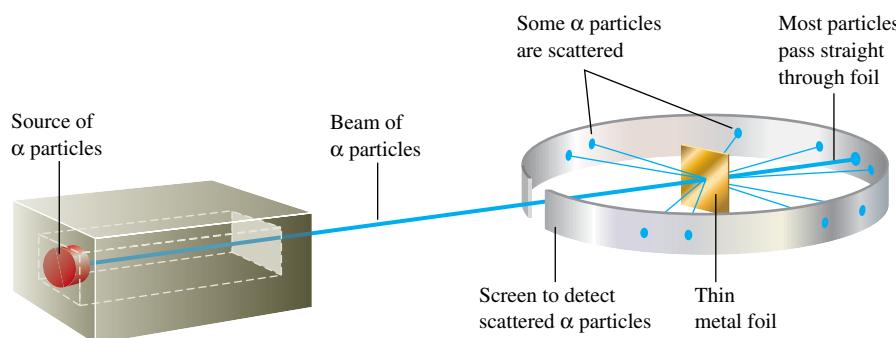
him to determine the magnitude of the electron charge (see Fig. 2.10). With this value and the charge-to-mass ratio determined by Thomson, Millikan was able to calculate the mass of the electron as 9.11×10^{-31} kilogram.

Radioactivity

In the late nineteenth century scientists discovered that certain elements produce high-energy radiation. For example, in 1896 the French scientist Henri Becquerel found accidentally that a piece of a mineral containing uranium could produce its image on a photographic plate in the absence of light. He attributed this phenomenon to a spontaneous emission of radiation by the uranium, which he called **radioactivity**. Studies in the early twentieth century demonstrated three types of radioactive emission: gamma (γ) rays, beta (β) particles, and alpha (α) particles. A γ ray is high-energy “light”; a β particle is a high-speed electron; and an α particle has a $2+$ charge, that is, a charge twice that of the electron and with the opposite sign. The mass of an α particle is 7300 times that of the electron. More modes of radioactivity are now known, and we will discuss them in Chapter 18. Here we will consider only α particles because they were used in some crucial early experiments.

The Nuclear Atom

In 1911 Ernest Rutherford (Fig. 2.11), who performed many of the pioneering experiments to explore radioactivity, carried out an experiment to test Thomson's plum pudding model. The experiment involved directing α particles at a thin sheet of metal foil, as illustrated in Fig. 2.12. Rutherford reasoned that if Thomson's model were accurate, the massive α particles should crash through the thin foil like cannonballs through gauze, as shown in Fig. 2.13(a). He expected the α particles to travel through the foil with, at the most, very minor deflections in their paths. The results of the experiment were very different from those Rutherford anticipated. Although most of the α particles passed straight through, many of the particles were deflected at large angles, as shown in Fig. 2.13(b), and some were reflected, never hitting the detector. This outcome was a great surprise to Rutherford. (He wrote that this result was comparable with shooting a howitzer at a piece of paper and having the shell reflected back.)

**FIGURE 2.12**

Rutherford's experiment on α -particle bombardment of metal foil.

Rutherford knew from these results that the plum pudding model for the atom could not be correct. The large deflections of the α particles could be caused only by a center of concentrated positive charge that contains most of the atom's mass, as illustrated in Fig. 2.13(b). Most of the α particles pass directly through the foil because the atom is mostly open space. The deflected α particles are those that had a “close encounter” with the massive positive center of the atom, and the few reflected α particles are those that made a “direct hit” on the much more massive positive center.

In Rutherford's mind these results could be explained only in terms of a **nuclear atom**—an atom with a dense center of positive charge (the **nucleus**) with electrons moving around the nucleus at a distance that is large relative to the nuclear radius.

2.5 The Modern View of Atomic Structure: An Introduction

The forces that bind the positively charged protons in the nucleus will be discussed in Chapter 18.

In the years since Thomson and Rutherford, a great deal has been learned about atomic structure. Because much of this material will be covered in detail in later chapters, only an introduction will be given here. The simplest view of the atom is that it consists of a tiny nucleus (with a diameter of about 10^{-13} cm) and electrons that move about the nucleus at an average distance of about 10^{-8} cm from it (see Fig. 2.14).

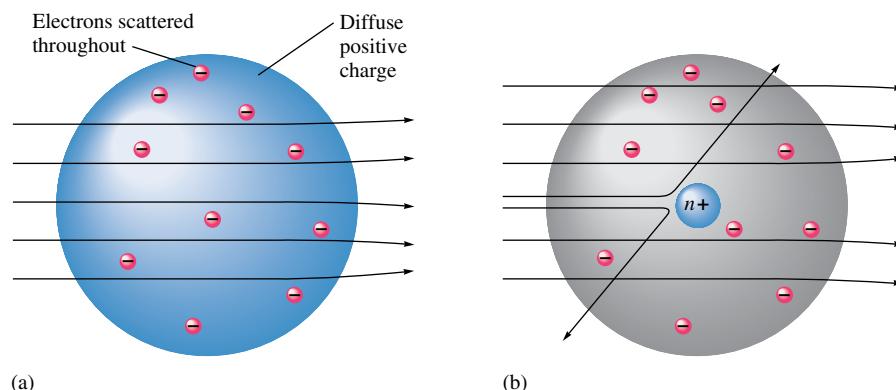
As we will see later, the chemistry of an atom mainly results from its electrons. For this reason, chemists can be satisfied with a relatively crude nuclear model. The nucleus is assumed to contain **protons**, which have a positive charge equal in magnitude to the electron's negative charge, and **neutrons**, which have virtually the same mass as a proton but no charge. The masses and charges of the electron, proton, and neutron are shown in Table 2.1.

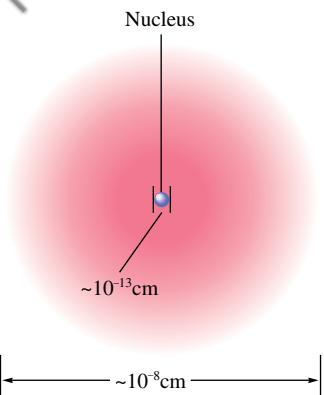


Visualization: Gold Foil Experiment

FIGURE 2.13

(a) The expected results of the metal foil experiment if Thomson's model were correct. (b) Actual results.



**FIGURE 2.14**

A nuclear atom viewed in cross section. Note that this drawing is not to scale.

The *chemistry* of an atom arises from its electrons.



If the atomic nucleus were the size of this ball bearing, a typical atom would be the size of this stadium.

Mass number
Atomic number → ${}_{\text{Z}}^{\text{A}}$ ← Element symbol

TABLE 2.1 The Mass and Charge of the Electron, Proton, and Neutron

Particle	Mass	Charge*
Electron	9.11×10^{-31} kg	1-
Proton	1.67×10^{-27} kg	1+
Neutron	1.67×10^{-27} kg	None

*The magnitude of the charge of the electron and the proton is 1.60×10^{-19} C.

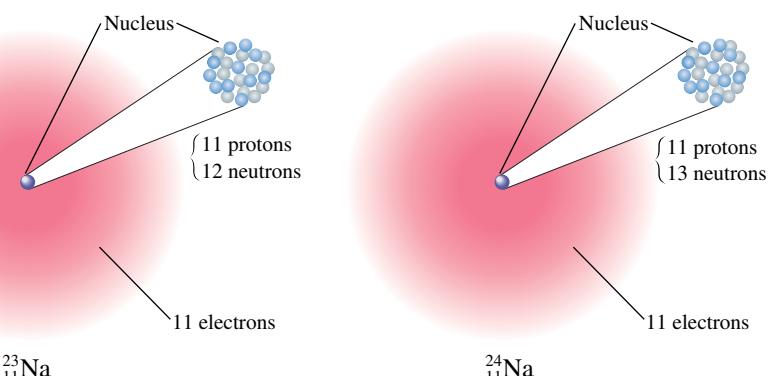
Two striking things about the nucleus are its small size compared with the overall size of the atom and its extremely high density. The tiny nucleus accounts for almost all the atom's mass. Its great density is dramatically demonstrated by the fact that a piece of nuclear material about the size of a pea would have a mass of 250 million tons!

An important question to consider at this point is, “*If all atoms are composed of these same components, why do different atoms have different chemical properties?*” The answer to this question lies in the number and the arrangement of the electrons. The electrons constitute most of the atomic volume and thus are the parts that “intermingle” when atoms combine to form molecules. Therefore, the number of electrons possessed by a given atom greatly affects its ability to interact with other atoms. As a result, the atoms of different elements, which have different numbers of protons and electrons, show different chemical behavior.

A sodium atom has 11 protons in its nucleus. Since atoms have no net charge, the number of electrons must equal the number of protons. Therefore, a sodium atom has 11 electrons moving around its nucleus. It is *always* true that a sodium atom has 11 protons and 11 electrons. However, each sodium atom also has neutrons in its nucleus, and different types of sodium atoms exist that have different numbers of neutrons. For example, consider the sodium atoms represented in Fig. 2.15. These two atoms are **isotopes**, or *atoms with the same number of protons but different numbers of neutrons*. Note that the symbol for one particular type of sodium atom is written



where the **atomic number Z** (number of protons) is written as a subscript, and the **mass number A** (the total number of protons and neutrons) is written as a superscript. (The particular atom represented here is called “sodium twenty-three.” It has 11 electrons, 11 protons, and 12 neutrons.) Because the chemistry of an atom is due to its electrons, isotopes show almost identical chemical properties. In nature most elements contain mixtures of isotopes.

**FIGURE 2.15**

Two isotopes of sodium. Both have 11 protons and 11 electrons, but they differ in the number of neutrons in their nuclei.



CHEMICAL IMPACT

Reading the History of Bogs

Scientists often “read” the history of the earth and its inhabitants using very different “books” than traditional historians. For example, the disappearance of the dinosaurs 65 million years ago in an “instant” of geological time was a great mystery until unusually high iridium and osmium levels were discovered at a position in the earth’s crust corresponding to that time. These high levels of iridium and osmium suggested that an extraterrestrial object had struck the earth 65 million years ago with catastrophic results for the dinosaurs. Since then, the huge buried crater caused by the object has been discovered on the Yucatan Peninsula, and virtually everyone is now convinced that this is the correct explanation for the disappearing dinosaurs.

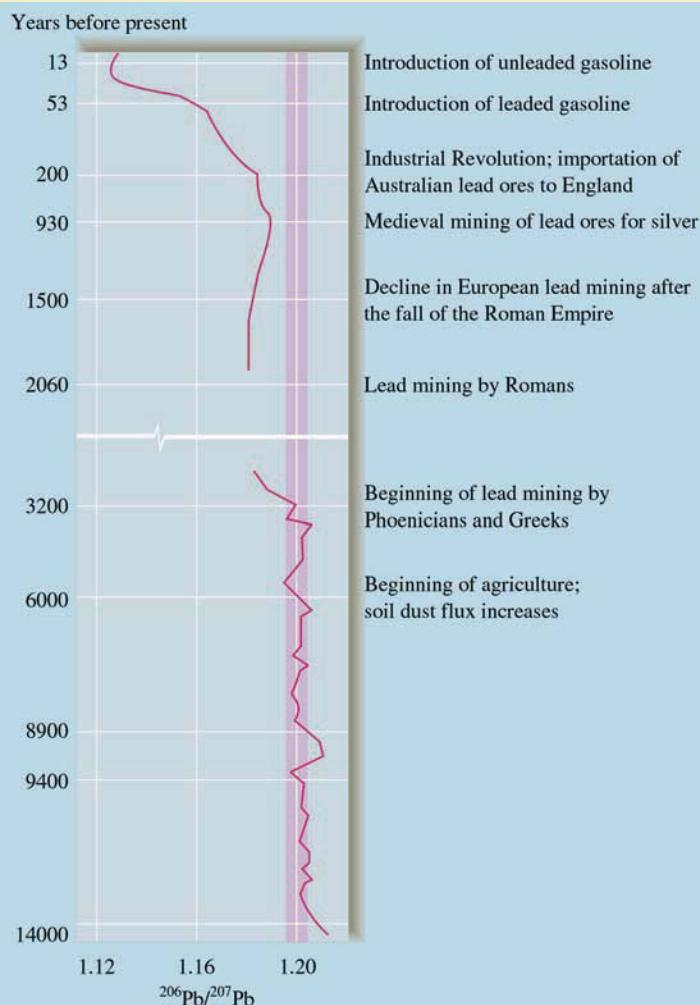
History is also being “read” by scientists studying ice cores from glaciers in Iceland. Now Swiss scientists have found that ancient peat bogs can furnish a reliable historical record. Geochemist William Shotyk of the University of Bern has found a 15,000-year window on history by analyzing the lead content of core samples from a Swiss mountainside peat bog [Science 281 (1998): 1635]. Various parts of the core samples were dated by ^{14}C dating techniques (see Chapter 18, Section 18.4, for more information) and analyzed for their scandium and lead contents. Also, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was measured for each sample. These data are represented in the accompanying figure. Notice that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio remains very close to 1.20 (see the red band in the figure) from 14,000 years to 3200 years. The value of 1.20 is the same as the average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the earth’s soil.

The core also reveals that the total lead and scandium levels increased simultaneously at the 6000-year mark but that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio remained close to 1.20. This coincides with the beginning of agriculture in Europe, which caused more soil dust to enter the atmosphere.

Significantly, about 3000 years ago the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreased markedly. This also corresponds in the core sample to an increase in total lead content out of proportion to the increase in scandium. This indicates the lead no longer resulted from soil dust but from other activities of humans—lead mining had begun. Since the 3000-year mark, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has remained well below 1.20, indicating that human use of lead ores has become the dominant source

of airborne lead. This is confirmed by the sharp decline in the ratio beginning 200 years ago that corresponds to the importation into England of Australian lead ores having low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios.

So far only lead has been used to read the history in the bog. However, Shotyk’s group is also measuring the changes in the levels of copper, zinc, cadmium, arsenic, mercury, and antimony. More interesting stories are sure to follow.



Geochemist William Shotyk’s analysis of the lead content of ice core samples reveals a 15,000-year history of lead levels. (Note: Dates are based on calibrated radiocarbon dating. Because the core was retrieved in two segments, a break in data occurs between 2060 and 3200 years before present.)

Sample Exercise 2.2**Writing the Symbols for Atoms**

Write the symbol for the atom that has an atomic number of 9 and a mass number of 19. How many electrons and how many neutrons does this atom have?

Solution

The atomic number 9 means the atom has 9 protons. This element is called *fluorine*, symbolized by F. The atom is represented as



and is called “fluorine nineteen.” Since the atom has 9 protons, it also must have 9 electrons to achieve electrical neutrality. The mass number gives the total number of protons and neutrons, which means that this atom has 10 neutrons.

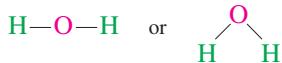
See Exercises 2.43 through 2.46.

2.6 Molecules and Ions

From a chemist’s viewpoint, the most interesting characteristic of an atom is its ability to combine with other atoms to form compounds. It was John Dalton who first recognized that chemical compounds are collections of atoms, but he could not determine the structure of atoms or their means for binding to each other. During the twentieth century we learned that atoms have electrons and that these electrons participate in bonding one atom to another. We will discuss bonding thoroughly in Chapters 8 and 9; here we will introduce some simple bonding ideas that will be useful in the next few chapters.

The forces that hold atoms together in compounds are called **chemical bonds**. One way that atoms can form bonds is by *sharing electrons*. These bonds are called **covalent bonds**, and the resulting collection of atoms is called a **molecule**. Molecules can be represented in several different ways. The simplest method is the **chemical formula**, in which the symbols for the elements are used to indicate the types of atoms present and subscripts are used to indicate the relative numbers of atoms. For example, the formula for carbon dioxide is CO₂, meaning that each molecule contains 1 atom of carbon and 2 atoms of oxygen.

Examples of molecules that contain covalent bonds are hydrogen (H₂), water (H₂O), oxygen (O₂), ammonia (NH₃), and methane (CH₄). More information about a molecule is given by its **structural formula**, in which the individual bonds are shown (indicated by lines). Structural formulas may or may not indicate the actual shape of the molecule. For example, water might be represented as



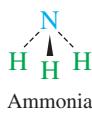
The structure on the right shows the actual shape of the water molecule. Scientists know from experimental evidence that the molecule looks like this. (We will study the shapes of molecules further in Chapter 8.) The structural formula for ammonia is shown in the margin at left.

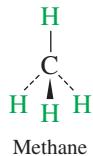
Note that atoms connected to the central atom by dashed lines are behind the plane of the paper, and atoms connected to the central atom by wedges are in front of the plane of the paper.

In a compound composed of molecules, the individual molecules move around as independent units. For example, a molecule of methane gas can be represented in several ways. The structural formula for methane (CH₄) is shown in Fig. 2.16. The **space-filling**

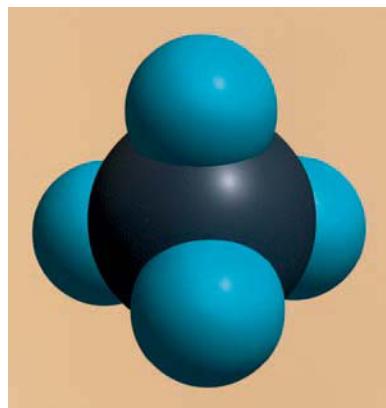


Visualization: Covalent Bonding



**FIGURE 2.16**

The structural formula for methane.

**FIGURE 2.17**

Space-filling model of methane. This type of model shows both the relative sizes of the atoms in the molecule and their spatial relationships.

**FIGURE 2.18**

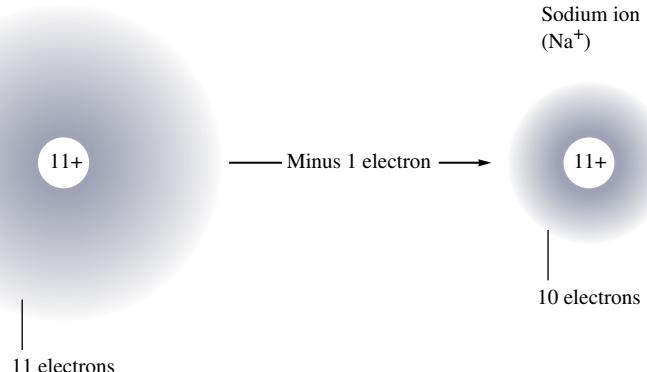
Ball-and-stick model of methane.

model of methane, which shows the relative sizes of the atoms as well as their relative orientation in the molecule, is given in Fig. 2.17. **Ball-and-stick models** are also used to represent molecules. The ball-and-stick structure of methane is shown in Fig. 2.18.

A second type of chemical bond results from attractions among ions. An **ion** is an atom or group of atoms that has a net positive or negative charge. The best-known ionic compound is common table salt, or sodium chloride, which forms when neutral chlorine and sodium react.

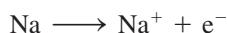
To see how the ions are formed, consider what happens when an electron is transferred from a sodium atom to a chlorine atom (the neutrons in the nuclei will be ignored):

Neutral sodium atom (Na)



Na^+ is usually called the *sodium ion* rather than the *sodium cation*. Also Cl^- is called the *chloride ion* rather than the *chloride anion*. In general, when a specific ion is referred to, the word *ion* rather than *cation* or *anion* is used.

With one electron stripped off, the sodium, with its 11 protons and only 10 electrons, now has a net $1+$ charge—it has become a *positive ion*. A positive ion is called a **cation**. The sodium ion is written as Na^+ , and the process can be represented in short-hand form as



If an electron is added to chlorine,

Chloride ion
(Cl^-)

Neutral chlorine
atom (Cl)

17+

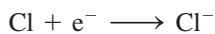
17 electrons

Plus 1 electron →

17+

18 electrons

the 18 electrons produce a net 1^- charge; the chlorine has become an *ion with a negative charge*—an **anion**. The chloride ion is written as Cl^- , and the process is represented as



Because anions and cations have opposite charges, they attract each other. This *force of attraction between oppositely charged ions* is called **ionic bonding**. As illustrated in Fig. 2.19, sodium metal and chlorine gas (a green gas composed of Cl_2 molecules) react

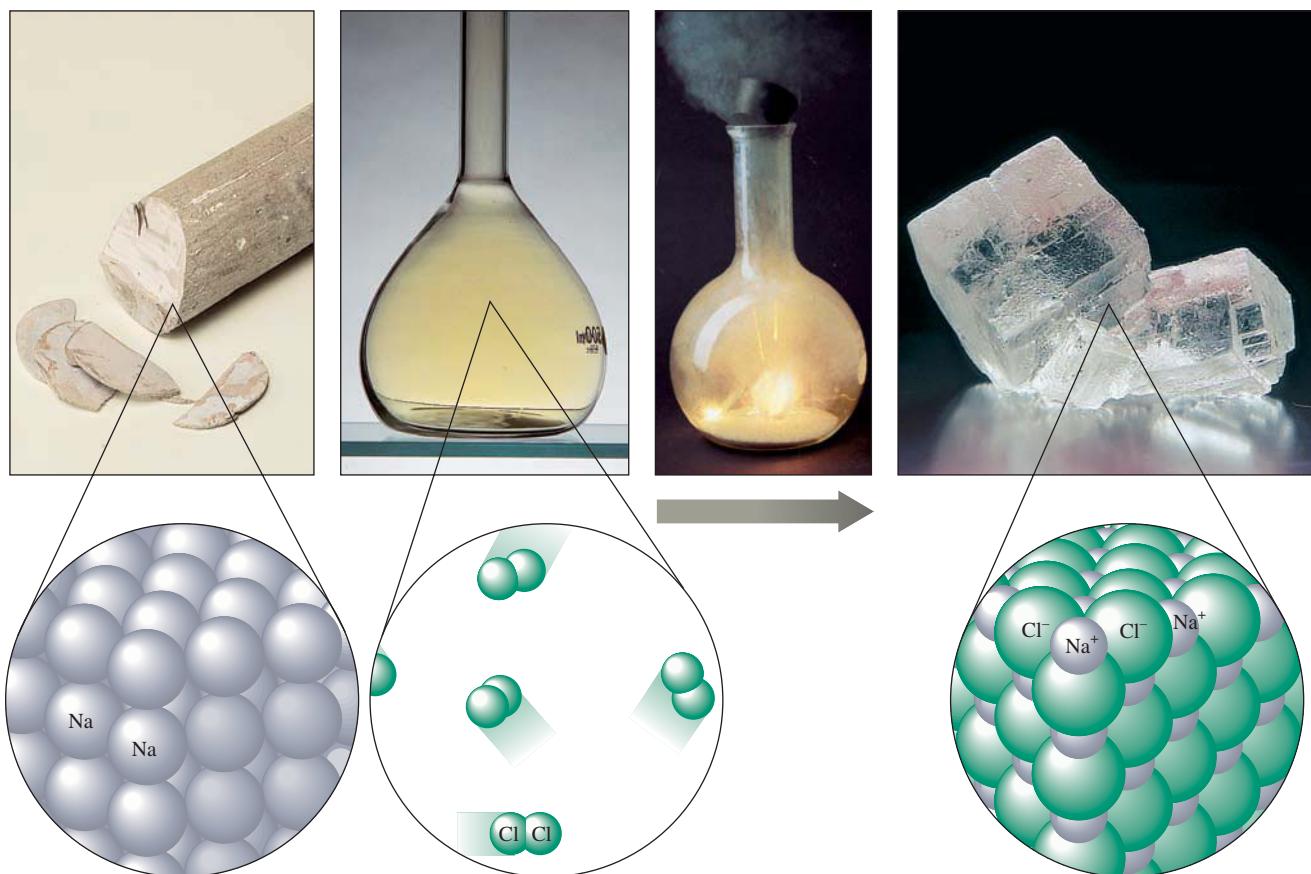
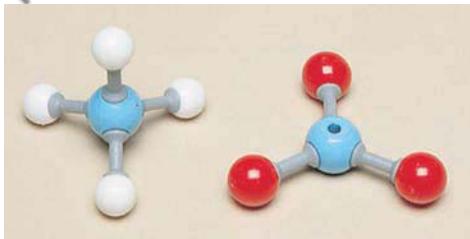


FIGURE 2.19

Sodium metal (which is so soft it can be cut with a knife and which consists of individual sodium atoms) reacts with chlorine gas (which contains Cl_2 molecules) to form solid sodium chloride (which contains Na^+ and Cl^- ions packed together).

**FIGURE 2.20**

Ball-and-stick models of the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-).



Visualization: Comparison of a Molecular Compound and an Ionic Compound

Metals tend to form positive ions; non-metals tend to form negative ions.

Elements in the same vertical column in the periodic table form a *group* (or *family*) and generally have similar properties.



Samples of chlorine gas, liquid bromine, and solid iodine.

to form solid sodium chloride, which contains many Na^+ and Cl^- ions packed together and forms the beautiful colorless cubic crystals shown in Fig. 2.19.

A solid consisting of oppositely charged ions is called an **ionic solid**, or a **salt**. Ionic solids can consist of simple ions, as in sodium chloride, or of **polyatomic** (many atom) **ions**, as in ammonium nitrate (NH_4NO_3), which contains ammonium ions (NH_4^+) and nitrate ions (NO_3^-). The ball-and-stick models of these ions are shown in Fig. 2.20.

2.7 An Introduction to the Periodic Table

In a room where chemistry is taught or practiced, a chart called the **periodic table** is almost certain to be found hanging on the wall. This chart shows all the known elements and gives a good deal of information about each. As our study of chemistry progresses, the usefulness of the periodic table will become more obvious. This section will simply introduce it to you.

A simplified version of the periodic table is shown in Fig. 2.21. The letters in the boxes are the symbols for the elements; these abbreviations are based on the current element names or the original names (see Table 2.2). The number shown above each symbol is the *atomic number* (number of protons) for that element. For example, carbon (C) has atomic number 6, and lead (Pb) has atomic number 82. Most of the elements are **metals**. Metals have characteristic physical properties such as efficient conduction of heat and electricity, malleability (they can be hammered into thin sheets), ductility (they can be pulled into wires), and (often) a lustrous appearance. Chemically, metals tend to *lose* electrons to form positive ions. For example, copper is a typical metal. It is lustrous (although it tarnishes readily); it is an excellent conductor of electricity (it is widely used in electrical wires); and it is readily formed into various shapes, such as pipes for water systems. Copper is also found in many salts, such as the beautiful blue copper sulfate, in which copper is present as Cu^{2+} ions. Copper is a member of the transition metals—the metals shown in the center of the periodic table.

The relatively few **nonmetals** appear in the upper-right corner of the table (to the right of the heavy line in Fig. 2.21), except hydrogen, a nonmetal that resides in the upper-left corner. The nonmetals lack the physical properties that characterize the metals. Chemically, they tend to *gain* electrons in reactions with metals to form negative ions. Nonmetals often bond to each other by forming covalent bonds. For example, chlorine is a typical nonmetal. Under normal conditions it exists as Cl_2 molecules; it reacts with metals to form salts containing Cl^- ions (NaCl , for example); and it forms covalent bonds with nonmetals (for example, hydrogen chloride gas, HCl).

The periodic table is arranged so that elements in the same vertical columns (called **groups** or **families**) have *similar chemical properties*. For example, all of the **alkali metals**, members of Group 1A—lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr)—are very active elements that readily form ions with a 1+ charge when they react with nonmetals. The members of Group 2A—beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra)—are called the **alkaline earth metals**. They all form ions with a 2+ charge when they react with nonmetals. The **halogens**, the members of Group 7A—fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At)—all form diatomic molecules. Fluorine, chlorine, bromine, and iodine all react with metals to form salts containing ions with a 1− charge (F^- , Cl^- , Br^- , and I^-). The members of Group 8A—helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn)—are known as the **noble gases**. They all exist under normal conditions as monatomic (single-atom) gases and have little chemical reactivity.

56 Chapter Two Atoms, Molecules, and Ions

The periodic table displays elements from hydrogen (H) to lawrencium (Lr). It highlights several groups: Alkaline earth metals (1A, 2A), Alkali metals (11), Halogens (17), Noble gases (2), and Transition metals (3-12). The Lanthanide and Actinide series are shown as rows below the main table.

Periodic Table of Elements																											
Alkaline earth metals		Transition metals														Noble gases											
1 1A H	2 2A Be	3 Li	4 Be	5	6	7	8	9	10	11	12	13 3A Al	14 4A Si	15 5A P	16 6A S	17 7A Cl	2 He Ne										
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
19 K	20 Ca	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe								
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn										
87 Fr	88 Ra	89 Ac [†]	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup													
*Lanthanides		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu												
		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr												

FIGURE 2.21

The periodic table.

TABLE 2.2 The Symbols for the Elements That Are Based on the Original Names

Current Name	Original Name	Symbol
Antimony	Stibium	Sb
Copper	Cuprum	Cu
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Mercury	Hydrargyrum	Hg
Potassium	Kalium	K
Silver	Argentum	Ag
Sodium	Natrium	Na
Tin	Stannum	Sn
Tungsten	Wolfram	W



CHEMICAL IMPACT

Hassium Fits Right in

Hassium, element 108, does not exist in nature but must be made in a particle accelerator. It was first created in 1984 and can be made by shooting magnesium-26 ($^{26}_{12}\text{Mg}$) atoms at curium-248 ($^{248}_{96}\text{Cm}$) atoms. The collisions between these atoms produce some hassium-265 ($^{265}_{108}\text{Hs}$) atoms. The position of hassium in the periodic table (see Fig. 2.21) in the vertical column containing iron, ruthenium, and osmium suggests that hassium should have chemical properties similar to these metals. However, it is not easy to test this prediction—only a few atoms of hassium can be made at a given time and they last for only about 9 seconds. Imagine having to get your next lab experiment done in 9 seconds!

Amazingly, a team of chemists from the Lawrence Berkeley National Laboratory in California, the Paul Scherrer

Institute and the University of Bern in Switzerland, and the Institute of Nuclear Chemistry in Germany have done experiments to characterize the chemical behavior of hassium. For example, they have observed that hassium atoms react with oxygen to form a hassium oxide compound of the type expected from its position on the periodic table. The team has also measured other properties of hassium, including the energy released as it undergoes nuclear decay to another atom.

This work would have surely pleased Dmitri Mendeleev (see Fig. 7.23), who originally developed the periodic table and showed its power to predict chemical properties.

Note from Fig. 2.21 that alternate sets of symbols are used to denote the groups. The symbols 1A through 8A are the traditional designations, whereas the numbers 1 to 18 have been suggested recently. In this text the 1A to 8A designations will be used.

The horizontal rows of elements in the periodic table are called **periods**. Horizontal row 1 is called the *first period* (it contains H and He); row 2 is called the *second period* (elements Li through Ne); and so on.

We will learn much more about the periodic table as we continue with our study of chemistry. Meanwhile, when an element is introduced in this text, you should always note its position on the periodic table.

Another format of the periodic table will be discussed in Section 7.11.

2.8 Naming Simple Compounds

When chemistry was an infant science, there was no system for naming compounds. Names such as sugar of lead, blue vitrol, quicklime, Epsom salts, milk of magnesia, gypsum, and laughing gas were coined by early chemists. Such names are called *common names*. As chemistry grew, it became clear that using common names for compounds would lead to unacceptable chaos. Nearly 5 million chemical compounds are currently known. Memorizing common names for these compounds would be an impossible task.

The solution, of course, is to adopt a *system* for naming compounds in which the name tells something about the composition of the compound. After learning the system, a chemist given a formula should be able to name the compound or, given a name, should be able to construct the compound's formula. In this section we will specify the most important rules for naming compounds other than organic compounds (those based on chains of carbon atoms).

We will begin with the systems for naming inorganic **binary compounds**—compounds composed of two elements—which we classify into various types for easier recognition. We will consider both ionic and covalent compounds.

TABLE 2.3 Common Monatomic Cations and Anions

Cation	Name	Anion	Name
H ⁺	Hydrogen	H ⁻	Hydride
Li ⁺	Lithium	F ⁻	Fluoride
Na ⁺	Sodium	Cl ⁻	Chloride
K ⁺	Potassium	Br ⁻	Bromide
Cs ⁺	Cesium	I ⁻	Iodide
Be ²⁺	Beryllium	O ²⁻	Oxide
Mg ²⁺	Magnesium	S ²⁻	Sulfide
Ca ²⁺	Calcium	N ³⁻	Nitride
Ba ²⁺	Barium	P ³⁻	Phosphide
Al ³⁺	Aluminum		
Ag ⁺	Silver		

Binary Ionic Compounds (Type I)

Binary ionic compounds contain a positive ion (cation) always written first in the formula and a negative ion (anion). In naming these compounds, the following rules apply:

1. The cation is always named first and the anion second.
2. A monatomic (meaning “one-atom”) cation takes its name from the name of the element. For example, Na⁺ is called sodium in the names of compounds containing this ion.
3. A monatomic anion is named by taking the root of the element name and adding *-ide*. Thus the Cl⁻ ion is called chloride.

Some common monatomic cations and anions and their names are given in Table 2.3.

The rules for naming binary ionic compounds are illustrated by the following examples:

A monatomic cation has the same name as its parent element.

In formulas of ionic compounds, simple ions are represented by the element symbol: Cl means Cl⁻, Na means Na⁺, and so on.

Compound	Ions Present	Name
NaCl	Na ⁺ , Cl ⁻	Sodium chloride
KI	K ⁺ , I ⁻	Potassium iodide
CaS	Ca ²⁺ , S ²⁻	Calcium sulfide
Li ₃ N	Li ⁺ , N ³⁻	Lithium nitride
CsBr	Cs ⁺ , Br ⁻	Cesium bromide
MgO	Mg ²⁺ , O ²⁻	Magnesium oxide

Sample Exercise 2.3

Naming Type I Binary Compounds

Name each binary compound.

- a. CsF b. AlCl₃ c. LiH

Solution

- a. CsF is cesium fluoride.
 b. AlCl₃ is aluminum chloride.
 c. LiH is lithium hydride.

Notice that, in each case, the cation is named first, and then the anion is named.

See Exercise 2.55.



Visualization: Formation of Ionic Compounds

TABLE 2.4 Common Type II Cations

Ion	Systematic Name
Fe ³⁺	Iron(III)
Fe ²⁺	Iron(II)
Cu ²⁺	Copper(II)
Cu ⁺	Copper(I)
Co ³⁺	Cobalt(III)
Co ²⁺	Cobalt(II)
Sn ⁴⁺	Tin(IV)
Sn ²⁺	Tin(II)
Pb ⁴⁺	Lead(IV)
Pb ²⁺	Lead(II)
Hg ²⁺	Mercury(II)
Hg ₂ ^{2+*}	Mercury(I)
Ag ⁺	Silver†
Zn ²⁺	Zinc†
Cd ²⁺	Cadmium†

*Note that mercury(I) ions always occur bound together to form Hg₂²⁺ ions.

†Although these are transition metals, they form only one type of ion, and a Roman numeral is not used.

Sample Exercise 2.4

Formulas from Names for Type I Binary Compounds

Given the following systematic names, write the formula for each compound:

- potassium iodide
- calcium oxide
- gallium bromide

Solution

Name	Formula	Comments
a. potassium iodide	KI	Contains K ⁺ and I ⁻ .
b. calcium oxide	CaO	Contains Ca ²⁺ and O ²⁻ .
c. gallium bromide	GaBr ₃	Contains Ga ³⁺ and Br ⁻ . Must have 3Br ⁻ to balance charge of Ga ³⁺ .

See Exercise 2.55.

Sample Exercise 2.5

Naming Type II Binary Compounds

- Give the systematic name for each of the following compounds:

- CuCl
- HgO
- Fe₂O₃

- Given the following systematic names, write the formula for each compound:

- Manganese(IV) oxide
- Lead(II) chloride

60 Chapter Two Atoms, Molecules, and Ions

Type II binary ionic compounds contain a metal that can form more than one type of cation.

A compound must be electrically neutral.

Solution

All of these compounds include a metal that can form more than one type of cation. Thus we must first determine the charge on each cation. This can be done by recognizing that a compound must be electrically neutral; that is, the positive and negative charges must exactly balance.

1.

Formula	Name	Comments
a. CuCl	Copper(I) chloride	Because the anion is Cl^- , the cation must be Cu^+ (for charge balance), which requires a Roman numeral I.
b. HgO	Mercury(II) oxide	Because the anion is O^{2-} , the cation must be Hg^{2+} [mercury(II)].
c. Fe_2O_3	Iron(III) oxide	The three O^{2-} ions carry a total charge of $6-$, so two Fe^{3+} ions [iron(III)] are needed to give a $6+$ charge.

2.

Name	Formula	Comments
a. Manganese(IV) oxide	MnO_2	Two O^{2-} ions (total charge $4-$) are required by the Mn^{4+} ion [manganese(IV)].
b. Lead(II) chloride	PbCl_2	Two Cl^- ions are required by the Pb^{2+} ion [lead(II)] for charge balance.

See Exercise 2.56.

A compound containing a transition metal usually requires a Roman numeral in its name.



Crystals of copper(II) sulfate.

Note that the use of a Roman numeral in a systematic name is required only in cases where more than one ionic compound forms between a given pair of elements. This case most commonly occurs for compounds containing transition metals, which often form more than one cation. *Elements that form only one cation do not need to be identified by a Roman numeral.* Common metals that do not require Roman numerals are the Group 1A elements, which form only $1+$ ions; the Group 2A elements, which form only $2+$ ions; and aluminum, which forms only Al^{3+} . The element silver deserves special mention at this point. In virtually all its compounds silver is found as the Ag^+ ion. Therefore, although silver is a transition metal (and can potentially form ions other than Ag^+), silver compounds are usually named without a Roman numeral. Thus AgCl is typically called silver chloride rather than silver(I) chloride, although the latter name is technically correct. Also, a Roman numeral is not used for zinc compounds, since zinc forms only the Zn^{2+} ion.

As shown in Sample Exercise 2.5, when a metal ion is present that forms more than one type of cation, the charge on the metal ion must be determined by balancing the positive and negative charges of the compound. To do this you must be able to recognize the common cations and anions and know their charges (see Tables 2.3 and 2.5).

Sample Exercise 2.6

Naming Binary Compounds

1. Give the systematic name for each of the following compounds:



2. Given the following systematic names, write the formula for each compound:

- a. Chromium(III) chloride
b. Gallium iodide

Solution**1.**

Formula	Name	Comments
a. CoBr_2	Cobalt(II) bromide	Cobalt is a transition metal; the compound name must have a Roman numeral. The two Br^- ions must be balanced by a Co^{2+} ion.
b. CaCl_2	Calcium chloride	Calcium, an alkaline earth metal, forms only the Ca^{2+} ion. A Roman numeral is not necessary.
c. Al_2O_3	Aluminum oxide	Aluminum forms only the Al^{3+} ion. A Roman numeral is not necessary.

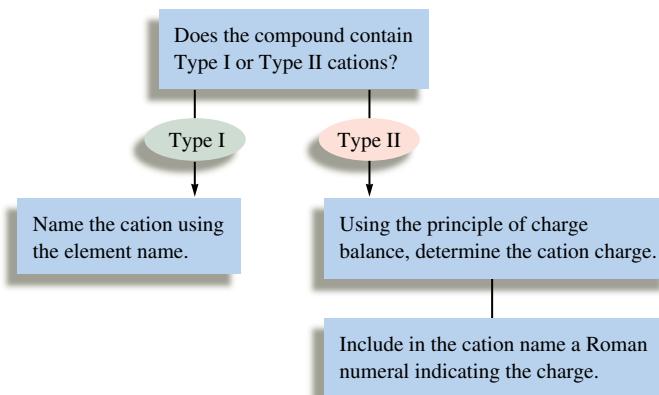
2.

Name	Formula	Comments
a. Chromium(III) chloride	CrCl_3	Chromium(III) indicates that Cr^{3+} is present, so 3 Cl^- ions are needed for charge balance.
b. Gallium iodide	GaI_3	Gallium always forms 3+ ions, so 3 I^- ions are required for charge balance.

See Exercises 2.57 and 2.58.

Various chromium compounds dissolved in water. From left to right: CrCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cr}(\text{NO}_3)_3$, CrCl_3 , K_2CrO_4 .

The following flowchart is useful when you are naming binary ionic compounds:



The common Type I and Type II ions are summarized in Fig. 2.22. Also shown in Fig. 2.22 are the common monatomic ions.

1A	2A											8A	
Li^+													
Na^+	Mg^{2+}												
K^+	Ca^{2+}				Cr^{2+} Cr^{3+}	Mn^{2+} Mn^{3+}	Fe^{2+} Fe^{3+}	Co^{2+} Co^{3+}	Cu^+ Cu^{2+}	Zn^{2+}			
Rb^+	Sr^{2+}								Ag^+	Cd^{2+}		Sn^{2+} Sn^{4+}	
Cs^+	Ba^{2+}									Hg^{2+} Hg^{4+}		Pb^{2+} Pb^{4+}	

FIGURE 2.22
The common cations and anions.

Common Type I cations

Common Type II cations

Common monatomic anions

TABLE 2.5 Common Polyatomic Ions

Ion	Name	Ion	Name
Hg_2^{2+}	Mercury(I)	NCS^-	Thiocyanate
NH_4^+	Ammonium	CO_3^{2-}	Carbonate
NO_2^-	Nitrite	HCO_3^-	Hydrogen carbonate (bicarbonate is a widely used common name)
NO_3^-	Nitrate		
SO_3^{2-}	Sulfite	ClO^-	Hypochlorite
SO_4^{2-}	Sulfate	ClO_2^-	Chlorite
HSO_4^-	Hydrogen sulfate (bisulfate is a widely used common name)	ClO_3^-	Chlorate
OH^-	Hydroxide	ClO_4^-	Perchlorate
CN^-	Cyanide	$\text{C}_2\text{H}_3\text{O}_2^-$	Acetate
PO_4^{3-}	Phosphate	MnO_4^-	Permanganate
HPO_4^{2-}	Hydrogen phosphate	$\text{Cr}_2\text{O}_7^{2-}$	Dichromate
H_2PO_4^-	Dihydrogen phosphate	CrO_4^{2-}	Chromate
		O_2^{2-}	Peroxide
		$\text{C}_2\text{O}_4^{2-}$	Oxalate

Polyatomic ion formulas must be memorized.

Ionic Compounds with Polyatomic Ions

We have not yet considered ionic compounds that contain polyatomic ions. For example, the compound ammonium nitrate, NH_4NO_3 , contains the polyatomic ions NH_4^+ and NO_3^- . Polyatomic ions are assigned special names that *must be memorized* to name the compounds containing them. The most important polyatomic ions and their names are listed in Table 2.5.

Note in Table 2.5 that several series of anions contain an atom of a given element and different numbers of oxygen atoms. These anions are called **oxyanions**. When there are two members in such a series, the name of the one with the smaller number of oxygen atoms ends in *-ite* and the name of the one with the larger number ends in *-ate*—for example, sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}). When more than two oxyanions make up a series, *hypo-* (less than) and *per-* (more than) are used as prefixes to name the members of the series with the fewest and the most oxygen atoms, respectively. The best example involves the oxyanions containing chlorine, as shown in Table 2.5.

Sample Exercise 2.7

Naming Compounds Containing Polyatomic Ions

1. Give the systematic name for each of the following compounds:

- a. Na_2SO_4
- b. KH_2PO_4
- c. $\text{Fe}(\text{NO}_3)_3$
- d. $\text{Mn}(\text{OH})_2$
- e. Na_2SO_3
- f. Na_2CO_3

2. Given the following systematic names, write the formula for each compound:

- a. Sodium hydrogen carbonate
- b. Cesium perchlorate

- c. Sodium hypochlorite
- d. Sodium selenate
- e. Potassium bromate

Solution

1.

Formula	Name	Comments
a. Na_2SO_4	Sodium sulfate	
b. KH_2PO_4	Potassium dihydrogen phosphate	
c. $\text{Fe}(\text{NO}_3)_3$	Iron(III) nitrate	Transition metal—name must contain a Roman numeral. The Fe^{3+} ion balances three NO_3^- ions.
d. $\text{Mn}(\text{OH})_2$	Manganese(II) hydroxide	Transition metal—name must contain a Roman numeral. The Mn^{2+} ion balances three OH^- ions.
e. Na_2SO_3	Sodium sulfite	
f. Na_2CO_3	Sodium carbonate	

2.

Name	Formula	Comments
a. Sodium hydrogen carbonate	NaHCO_3	Often called sodium bicarbonate.
b. Cesium perchlorate	CsClO_4	
c. Sodium hypochlorite	NaOCl	
d. Sodium selenate	Na_2SeO_4	Atoms in the same group, like sulfur and selenium, often form similar ions that are named similarly. Thus SeO_4^{2-} is selenate, like SO_4^{2-} (sulfate).
e. Potassium bromate	KBrO_3	As above, BrO_3^- is bromate, like ClO_3^- (chlorate).

See Exercises 2.59 and 2.60.

Binary Covalent Compounds (Type III)

In *binary covalent compounds*, the element names follow the same rules as for binary ionic compounds.

Binary covalent compounds are formed between *two nonmetals*. Although these compounds do not contain ions, they are named very similarly to binary ionic compounds.

In the naming of binary covalent compounds, the following rules apply:

1. The first element in the formula is named first, using the full element name.
2. The second element is named as if it were an anion.
3. Prefixes are used to denote the numbers of atoms present. These prefixes are given in Table 2.6.
4. The prefix *mono-* is never used for naming the first element. For example, CO is called carbon monoxide, *not* monocarbon monoxide.

TABLE 2.6 Prefixes Used to Indicate Number in Chemical Names

Prefix	Number Indicated
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

To see how these rules apply, we will now consider the names of the several covalent compounds formed by nitrogen and oxygen:

Compound	Systematic Name	Common Name
N ₂ O	Dinitrogen monoxide	Nitrous oxide
NO	Nitrogen monoxide	Nitric oxide
NO ₂	Nitrogen dioxide	
N ₂ O ₃	Dinitrogen trioxide	
N ₂ O ₄	Dinitrogen tetroxide	
N ₂ O ₅	Dinitrogen pentoxide	

Notice from the preceding examples that to avoid awkward pronunciations, we often drop the final *o* or *a* of the prefix when the element begins with a vowel. For example, N₂O₄ is called dinitrogen tetroxide, *not* dinitrogen tetraoxide, and CO is called carbon monoxide, *not* carbon monooxide.

Some compounds are always referred to by their common names. The two best examples are water and ammonia. The systematic names for H₂O and NH₃ are never used.

Sample Exercise 2.8

Naming Type III Binary Compounds

1. Name each of the following compounds:

- a. PCl₅
- b. PCl₃
- c. SO₂

2. From the following systematic names, write the formula for each compound:

- a. Sulfur hexafluoride
- b. Sulfur trioxide
- c. Carbon dioxide

Solution

1.

Formula	Name
a. PCl ₅	Phosphorus pentachloride
b. PCl ₃	Phosphorus trichloride
c. SO ₂	Sulfur dioxide

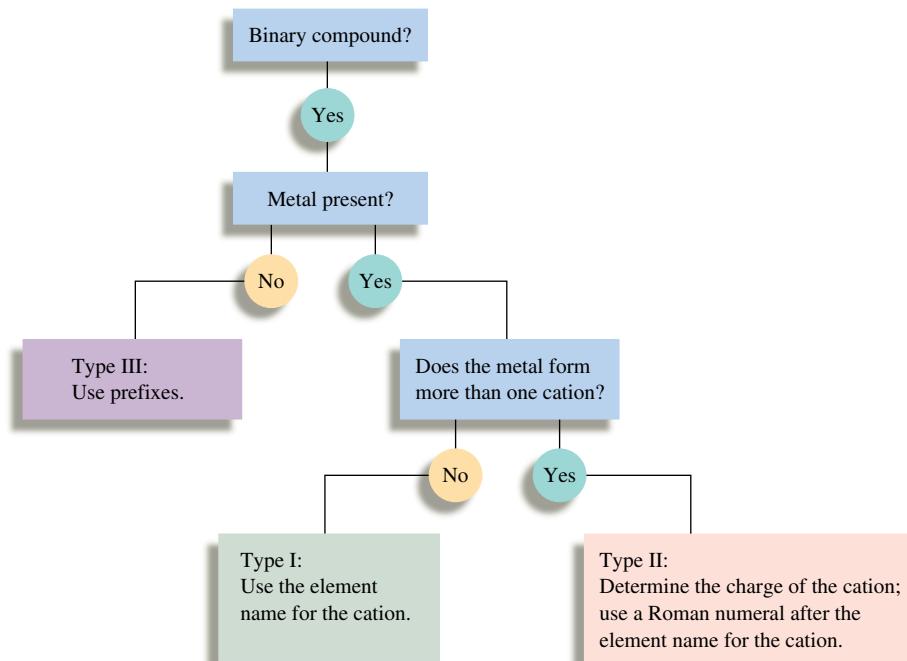
2.

Name	Formula
a. Sulfur hexafluoride	SF ₆
b. Sulfur trioxide	SO ₃
c. Carbon dioxide	CO ₂

See Exercises 2.61 and 2.62.

The rules for naming binary compounds are summarized in Fig. 2.23. Prefixes to indicate the number of atoms are used only in Type III binary compounds (those containing two nonmetals). An overall strategy for naming compounds is given in Fig. 2.24.

FÉUEWH

**FIGURE 2.23**

A flowchart for naming binary compounds.

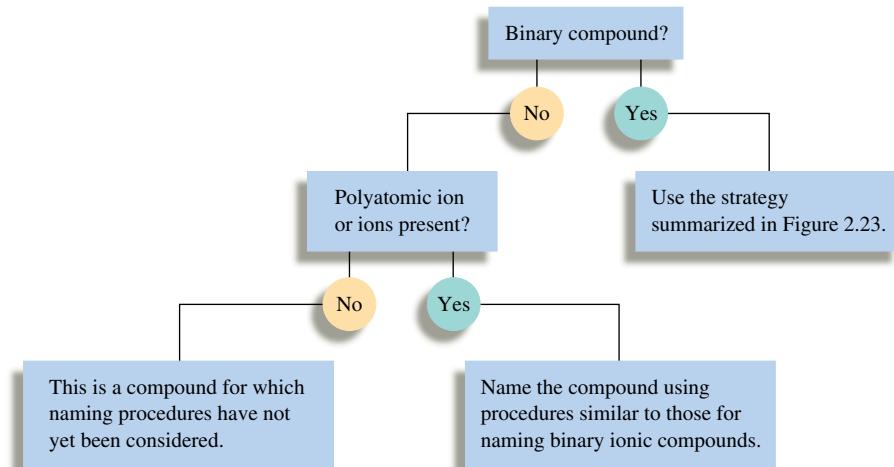
Sample Exercise 2.9**Naming Various Types of Compounds**

1. Give the systematic name for each of the following compounds:

- P_4O_{10}
- Nb_2O_5
- Li_2O_2
- $Ti(NO_3)_4$

2. Given the following systematic names, write the formula for each compound:

- Vanadium(V) fluoride
- Dioxygen difluoride
- Rubidium peroxide
- Gallium oxide

**FIGURE 2.24**

Overall strategy for naming chemical compounds.

Solution**1.**

Compound	Name	Comment
a. P_4O_{10}	Tetraphosphorus decaoxide	Binary covalent compound (Type III), so prefixes are used. The <i>a</i> in <i>deca-</i> is sometimes dropped.
b. Nb_2O_5	Niobium(V) oxide	Type II binary compound containing Nb^{5+} and O_2^{2-} ions. Niobium is a transition metal and requires a Roman numeral.
c. Li_2O_2	Lithium peroxide	Type I binary compound containing the Li^+ and O_2^{2-} (peroxide) ions.
d. $Ti(NO_3)_4$	Titanium(IV) nitrate	Not a binary compound. Contains the Ti^{4+} and NO_3^- ions. Titanium is a transition metal and requires a Roman numeral.

2.

Name	Chemical Formula	Comment
a. Vanadium(V) fluoride	VF_5	The compound contains V^{5+} ions and requires five F^- ions for charge balance.
b. Dioxygen difluoride	O_2F_2	The prefix <i>di-</i> indicates two of each atom.
c. Rubidium peroxide	Rb_2O_2	Because rubidium is in Group 1A, it forms only $1+$ ions. Thus two Rb^+ ions are needed to balance the $2-$ charge on the peroxide ion (O_2^{2-}).
d. Gallium oxide	Ga_2O_3	Because gallium is in Group 3A, like aluminum, it forms only $3+$ ions. Two Ga^{3+} ions are required to balance the charge on three O^{2-} ions.

*See Exercises 2.63, 2.65, and 2.66.***Acids**

Acids can be recognized by the hydrogen that appears first in the formula.

When dissolved in water, certain molecules produce a solution containing free H^+ ions (protons). These substances, **acids**, will be discussed in detail in Chapters 4, 14, and 15. Here we will simply present the rules for naming acids.

An acid can be viewed as a molecule with one or more H^+ ions attached to an anion. The rules for naming acids depend on whether the anion contains oxygen. If the *anion does not contain oxygen*, the acid is named with the prefix *hydro-* and the suffix *-ic*. For example, when gaseous HCl is dissolved in water, it forms hydrochloric acid. Similarly, HCN and H_2S dissolved in water are called hydrocyanic and hydrosulfuric acids, respectively.

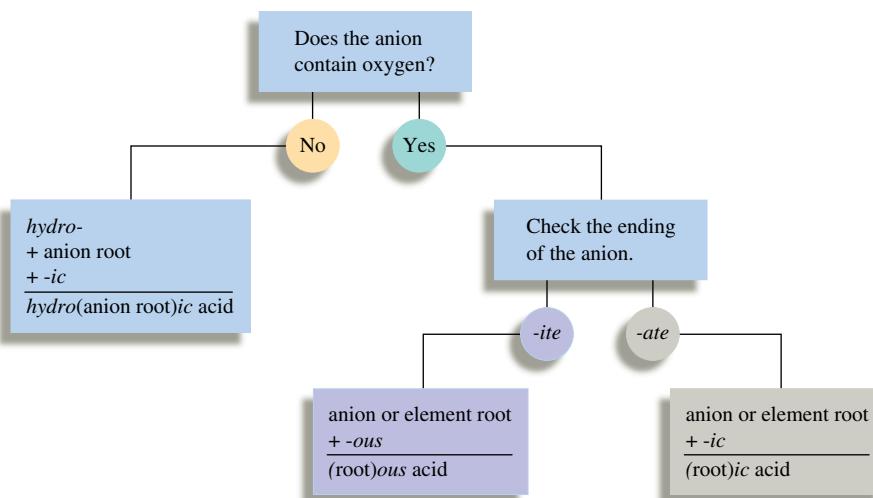
When the *anion contains oxygen*, the acidic name is formed from the root name of the anion with a suffix of *-ic* or *-ous*, depending on the name of the anion.

- If the anion name ends in *-ate*, the suffix *-ic* is added to the root name. For example, H_2SO_4 contains the sulfate anion (SO_4^{2-}) and is called sulfuric acid; H_3PO_4 contains the phosphate anion (PO_4^{3-}) and is called phosphoric acid; and $HC_2H_3O_2$ contains the acetate ion ($C_2H_3O_2^-$) and is called acetic acid.
- If the anion has an *-ite* ending, the *-ite* is replaced by *-ous*. For example, H_2SO_3 , which contains sulfite (SO_3^{2-}), is named sulfurous acid; and HNO_2 , which contains nitrite (NO_2^-), is named nitrous acid.

TABLE 2.7 Names of Acids* That Do Not Contain Oxygen

Acid	Name
HF	Hydrofluoric acid
HCl	Hydrochloric acid
HBr	Hydrobromic acid
HI	Hydroiodic acid
HCN	Hydrocyanic acid
H ₂ S	Hydrosulfuric acid

*Note that these acids are aqueous solutions containing these substances.

**FIGURE 2.25**

A flowchart for naming acids. An acid is best considered as one or more H⁺ ions attached to an anion.

TABLE 2.8 Names of Some Oxygen-Containing Acids

Acid	Name
HNO ₃	Nitric acid
HNO ₂	Nitrous acid
H ₂ SO ₄	Sulfuric acid
H ₂ SO ₃	Sulfurous acid
H ₃ PO ₄	Phosphoric acid
HC ₂ H ₃ O ₂	Acetic Acid

The application of these rules can be seen in the names of the acids of the oxyanions of chlorine:

Acid	Anion	Name
HClO ₄	Perchlorate	Perchloric acid
HClO ₃	Chlorate	Chloric acid
HClO ₂	Chlorite	Chlorous acid
HClO	Hypochlorite	Hypochlorous acid

The names of the most important acids are given in Tables 2.7 and 2.8. An overall strategy for naming acids is shown in Fig. 2.25.

Key Terms

Section 2.2

law of conservation of mass
law of definite proportion
law of multiple proportions

Section 2.3

atomic masses
atomic weights
Avogadro's hypothesis

Section 2.4

cathode-ray tube
electron
radioactivity
nuclear atom
nucleus

Section 2.5

proton
neutron
isotopes
atomic number
mass number

For Review

Fundamental laws

- Conservation of mass
- Definite proportion
- Multiple proportions

Dalton's atomic theory

- All elements are composed of atoms.
- All atoms of a given element are identical.
- Chemical compounds are formed when atoms combine.
- Atoms are not changed in chemical reactions but the way they are bound together changes.

Early atomic experiments and models

- Thomson model
- Millikan experiment
- Rutherford experiment
- Nuclear model

Section 2.6

chemical bond
covalent bond
molecule
chemical formula
structural formula
space-filling model
ball-and-stick model
ion
cation
anion
ionic bond
ionic solid (salt)
polyatomic ion

Section 2.7

periodic table
metal
nonmetal
group (family)
alkali metals
alkaline earth metals
halogens
noble gases
period

Section 2.8

binary compounds
binary ionic compounds
oxyanions
binary covalent compounds
acid

Atomic structure

- Small dense nucleus contains protons and neutrons.
 - Protons—positive charge
 - Neutrons—no charge
- Electrons reside outside the nucleus in the relatively large remaining atomic volume.
 - Electrons—negative charge, small mass (1/1840 of proton)
- Isotopes have the same atomic number but different mass numbers.

Atoms combine to form molecules by sharing electrons to form covalent bonds.

- Molecules are described by chemical formulas.
- Chemical formulas show number and type of atoms.
 - Structural formula
 - Ball-and-stick model
 - Space-filling model

Formation of ions

- Cation—formed by loss of an electron, positive charge
- Anion—formed by gain of an electron, negative charge
- Ionic bonds—formed by interaction of cations and anions

The periodic table organizes elements in order of increasing atomic number.

- Elements with similar properties are in columns, or groups.
- Metals are in the majority and tend to form cations.
- Nonmetals tend to form anions.

Compounds are named using a system of rules depending on the type of compound.

- Binary compounds
 - Type I—contain a metal that always forms the same cation
 - Type II—contain a metal that can form more than one cation
 - Type III—contain two nonmetals
- Compounds containing a polyatomic ion

REVIEW QUESTIONS

1. Use Dalton's atomic theory to account for each of the following.
 - a. the law of conservation of mass
 - b. the law of definite proportion
 - c. the law of multiple proportions
2. What evidence led to the conclusion that cathode rays had a negative charge?
3. What discoveries were made by J. J. Thomson, Henri Becquerel, and Lord Rutherford? How did Dalton's model of the atom have to be modified to account for these discoveries?
4. Consider Ernest Rutherford's alpha-particle bombardment experiment illustrated in Figure 2.12. How did the results of this experiment lead Rutherford away from the plum pudding model of the atom to propose the nuclear model of the atom?
5. Do the proton and the neutron have exactly the same mass? How do the masses of the proton and neutron compare to the mass of the electron? Which particles make the greatest contribution to the mass of an atom? Which particles make the greatest contribution to the chemical properties of an atom?
6. What is the distinction between atomic number and mass number? Between mass number and atomic mass?
7. Distinguish between the terms *family* and *period* in connection with the periodic table. For which of these terms is the term *group* also used?
8. The compounds AlCl_3 , CrCl_3 , and ICl_3 have similar formulas, yet each follows a different set of rules to name it. Name these compounds, and then compare and contrast the nomenclature rules used in each case.

9. When metals react with nonmetals, an ionic compound generally results. What is the predicted general formula for the compound formed between an alkali metal and sulfur? Between an alkaline earth metal and nitrogen? Between aluminum and a halogen?
10. How would you name HBrO_4 , KIO_3 , NaBrO_2 , and HIO ? Refer to Table 2.5 and the acid nomenclature discussion in the text.

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- Which of the following is true about an individual atom? Explain.
 - An individual atom should be considered to be a solid.
 - An individual atom should be considered to be a liquid.
 - An individual atom should be considered to be a gas.
 - The state of the atom depends on which element it is.
 - An individual atom cannot be considered to be a solid, liquid, or gas.

Justify your choice, and for choices you did not pick, explain what is wrong with them.
- How would you go about finding the number of “chalk molecules” it takes to write your name on the board? Provide an explanation of all you would need to do and a sample calculation.
- These questions concern the work of J. J. Thomson.
 - From Thomson’s work, which particles do you think he would feel are most important for the formation of compounds (chemical changes) and why?
 - Of the remaining two subatomic particles, which do you place second in importance for forming compounds and why?
 - Propose three models that explain Thomson’s findings and evaluate them. To be complete you should include Thomson’s findings.
- Heat is applied to an ice cube in a closed container until only steam is present. Draw a representation of this process, assuming you can see it at an extremely high level of magnification. What happens to the size of the molecules? What happens to the total mass of the sample?
- You have a chemical in a sealed glass container filled with air. The setup is sitting on a balance as shown below. The chemical is ignited by means of a magnifying glass focusing sunlight on the reactant. After the chemical has completely burned, which of the following is true? Explain your answer.



- The balance will read less than 250.0 g.
- The balance will read 250.0 g.
- The balance will read greater than 250.0 g.
- Cannot be determined without knowing the identity of the chemical.

6. You take three compounds consisting of two elements and decompose them. To determine the relative masses of X, Y, and Z, you collect and weigh the elements, obtaining the following data:

Elements in Compound	Masses of Elements
X and Y	$X = 0.4 \text{ g}, Y = 4.2 \text{ g}$
Y and Z	$Y = 1.4 \text{ g}, Z = 1.0 \text{ g}$
X and Y	$X = 2.0 \text{ g}, Y = 7.0 \text{ g}$

- What are the assumptions in solving this problem?
 - What are the relative masses of X, Y, and Z?
 - What are the chemical formulas of the three compounds?
 - If you decompose 21 g of compound XY, how much of each element is present?
- The vitamin niacin (nicotinic acid, $\text{C}_6\text{H}_5\text{NO}_2$) can be isolated from a variety of natural sources such as liver, yeast, milk, and whole grain. It also can be synthesized from commercially available materials. Which source of nicotinic acid, from a nutritional view, is best for use in a multivitamin tablet? Why?
 - One of the best indications of a useful theory is that it raises more questions for further experimentation than it originally answered. Does this apply to Dalton’s atomic theory? Give examples.
 - Dalton assumed that all atoms of the same element were identical in all their properties. Explain why this assumption is not valid.
 - Evaluate each of the following as an acceptable name for water:

a. dihydrogen oxide	c. hydrogen hydroxide
b. hydroxide hydride	d. oxygen dihydride
 - Why do we call $\text{Ba}(\text{NO}_3)_2$ barium nitrate, but we call $\text{Fe}(\text{NO}_3)_2$ iron(II) nitrate?
 - Why is calcium dichloride not the correct systematic name for CaCl_2 ?
 - The common name for NH_3 is ammonia. What would be the systematic name for NH_3 ? Support your answer.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

- What refinements had to be made in Dalton’s atomic theory to account for Gay-Lussac’s results on the combining volumes of gases?

70 Chapter Two Atoms, Molecules, and Ions

- 15.** When hydrogen is burned in oxygen to form water, the composition of water formed does not depend on the amount of oxygen reacted. Interpret this in terms of the law of definite proportion.
- 16.** The two most reactive families of elements are the halogens and the alkali metals. How do they differ in their reactivities?
- 17.** Explain the law of conservation of mass, the law of definite proportion, and the law of multiple proportions.
- 18.** Section 2.3 describes the postulates of Dalton's atomic theory. With some modifications, these postulates hold up very well regarding how we view elements, compounds, and chemical reactions today. Answer the following questions concerning Dalton's atomic theory and the modifications made today.
- The atom can be broken down into smaller parts. What are the smaller parts?
 - How are atoms of hydrogen identical to each other and how can they be different from each other?
 - How are atoms of hydrogen different from atoms of helium? How can H atoms be similar to He atoms?
 - How is water different from hydrogen peroxide (H_2O_2) even though both compounds are composed of only hydrogen and oxygen?
 - What happens in a chemical reaction and why is mass conserved in a chemical reaction?
- 19.** The contributions of J. J. Thomson and Ernest Rutherford led the way to today's understanding of the structure of the atom. What were their contributions?
- 20.** What is the modern view of the structure of the atom?
- 21.** The number of protons in an atom determines the identity of the atom. What does the number and arrangement of the electrons in an atom determine? What does the number of neutrons in an atom determine?
- 22.** Distinguish between the following terms.
- molecule versus ion
 - covalent bonding versus ionic bonding
 - molecule versus compound
 - anion versus cation
- 23.** Which of the following statements are true? For the false statements, correct them.
- Most of the known elements are metals.
 - Element 118 should be a nonmetal.
 - Hydrogen has mostly metallic properties.
 - A family of elements is also known as a period of elements.
 - When an alkaline earth metal, A, reacts with a halogen, X, the formula of the covalent compound formed should be A_2X .
- 24.** Each of the following compounds has three possible names listed for it. For each compound, what is the correct name and why aren't the other names used?
- N_2O : nitrogen oxide, nitrogen(I) oxide, dinitrogen monoxide
 - Cu_2O : copper oxide, copper(I) oxide, dicopper monoxide
 - Li_2O : lithium oxide, lithium(I) oxide, dilithium monoxide

Exercises

In this section similar exercises are paired.

Development of the Atomic Theory

- 25.** When mixtures of gaseous H_2 and gaseous Cl_2 react, a product forms that has the same properties regardless of the relative amounts of H_2 and Cl_2 used.

- How is this result interpreted in terms of the law of definite proportion?
 - When a volume of H_2 reacts with an equal volume of Cl_2 at the same temperature and pressure, what volume of product having the formula HCl is formed?
- 26.** A reaction of 1 liter of chlorine gas (Cl_2) with 3 liters of fluorine gas (F_2) yields 2 liters of a gaseous product. All gas volumes are at the same temperature and pressure. What is the formula of the gaseous product?
- 27.** Hydrazine, ammonia, and hydrogen azide all contain only nitrogen and hydrogen. The mass of hydrogen that combines with 1.00 g of nitrogen for each compound is 1.44×10^{-1} g, 2.16×10^{-1} g, and 2.40×10^{-2} g, respectively. Show how these data illustrate the law of multiple proportions.
- 28.** Consider 100.0-g samples of two different compounds consisting only of carbon and oxygen. One compound contains 27.2 g of carbon and the other has 42.9 g of carbon. How can these data support the law of multiple proportions if 42.9 is not a multiple of 27.2? Show that these data support the law of multiple proportions.
- 29.** Early tables of atomic weights (masses) were generated by measuring the mass of a substance that reacts with 1.00 g of oxygen. Given the following data and taking the atomic mass of hydrogen as 1.00, generate a table of relative atomic masses for oxygen, sodium, and magnesium.

Element	Mass That Combines with 1.00 g Oxygen	Assumed Formula
Hydrogen	0.126 g	HO
Sodium	2.875 g	NaO
Magnesium	1.500 g	MgO

How do your values compare with those in the periodic table? How do you account for any differences?

- 30.** Indium oxide contains 4.784 g of indium for every 1.000 g of oxygen. In 1869, when Mendeleev first presented his version of the periodic table, he proposed the formula In_2O_3 for indium oxide. Before that time it was thought that the formula was InO . What values for the atomic mass of indium are obtained using these two formulas? Assume that oxygen has an atomic mass of 16.00.

The Nature of the Atom

- 31.** From the information in this chapter on the mass of the proton, the mass of the electron, and the sizes of the nucleus and the atom, calculate the densities of a hydrogen nucleus and a hydrogen atom.
- 32.** If you wanted to make an accurate scale model of the hydrogen atom and decided that the nucleus would have a diameter of 1 mm, what would be the diameter of the entire model?
- 33.** In an experiment it was found that the total charge on an oil drop was 5.93×10^{-18} C. How many negative charges does the drop contain?
- 34.** A chemist in a galaxy far, far away performed the Millikan oil drop experiment and got the following results for the charges on

various drops. Use these data to calculate the charge of the electron in zirkombs.

$$\begin{array}{ll} 2.56 \times 10^{-12} \text{ zirkombs} & 7.68 \times 10^{-12} \text{ zirkombs} \\ 3.84 \times 10^{-12} \text{ zirkombs} & 6.40 \times 10^{-13} \text{ zirkombs} \end{array}$$

35. What are the symbols of the following metals: sodium, radium, iron, gold, manganese, lead?

36. What are the symbols of the following nonmetals: fluorine, chlorine, bromine, sulfur, oxygen, phosphorus?

37. Give the names of the metals that correspond to the following symbols: Sn, Pt, Hg, Mg, K, Ag.

38. Give the names of the nonmetals that correspond to the following symbols: As, I, Xe, He, C, Si.

39. a. Classify the following elements as metals or nonmetals:

Mg	Si	Rn
Ti	Ge	Eu
Au	B	Am
Bi	At	Br

b. The distinction between metals and nonmetals is really not a clear one. Some elements, called *metalloids*, are intermediate in their properties. Which of these elements would you reclassify as metalloids? What other elements in the periodic table would you expect to be metalloids?

40. a. List the noble gas elements. Which of the noble gases has only radioactive isotopes? (This situation is indicated on most periodic tables by parentheses around the mass of the element. See inside front cover.)

b. Which lanthanide element and which transition element have only radioactive isotopes?

41. In the periodic table, how many elements are found in

- a. Group 2A? c. the nickel group?
- b. the oxygen family? d. Group 8A?

42. In the periodic table, how many elements are found

- a. in the halogen group?
- b. in the alkali family?
- c. in the lanthanide series?
- d. classified as transition metals?

43. How many protons and neutrons are in the nucleus of each of the following atoms? In a neutral atom of each element, how many electrons are present?

- a. ^{79}Br d. ^{133}Cs
- b. ^{81}Br e. ^3H
- c. ^{239}Pu f. ^{56}Fe

44. What number of protons and neutrons are contained in the nucleus of each of the following atoms? Assuming each atom is uncharged, what number of electrons are present?

- a. ^{235}U d. ^{208}Pb
- b. ^{13}C e. ^{86}Rb
- c. ^{57}Fe f. ^{41}Ca

45. Write the atomic symbol (${}^A_Z\text{X}$) for each of the following isotopes.

- a. $Z = 8$, number of neutrons = 9
- b. the isotope of chlorine in which $A = 37$

c. $Z = 27$, $A = 60$

d. number of protons = 26, number of neutrons = 31

e. the isotope of I with a mass number of 131

f. $Z = 3$, number of neutrons = 4

46. Write the atomic symbol (${}^A_Z\text{X}$) for each of the isotopes described below.

a. number of protons = 27, number of neutrons = 31

b. the isotope of boron with mass number 10

c. $Z = 12$, $A = 23$

d. atomic number 53, number of neutrons = 79

e. $Z = 9$, number of neutrons = 10

f. number of protons = 29, mass number 65

47. What is the symbol for an ion with 63 protons, 60 electrons, and 88 neutrons? If an ion contains 50 protons, 68 neutrons, and 48 electrons, what is its symbol?

48. What is the symbol of an ion with 16 protons, 18 neutrons, and 18 electrons? What is the symbol for an ion that has 16 protons, 16 neutrons, and 18 electrons?

49. Complete the following table:

Symbol	Number of Protons in Nucleus	Number of Neutrons in Nucleus	Number of Electrons	Net Charge
$^{238}_{92}\text{U}$	20	20		2+
	23	28	20	
$^{89}_{39}\text{Y}$	35	44	36	
	15	16		3-

50.

Symbol	Number of Protons in Nucleus	Number of Neutrons in Nucleus	Number of Electrons	Net Charge
$^{53}_{26}\text{Fe}^{2+}$	26	33		3+
	85	125	86	
	13	14	10	
	76	54		2-

51. For each of the following sets of elements, label each as either noble gases, halogens, alkali metals, alkaline earth metals, or transition metals.

- a. Ti, Fe, Ag d. Ne, Kr, Xe
- b. Mg, Sr, Ba e. F, Br, I
- c. Li, K, Rb

52. Consider the elements of Group 4A (the “carbon family”): C, Si, Ge, Sn, and Pb. What is the trend in metallic character as one goes down this group? What is the trend in metallic character going from left to right across a period in the periodic table?

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53. Would you expect each of the following atoms to gain or lose electrons when forming ions? What ion is the most likely in each case?

- a. Ra c. P e. Br
- b. In d. Te f. Rb

54. For each of the following atomic numbers, use the periodic table to write the formula (including the charge) for the simple *ion* that the element is most likely to form in ionic compounds.

- a. 13 c. 56 e. 87
- b. 34 d. 7 f. 35

Nomenclature

55. Name the compounds in parts a–d and write the formulas for the compounds in parts e–h.

- a. NaBr e. strontium fluoride
- b. Rb₂O f. aluminum selenide
- c. CaS g. potassium nitride
- d. AlI₃ h. magnesium phosphide

56. Name the compounds in parts a–d and write the formulas for the compounds in parts e–h.

- a. Hg₂O e. tin(II) nitride
- b. FeBr₃ f. cobalt(III) iodide
- c. CoS g. mercury(II) oxide
- d. TiCl₄ h. chromium(VI) sulfide

57. Name each of the following compounds:

- a. CsF c. Ag₂S e. TiO₂
- b. Li₃N d. MnO₂ f. Sr₃P₂

58. Write the formula for each of the following compounds:

- a. zinc chloride d. aluminum sulfide
- b. tin(IV) fluoride e. mercury(I) selenide
- c. calcium nitride f. silver iodide

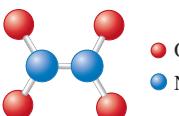
59. Name each of the following compounds:

- a. BaSO₃ c. KMnO₄
- b. NaNO₂ d. K₂Cr₂O₇

60. Write the formula for each of the following compounds:

- a. chromium(III) hydroxide c. lead(IV) carbonate
- b. magnesium cyanide d. ammonium acetate

61. Name each of the following compounds:

- a. 
- b. 
- c. SO₂
- d. P₂S₅

62. Write the formula for each of the following compounds:

- a. diboron trioxide c. dinitrogen monoxide
- b. arsenic pentafluoride d. sulfur hexachloride

63. Name each of the following compounds:

- a. CuI c. CoI₂
- b. CuI₂ d. Na₂CO₃

- e. NaHCO₃
- f. S₄N₄
- g. SF₆
- h. NaOCl
- i. BaCrO₄
- j. NH₄NO₃

64. Name each of the following compounds:

- a. HC₂H₃O₂
- b. NH₄NO₂
- c. Co₂S₃
- d. ICl
- e. Pb₃(PO₄)₂
- f. KIO₃
- g. H₂SO₄
- h. Sr₃N₂
- i. Al₂(SO₄)₃
- j. SnO₂
- k. Na₂CrO₄
- l. HClO

65. Write the formula for each of the following compounds:

- a. sulfur difluoride
- b. sulfur hexafluoride
- c. sodium dihydrogen phosphate
- d. lithium nitride
- e. chromium(III) carbonate
- f. tin(II) fluoride
- g. ammonium acetate
- h. ammonium hydrogen sulfate
- i. cobalt(III) nitrate
- j. mercury(I) chloride
- k. potassium chlorate
- l. sodium hydride

66. Write the formula for each of the following compounds:

- a. chromium(VI) oxide
- b. disulfur dichloride
- c. nickel(II) fluoride
- d. potassium hydrogen phosphate
- e. aluminum nitride
- f. ammonia
- g. manganese(IV) sulfide
- h. sodium dichromate
- i. ammonium sulfite
- j. carbon tetraiodide

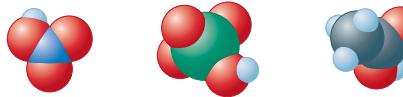
67. Write the formula for each of the following compounds:

- a. sodium oxide
- b. sodium peroxide
- c. potassium cyanide
- d. copper(II) nitrate
- e. selenium tetrabromide
- f. iodous acid
- g. lead(IV) sulfide
- h. copper(I) chloride
- i. gallium arsenide
- j. cadmium selenide
- k. zinc sulfide
- l. nitrous acid
- m. diphosphorus pentoxide

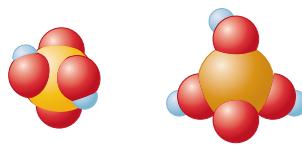
68. Write the formula for each of the following compounds:

- a. ammonium hydrogen phosphate
- b. mercury(I) sulfide
- c. silicon dioxide
- d. sodium sulfite
- e. aluminum hydrogen sulfate
- f. nitrogen trichloride
- g. hydrobromic acid
- h. bromous acid
- i. perbromic acid
- j. potassium hydrogen sulfide
- k. calcium iodide
- l. cesium perchlorate

69. Name the following acids illustrated below.



a. b. c.



d. e.

70. Each of the following compounds is incorrectly named. What is wrong with each name, and what is the correct name for each compound?

- a. FeCl_3 , iron chloride
- b. NO_2 , nitrogen(IV) oxide
- c. CaO , calcium(II) monoxide
- d. Al_2S_3 , dialuminum trisulfide
- e. $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$, manganese diacetate
- f. FePO_4 , iron(II) phosphide
- g. P_2S_5 , phosphorous sulfide
- h. Na_2O_2 , sodium oxide
- i. HNO_3 , nitrate acid
- j. H_2S , sulfuric acid

Additional Exercises

71. Chlorine has two natural isotopes: ^{37}Cl and ^{35}Cl . Hydrogen reacts with chlorine to form the compound HCl . Would a given amount of hydrogen react with different masses of the two chlorine isotopes? Does this conflict with the law of definite proportion? Why or why not?

72. Which of the following statements is(are) *true*? For the false statements, correct them.

- a. All particles in the nucleus of an atom are charged.
- b. The atom is best described as a uniform sphere of matter in which electrons are embedded.
- c. The mass of the nucleus is only a very small fraction of the mass of the entire atom.
- d. The volume of the nucleus is only a very small fraction of the total volume of the atom.
- e. The number of neutrons in a neutral atom must equal the number of electrons.

73. The isotope of an unknown element, X, has a mass number of 79. The most stable ion of the isotope has 36 electrons and forms a binary compound with sodium having a formula of Na_2X . Which of the following statements is(are) *true*? For the false statements, correct them.

- a. The binary compound formed between X and fluorine will be a covalent compound.
- b. The isotope of X contains 38 protons.
- c. The isotope of X contains 41 neutrons.
- d. The identity of X is strontium, Sr.

74. For each of the following ions, indicate the total number of protons and electrons in the ion. For the positive ions in the list, predict

the formula of the simplest compound formed between each positive ion and the oxide ion. For the negative ions in the list, predict the formula of the simplest compound formed between each negative ion and the aluminum ion.

- a. Fe^{2+}
- e. S^{2-}
- b. Fe^{3+}
- f. P^{3-}
- c. Ba^{2+}
- g. Br^-
- d. Cs^+
- h. N^{3-}

75. The formulas and common names for several substances are given below. Give the systematic names for these substances.

- | | |
|---------------------|---|
| a. sugar of lead | $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ |
| b. blue vitrol | CuSO_4 |
| c. quicklime | CaO |
| d. Epsom salts | MgSO_4 |
| e. milk of magnesia | $\text{Mg}(\text{OH})_2$ |
| f. gypsum | CaSO_4 |
| g. laughing gas | N_2O |

76. Identify each of the following elements:

- a. a member of the same family as oxygen whose most stable ion contains 54 electrons
- b. a member of the alkali metal family whose most stable ion contains 36 electrons
- c. a noble gas with 18 protons in the nucleus
- d. a halogen with 85 protons and 85 electrons

77. An element's most stable ion forms an ionic compound with bromine, having the formula XBr_2 . If the ion of element X has a mass number of 230 and has 86 electrons, what is the identity of the element, and how many neutrons does it have?

78. A certain element has only two naturally occurring isotopes: one with 18 neutrons and the other with 20 neutrons. The element forms 1 $-$ charged ions when in ionic compounds. Predict the identity of the element. What number of electrons does the 1 $-$ charged ion have?

79. The designations 1A through 8A used for certain families of the periodic table are helpful for predicting the charges on ions in binary ionic compounds. In these compounds, the metals generally take on a positive charge equal to the family number, while the nonmetals take on a negative charge equal to the family number minus eight. Thus the compound between sodium and chlorine contains Na^+ ions and Cl^- ions and has the formula NaCl . Predict the formula and the name of the binary compound formed from the following pairs of elements.

- a. Ca and N
- e. Ba and I
- b. K and O
- f. Al and Se
- c. Rb and F
- g. Cs and P
- d. Mg and S
- h. In and Br

80. By analogy with phosphorous compounds, name the following: Na_3AsO_4 , H_3AsO_4 , $\text{Mg}_3(\text{SbO}_4)_2$.

81. A sample of H_2SO_4 contains 2.02 g of hydrogen, 32.07 g of sulfur, and 64.00 g of oxygen. How many grams of sulfur and grams of oxygen are present in a second sample of H_2SO_4 containing 7.27 g of hydrogen?

82. In a reaction, 34.0 g of chromium(III) oxide reacts with 12.1 g of aluminum to produce chromium and aluminum oxide. If 23.3 g of chromium is produced, what mass of aluminum oxide is produced?

Challenge Problems

83. The elements in one of the groups in the periodic table are often called the coinage metals. Identify the elements in this group based on your own experience.
84. Reaction of 2.0 L of hydrogen gas with 1.0 L of oxygen gas yields 2.0 L of water vapor. All gases are at the same temperature and pressure. Show how these data support the idea that oxygen gas is a diatomic molecule. Must we consider hydrogen to be a diatomic molecule to explain these results?
85. A combustion reaction involves the reaction of a substance with oxygen gas. The complete combustion of any hydrocarbon (binary compound of carbon and hydrogen) produces carbon dioxide and water as the only products. Octane is a hydrocarbon that is found in gasoline. Complete combustion of octane produces 8 liters of carbon dioxide for every 9 liters of water vapor (both measured at the same temperature and pressure). What is the ratio of carbon atoms to hydrogen atoms in a molecule of octane?
86. A chemistry instructor makes the following claim: "Consider that if the nucleus were the size of a grape, the electrons would be about 1 mile away on average." Is this claim reasonably accurate? Provide mathematical support.
87. Two elements, R and Q, combine to form two binary compounds. In the first compound, 14.0 g of R combines with 3.00 g of Q. In the second compound, 7.00 g of R combines with 4.50 g of Q. Show that these data are in accord with the law of multiple proportions. If the formula of the second compound is RQ, what is the formula of the first compound?
88. The early alchemists used to do an experiment in which water was boiled for several days in a sealed glass container. Eventually, some solid residue would appear in the bottom of the flask, which was interpreted to mean that some of the water in the flask had been converted into "earth." When Lavoisier repeated this experiment, he found that the water weighed the same before and after heating and the mass of the flask plus the solid residue equaled the original mass of the flask. Were the alchemists correct? Explain what really happened. (This experiment is described in the article by A. F. Scott in *Scientific American*, January 1984.)
89. Each of the following statements is true, but Dalton might have had trouble explaining some of them with his atomic theory. Give explanations for the following statements.
- The space-filling models for ethyl alcohol and dimethyl ether are shown below.



These two compounds have the same composition by mass (52% carbon, 13% hydrogen, and 35% oxygen), yet the two have different melting points, boiling points, and solubilities in water.

- Burning wood leaves an ash that is only a small fraction of the mass of the original wood.
- Atoms can be broken down into smaller particles.

- d. One sample of lithium hydride is 87.4% lithium by mass, while another sample of lithium hydride is 74.9% lithium by mass. However, the two samples have the same properties.

90. You have two distinct gaseous compounds made from element X and element Y. The mass percents are as follows:

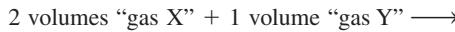
Compound I: 30.43% X, 69.57% Y

Compound II: 63.64% X, 36.36% Y

In their natural standard states, element X and element Y exist as gases. (Monatomic? Diatomic? Triatomic? That is for you to determine.) When you react "gas X" with "gas Y" to make the products, you get the following data (all at standard pressure and temperature):



2 volumes compound I



2 volumes compound II

Assume the simplest possible formulas for reactants and products in the chemical equations above. Then, determine the relative atomic masses of element X and element Y.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

91. What is the systematic name of Ta_2O_5 ? If the charge on the metal remained constant and then sulfur was substituted for oxygen, how would the formula change? What is the difference in the total number of protons between Ta_2O_5 and its sulfur analog?
92. A binary ionic compound is known to contain a cation with 51 protons and 48 electrons. The anion contains one-third the number of protons as the cation. The number of electrons in the anion is equal to the number of protons plus 1. What is the formula of this compound? What is the name of this compound?
93. Using the information in Table 2.1, answer the following questions. In an ion with an unknown charge, the total mass of all the electrons was determined to be 2.55×10^{-26} g, while the total mass of its protons was 5.34×10^{-23} g. What is the identity and charge of this ion? What is the symbol and mass number of a neutral atom whose total mass of its electrons is 3.92×10^{-26} g, while its neutrons have a mass of 9.35×10^{-23} g?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

94. You have gone back in time and are working with Dalton on a table of relative masses. Following are his data.

0.602 g gas A reacts with 0.295 g gas B

0.172 g gas B reacts with 0.401 g gas C

0.320 g gas A reacts with 0.374 g gas C

- Assuming simplest formulas (AB, BC, and AC), construct a table of relative masses for Dalton.

- b. Knowing some history of chemistry, you tell Dalton that if he determines the volumes of the gases reacted at constant temperature and pressure, he need not assume simplest formulas. You collect the following data:

6 volumes gas A + 1 volume gas B \rightarrow 4 volumes product

1 volume gas B + 4 volumes gas C \rightarrow 4 volumes product

3 volumes gas A + 2 volumes gas C \rightarrow 6 volumes product

Write the simplest balanced equations, and find the actual relative masses of the elements. Explain your reasoning.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

3 Stoichiometry

Contents

- 3.1 Counting by Weighing
- 3.2 Atomic Masses
- 3.3 The Mole
- 3.4 Molar Mass
- 3.5 Percent Composition of Compounds
- 3.6 Determining the Formula of a Compound
- 3.7 Chemical Equations
 - Chemical Reactions
 - The Meaning of a Chemical Equation
- 3.8 Balancing Chemical Equations
- 3.9 Stoichiometric Calculations: Amounts of Reactants and Products
- 3.10 Calculations Involving a Limiting Reactant

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The violent chemical reaction of bromine and phosphorus.

C

hemical reactions have a profound effect on our lives. There are many examples: Food is converted to energy in the human body; nitrogen and hydrogen are combined to form ammonia, which is used as a fertilizer; fuels and plastics are produced from petroleum; the starch in plants is synthesized from carbon dioxide and water using energy from sunlight; human insulin is produced in laboratories by bacteria; cancer is induced in humans by substances from our environment; and so on, in a seemingly endless list. The central activity of chemistry is to understand chemical changes such as these, and the study of reactions occupies a central place in this book. We will examine why reactions occur, how fast they occur, and the specific pathways they follow.

In this chapter we will consider the quantities of materials consumed and produced in chemical reactions. This area of study is called **chemical stoichiometry** (pronounced stoy-kē-om'-etry). To understand chemical stoichiometry, you must first understand the concept of relative atomic masses.

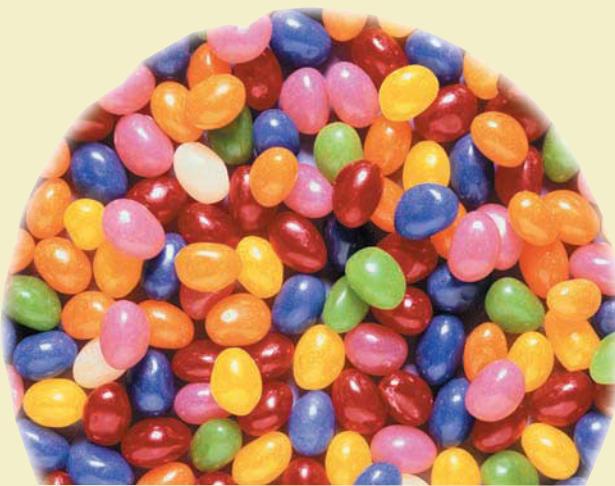
3.1 Counting by Weighing

Suppose you work in a candy store that sells gourmet jelly beans by the bean. People come in and ask for 50 beans, 100 beans, 1000 beans, and so on, and you have to count them out—a tedious process at best. As a good problem solver, you try to come up with a better system. It occurs to you that it might be far more efficient to buy a scale and count the jelly beans by weighing them. How can you count jelly beans by weighing them? What information about the individual beans do you need to know?

Assume that all of the jelly beans are identical and that each has a mass of 5 g. If a customer asks for 1000 jelly beans, what mass of jelly beans would be required? Each bean has a mass of 5 g, so you would need 1000 beans \times 5 g/bean, or 5000 g (5 kg). It takes just a few seconds to weigh out 5 kg of jelly beans. It would take much longer to count out 1000 of them.

In reality, jelly beans are not identical. For example, let's assume that you weigh 10 beans individually and get the following results:

Bean	Mass
1	5.1 g
2	5.2 g
3	5.0 g
4	4.8 g
5	4.9 g
6	5.0 g
7	5.0 g
8	5.1 g
9	4.9 g
10	5.0 g



Jelly beans can be counted by weighing.

Can we count these nonidentical beans by weighing? Yes. The key piece of information we need is the *average mass* of the jelly beans. Let's compute the average mass for our 10-bean sample.

$$\begin{aligned}\text{Average mass} &= \frac{\text{total mass of beans}}{\text{number of beans}} \\ &= \frac{5.1 \text{ g} + 5.2 \text{ g} + 5.0 \text{ g} + 4.8 \text{ g} + 4.9 \text{ g} + 5.0 \text{ g} + 5.0 \text{ g} + 5.1 \text{ g} + 4.9 \text{ g} + 5.0 \text{ g}}{10} \\ &= \frac{50.0}{10} = 5.0 \text{ g}\end{aligned}$$

The average mass of a jelly bean is 5.0 g. Thus, to count out 1000 beans, we need to weigh out 5000 g of beans. This sample of beans, in which the beans have an average mass of 5.0 g, can be treated exactly like a sample where all of the beans are identical. Objects do not need to have identical masses to be counted by weighing. We simply need to know the average mass of the objects. For purposes of counting, the objects *behave as though they were all identical*, as though they each actually had the average mass.

We count atoms in exactly the same way. Because atoms are so small, we deal with samples of matter that contain huge numbers of atoms. Even if we could see the atoms it would not be possible to count them directly. Thus we determine the number of atoms in a given sample by finding its mass. However, just as with jelly beans, to relate the mass to a number of atoms, we must know the average mass of the atoms.

3.2 Atomic Masses

As we saw in Chapter 2, the first quantitative information about atomic masses came from the work of Dalton, Gay-Lussac, Lavoisier, Avogadro, and Berzelius. By observing the proportions in which elements combine to form various compounds, nineteenth-century chemists calculated relative atomic masses. The modern system of atomic masses, instituted in 1961, is based on ^{12}C ("carbon twelve") as the standard. In this system, ^{12}C is assigned a mass of exactly 12 atomic mass units (amu), and the masses of all other atoms are given relative to this standard.

The most accurate method currently available for comparing the masses of atoms involves the use of the **mass spectrometer**. In this instrument, diagramed in Fig. 3.1, atoms or molecules are passed into a beam of high-speed electrons, which knock electrons off the atoms or molecules being analyzed and change them into positive ions. An applied

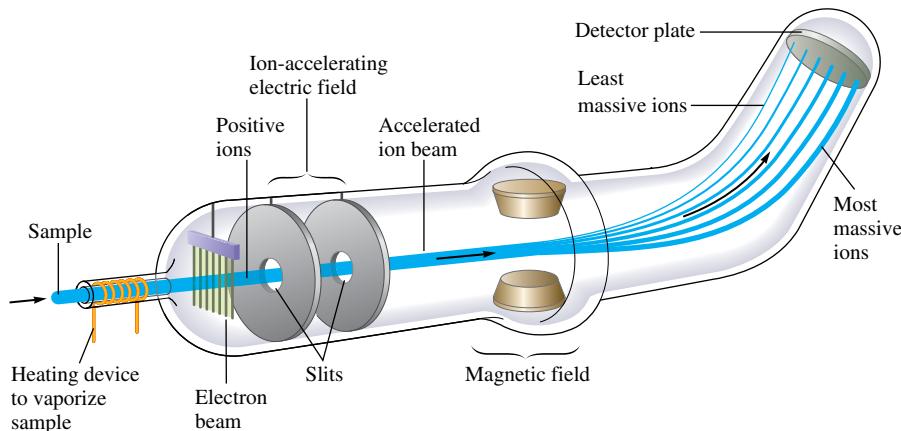


FIGURE 3.1

(left) A scientist injecting a sample into a mass spectrometer. (above) Schematic diagram of a mass spectrometer.

electric field then accelerates these ions into a magnetic field. Because an accelerating ion produces its own magnetic field, an interaction with the applied magnetic field occurs, which tends to change the path of the ion. The amount of path deflection for each ion depends on its mass—the most massive ions are deflected the smallest amount—which causes the ions to separate, as shown in Fig. 3.1. A comparison of the positions where the ions hit the detector plate gives very accurate values of their relative masses. For example, when ^{12}C and ^{13}C are analyzed in a mass spectrometer, the ratio of their masses is found to be

$$\frac{\text{Mass } ^{13}\text{C}}{\text{Mass } ^{12}\text{C}} = 1.0836129$$

Since the atomic mass unit is defined such that the mass of ^{12}C is *exactly* 12 atomic mass units, then on this same scale,

$$\text{Mass of } ^{13}\text{C} = (1.0836129)(12 \text{ amu}) = 13.003355 \text{ amu}$$

↑
Exact number
by definition

The masses of other atoms can be determined in a similar fashion.

The mass for each element is given in the table inside the front cover of this text. This value, even though it is actually a mass, is (for historical reasons) sometimes called the *atomic weight* for each element.

Look at the value of the atomic mass of carbon given in this table. You might expect to see 12, since we said the system of atomic masses is based on ^{12}C . However, the number given for carbon is not 12 but 12.01. Why? The reason for this apparent discrepancy is that the carbon found on earth (natural carbon) is a mixture of the isotopes ^{12}C , ^{13}C , and ^{14}C . All three isotopes have six protons, but they have six, seven, and eight neutrons, respectively. Because natural carbon is a mixture of isotopes, the atomic mass we use for carbon is an *average value* reflecting the average of the isotopes composing it.

The average atomic mass for carbon is computed as follows: It is known that natural carbon is composed of 98.89% ^{12}C atoms and 1.11% ^{13}C atoms. The amount of ^{14}C is negligibly small at this level of precision. Using the masses of ^{12}C (exactly 12 amu) and ^{13}C (13.003355 amu), we can calculate the average atomic mass for natural carbon as follows:

$$98.89\% \text{ of } 12 \text{ amu} + 1.11\% \text{ of } 13.0034 \text{ amu} = \\ (0.9889)(12 \text{ amu}) + (0.0111)(13.0034 \text{ amu}) = 12.01 \text{ amu}$$

In this text we will call the average mass for an element the **average atomic mass** or, simply, the *atomic mass* for that element.

Even though natural carbon does not contain a single atom with mass 12.01, for stoichiometric purposes, we can consider carbon to be composed of only one type of atom with a mass of 12.01. This enables us to count atoms of natural carbon by weighing a sample of carbon.

Recall from Section 3.1 that counting by weighing works if you know the *average* mass of the units being counted. Counting by weighing works just the same for atoms as for jelly beans. For natural carbon with an average mass of 12.01 atomic mass units, to obtain 1000 atoms would require weighing out 12,010 atomic mass units of natural carbon (a mixture of ^{12}C and ^{13}C).

As in the case of carbon, the mass for each element listed in the table inside the front cover of the text is an average value based on the isotopic composition of the naturally occurring element. For instance, the mass listed for hydrogen (1.008) is the average mass for natural hydrogen, which is a mixture of ^1H and ^2H (deuterium). *No* atom of hydrogen actually has the mass 1.008.



It is much easier to weigh out 600 hex nuts than count them one by one.

Most elements occur in nature as mixtures of isotopes; thus atomic masses are usually average values.



CHEMICAL IMPACT

Buckyballs Teach Some History

About 250 million years ago, 90% of life on earth was destroyed in some sort of cataclysmic event. This event, which ended the Permian period and began the Triassic (the P-T boundary), is the most devastating mass extinction in the earth's history—far surpassing the catastrophe 65 million years ago that wiped out the dinosaurs (the K-T boundary). In 1979 geologist Walter Alvarez and his Nobel Prize-winning physicist father Luis Alvarez suggested that unusually high concentrations of iridium in rocks laid down at the K-T boundary meant that an asteroid had hit the earth, causing tremendous devastation. In the last 20 years much evidence has accumulated to support this hypothesis, including identification of the location of the probable crater caused by the impact in the ocean near Mexico.

Were the P-T boundary extinctions also caused by an extraterrestrial object or by some event on earth, such as a massive volcano explosion? Recent discoveries by geochemists Luann Becker of the University of Washington and

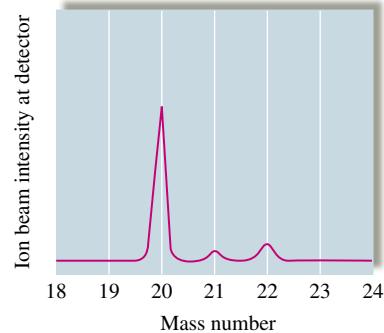
Robert J. Poreda of the University of Rochester seem to strongly support the impact theory. Examining sediment from China and Japan, the team found fullerenes encapsulating argon and helium gas atoms whose isotopic composition indicates that they are extraterrestrial in origin. For example, the ratio of ^3He to ^4He found in the fullerenes is 100 times greater than the ratio for helium found in the earth's atmosphere. Likewise, the isotopic composition of the fullerene-trapped argon atoms is quite different from that found on earth.

Fullerenes include spherical C_{60} carbon molecules (“buckyballs”) whose cavities can trap other atoms such as helium and argon. (See the accompanying figure.) The scientists postulate that the fullerenes originated in stars or collapsing gas clouds where the noble gas atoms were trapped as the fullerenes formed. These fullerenes were then somehow incorporated into the object that eventually hit the earth. Based on the isotopic compositions, the geochemists estimate that the impacting body must have

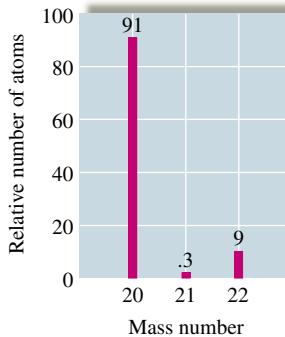
In addition to being useful for determining accurate mass values for individual atoms, the mass spectrometer is used to determine the isotopic composition of a natural element. For example, when a sample of natural neon is injected into a mass spectrometer, the mass spectrum shown in Fig. 3.2 is obtained. The areas of the “peaks” or the heights of the bars indicate the relative abundances of ^{20}Ne , ^{21}Ne , and ^{22}Ne atoms.



(a)



(b)



(c)

FIGURE 3.2

(a) Neon gas glowing in a discharge tube. The relative intensities of the signals recorded when natural neon is injected into a mass spectrometer, represented in terms of (b) “peaks” and (c) a bar graph. The relative areas of the peaks are 0.9092 (^{20}Ne), 0.00257 (^{21}Ne), and 0.0882 (^{22}Ne); natural neon is therefore 90.92% ^{20}Ne , 0.257% ^{21}Ne , and 8.82% ^{22}Ne .

been 10 kilometers in diameter, which is comparable in size to the asteroid that is assumed to have killed the dinosaurs.

One factor that had previously cast doubt on an asteroid collision as the cause of the P-T catastrophe was the lack of iridium found in sediments from this period. However, Becker and other scientists argue that this absence probably means the impacting object may have been a comet rather than an asteroid. It is also possible that such a blow could have intensified the volcanism already under way on earth at that time, delivering a “one-two punch” that almost obliterated life on earth, according to Becker.

It is ironic that “buckyballs,” which made big news when they were recently synthesized for the first time in the laboratory, actually have been around for millions of years and have some very interesting history to teach us.

Figure from *Chemical and Engineering News*, Feb. 26, 2001, p. 9.
Reprinted by permission of Joseph Wilmhoff.

Isotope ratios of the noble gas atoms inside celestial buckyballs indicate that these ancient carbon cages formed in a stellar environment, not on earth.

Sample Exercise 3.1

The Average Mass of an Element



Copper nugget.

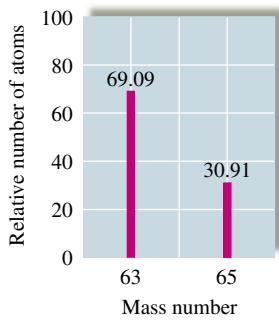


FIGURE 3.3
Mass spectrum of natural copper.

When a sample of natural copper is vaporized and injected into a mass spectrometer, the results shown in Fig. 3.3 are obtained. Use these data to compute the average mass of natural copper. (The mass values for ^{63}Cu and ^{65}Cu are 62.93 amu and 64.93 amu, respectively.)

Solution

As shown by the graph, of every 100 atoms of natural copper, 69.09 are ^{63}Cu and 30.91 are ^{65}Cu . Thus the mass of 100 atoms of natural copper is

$$(69.09 \text{ atoms})\left(62.93 \frac{\text{amu}}{\text{atom}}\right) + (30.91 \text{ atoms})\left(64.93 \frac{\text{amu}}{\text{atom}}\right) = 6355 \text{ amu}$$

The *average mass* of a copper atom is

$$\frac{6355 \text{ amu}}{100 \text{ atoms}} = 63.55 \text{ amu/atom}$$

This mass value is used in doing calculations involving the reactions of copper and is the value given in the table inside the front cover of this book.

Reality Check: When you finish a calculation, you should always check whether your answer makes sense. In this case our answer of 63.55 amu is between the masses of the atoms that make up natural copper. This makes sense. The answer could not be smaller than 62.93 amu or larger than 64.93 amu.

See Exercises 3.27 and 3.28.

3.3 The Mole

The SI definition of the mole is the amount of a substance that contains as many entities as there are in exactly 12 g of carbon-12.

Avogadro's number is 6.022×10^{23} . One mole of anything is 6.022×10^{23} units of that substance.

Because samples of matter typically contain so many atoms, a unit of measure called the **mole** has been established for use in counting atoms. For our purposes, it is most convenient to define the **mole** (abbreviated mol) as *the number equal to the number of carbon atoms in exactly 12 grams of pure ^{12}C* . Techniques such as mass spectrometry, which count atoms very precisely, have been used to determine this number as 6.02214×10^{23} (6.022×10^{23} will be sufficient for our purposes). This number is called **Avogadro's number** to honor his contributions to chemistry. *One mole of something consists of 6.022×10^{23} units of that substance*. Just as a dozen eggs is 12 eggs, a mole of eggs is 6.022×10^{23} eggs.

The magnitude of the number 6.022×10^{23} is very difficult to imagine. To give you some idea, 1 mole of seconds represents a span of time 4 million times as long as the earth has already existed, and 1 mole of marbles is enough to cover the entire earth to a depth of 50 miles! However, since atoms are so tiny, a mole of atoms or molecules is a perfectly manageable quantity to use in a reaction (see Fig. 3.4).

How do we use the mole in chemical calculations? Recall that Avogadro's number is defined as the number of atoms in exactly 12 grams of ^{12}C . This means that 12 grams of ^{12}C contains 6.022×10^{23} atoms. It also means that a 12.01-gram sample of natural carbon contains 6.022×10^{23} atoms (a mixture of ^{12}C , ^{13}C , and ^{14}C atoms, with an average atomic mass of 12.01). Since the ratio of the masses of the samples (12 g/12.01 g) is the same as the ratio of the masses of the individual components (12 amu/12.01 amu), the two samples contain the *same number* of atoms (6.022×10^{23}).

To be sure this point is clear, think of oranges with an average mass of 0.5 pound each and grapefruit with an average mass of 1.0 pound each. Any two sacks for which the sack of grapefruit weighs twice as much as the sack of oranges will contain the same number of pieces of fruit. The same idea extends to atoms. Compare natural carbon (average mass of 12.01) and natural helium (average mass of 4.003). A sample of 12.01 grams of natural carbon contains the same number of atoms as 4.003 grams of natural helium. Both samples contain 1 mole of atoms (6.022×10^{23}). Table 3.1 gives more examples that illustrate this basic idea.

Thus the mole is defined such that a sample of a natural element with a mass equal to the element's atomic mass expressed in grams contains 1 mole of atoms. This definition

The mass of 1 mole of an element is equal to its atomic mass in grams.



FIGURE 3.4

Proceeding clockwise from the top, samples containing one mole each of copper, aluminum, iron, sulfur, iodine, and (in the center) mercury.

TABLE 3.1 Comparison of 1 Mole Samples of Various Elements

Element	Number of Atoms Present	Mass of Sample (g)
Aluminum	6.022×10^{23}	26.98
Copper	6.022×10^{23}	63.55
Iron	6.022×10^{23}	55.85
Sulfur	6.022×10^{23}	32.07
Iodine	6.022×10^{23}	126.9
Mercury	6.022×10^{23}	200.6

also fixes the relationship between the atomic mass unit and the gram. Since 6.022×10^{23} atoms of carbon (each with a mass of 12 amu) have a mass of 12 g, then

$$(6.022 \times 10^{23} \text{ atoms}) \left(\frac{12 \text{ amu}}{\text{atom}} \right) = 12 \text{ g}$$

and

$$6.022 \times 10^{23} \text{ amu} = 1 \text{ g}$$

↑
 Exact
 number

This relationship can be used to derive the unit factor needed to convert between atomic mass units and grams.

Sample Exercise 3.2

Determining the Mass of a Sample of Atoms

Americium is an element that does not occur naturally. It can be made in very small amounts in a device known as a *particle accelerator*. Compute the mass in grams of a sample of americium containing six atoms.

Solution

From the table inside the front cover of the text, we note that one americium atom has a mass of 243 amu. Thus the mass of six atoms is

$$6 \text{ atoms} \times 243 \frac{\text{amu}}{\text{atom}} = 1.46 \times 10^3 \text{ amu}$$

Using the relationship

$$6.022 \times 10^{23} \text{ amu} = 1 \text{ g}$$

we write the conversion factor for converting atomic mass units to grams:

$$\frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}}$$

The mass of six americium atoms in grams is

$$1.46 \times 10^3 \text{ amu} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} = 2.42 \times 10^{-21} \text{ g}$$

Reality Check: Since this sample contains only six atoms, the mass should be very small as the amount $2.42 \times 10^{-21} \text{ g}$ indicates.

See Exercise 3.33.



CHEMICAL IMPACT

Elemental Analysis Catches Elephant Poachers

In an effort to combat the poaching of elephants by controlling illegal exports of ivory, scientists are now using the isotopic composition of ivory trinkets and elephant tusks to identify the region of Africa where the elephant lived. Using a mass spectrometer, scientists analyze the ivory for the relative amounts of ^{12}C , ^{13}C , ^{14}N , ^{15}N , ^{86}Sr , and ^{87}Sr to determine the diet of the elephant and thus its place of origin. For example, because grasses use a different photosynthetic pathway to produce glucose than do trees, grasses have a slightly different $^{13}\text{C}/^{12}\text{C}$ ratio from that of trees. They have different ratios because each time a carbon atom is added in going from simpler to more complex compounds, the more massive ^{13}C is disfavored relative to ^{12}C because it reacts more slowly. Because trees use more steps to build up glucose, they end up with a smaller $^{13}\text{C}/^{12}\text{C}$ ratio in their leaves relative to grasses, and this difference is then reflected in the tissues of elephants. Thus

scientists can tell whether a particular tusk came from a savanna-dwelling elephant (grass-eating) or from a tree-browsing elephant.

Similarly, because the ratios of $^{15}\text{N}/^{14}\text{N}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in elephant tusks also vary depending on the region of Africa the elephant inhabits, they can be used to trace the elephant's origin. In fact, using these techniques, scientists have reported being able to discriminate between elephants living only about 100 miles apart.

There is now international concern about the dwindling elephant populations in Africa—their numbers have decreased significantly in recent years. This concern has led to bans in the export of ivory from many countries in Africa. However, a few nations still allow ivory to be exported. Thus, to enforce the trade restrictions, the origin of a given piece of ivory must be established. It is hoped that the “isotope signature” of the ivory can be used for this purpose.

To do chemical calculations, you must understand what the mole means and how to determine the number of moles in a given mass of a substance. These procedures are illustrated in Sample Exercises 3.3 and 3.4.

Sample Exercise 3.3

Determining Moles of Atoms

Aluminum (Al) is a metal with a high strength-to-mass ratio and a high resistance to corrosion; thus it is often used for structural purposes. Compute both the number of moles of atoms and the number of atoms in a 10.0-g sample of aluminum.



(left) Pure aluminum. (right) Aluminum alloys are used for many high-quality bicycle components, such as this chain wheel.

Solution

The mass of 1 mole (6.022×10^{23} atoms) of aluminum is 26.98 g. The sample we are considering has a mass of 10.0 g. Since the mass is less than 26.98 g, this sample contains less than 1 mole of aluminum atoms. We can calculate the number of moles of aluminum atoms in 10.0 g as follows:

$$10.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 0.371 \text{ mol Al atoms}$$

The number of atoms in 10.0 g (0.371 mol) of aluminum is

$$0.371 \text{ mol Al} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Al}} = 2.23 \times 10^{23} \text{ atoms}$$

Reality Check: One mole of Al has a mass of 26.98 g and contains 6.022×10^{23} atoms. Our sample is 10.0 g, which is roughly 1/3 of 26.98. Thus the calculated amount should be on the order of 1/3 of 6×10^{23} , which it is.

See Exercise 3.34.

Sample Exercise 3.4

Calculating Numbers of Atoms

A silicon chip used in an integrated circuit of a microcomputer has a mass of 5.68 mg. How many silicon (Si) atoms are present in the chip?

Solution

The strategy for doing this problem is to convert from milligrams of silicon to grams of silicon, then to moles of silicon, and finally to atoms of silicon:

$$5.68 \text{ mg Si} \times \frac{1 \text{ g Si}}{1000 \text{ mg Si}} = 5.68 \times 10^{-3} \text{ g Si}$$

$$5.68 \times 10^{-3} \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 2.02 \times 10^{-4} \text{ mol Si}$$

$$2.02 \times 10^{-4} \text{ mol Si} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Si}} = 1.22 \times 10^{20} \text{ atoms}$$

Reality Check: Note that 5.68 mg of silicon is clearly much less than 1 mol of silicon (which has a mass of 28.09 g), so the final answer of 1.22×10^{20} atoms (compared with 6.022×10^{23} atoms) is in the right direction.

See Exercise 3.35.

Sample Exercise 3.5

Calculating the Number of Moles and Mass

Cobalt (Co) is a metal that is added to steel to improve its resistance to corrosion. Calculate both the number of moles in a sample of cobalt containing 5.00×10^{20} atoms and the mass of the sample.

Solution

Note that the sample of 5.00×10^{20} atoms of cobalt is less than 1 mole (6.022×10^{23} atoms) of cobalt. What fraction of a mole it represents can be determined as follows:

$$5.00 \times 10^{20} \text{ atoms Co} \times \frac{1 \text{ mol Co}}{6.022 \times 10^{23} \text{ atoms Co}} = 8.30 \times 10^{-4} \text{ mol Co}$$

Since the mass of 1 mole of cobalt atoms is 58.93 g, the mass of 5.00×10^{20} atoms can be determined as follows:

$$8.30 \times 10^{-4} \text{ mol Co} \times \frac{58.93 \text{ g Co}}{1 \text{ mol Co}} = 4.89 \times 10^{-2} \text{ g Co}$$

Reality Check: In this case the sample contains 5×10^{20} atoms, which is approximately 1/1000 of a mole. Thus the sample should have a mass of about $(1/1000)(58.93) \cong 0.06$. Our answer of ~ 0.05 makes sense.

See Exercise 3.36.



Fragments of cobalt metal.

3.4 Molar Mass

A chemical compound is, ultimately, a collection of atoms. For example, methane (the major component of natural gas) consists of molecules that each contain one carbon and four hydrogen atoms (CH_4). How can we calculate the mass of 1 mole of methane; that is, what is the mass of 6.022×10^{23} CH_4 molecules? Since each CH_4 molecule contains one carbon atom and four hydrogen atoms, 1 mole of CH_4 molecules contains 1 mole of carbon atoms and 4 moles of hydrogen atoms. The mass of 1 mole of methane can be found by summing the masses of carbon and hydrogen present:

$$\begin{aligned}\text{Mass of 1 mol C} &= 12.01 \text{ g} \\ \text{Mass of 4 mol H} &= 4 \times 1.008 \text{ g} \\ \text{Mass of 1 mol } \text{CH}_4 &= 16.04 \text{ g}\end{aligned}$$

In this case, the term 12.01 limits the number of significant figures.

A substance's molar mass is the mass in grams of 1 mole of the substance.

Because 16.04 g represents the mass of 1 mole of methane molecules, it makes sense to call it the *molar mass* for methane. Thus the **molar mass** of a substance is *the mass in grams of one mole of the compound*. Traditionally, the term *molecular weight* has been used for this quantity. However, we will use molar mass exclusively in this text. The molar mass of a known substance is obtained by summing the masses of the component atoms as we did for methane.

Sample Exercise 3.6

Calculating Molar Mass I

Juglone, a dye known for centuries, is produced from the husks of black walnuts. It is also a natural herbicide (weed killer) that kills off competitive plants around the black walnut tree but does not affect grass and other noncompetitive plants. The formula for juglone is $\text{C}_{10}\text{H}_6\text{O}_3$.

- Calculate the molar mass of juglone.
- A sample of 1.56×10^{-2} g of pure juglone was extracted from black walnut husks. How many moles of juglone does this sample represent?

Solution

- The molar mass is obtained by summing the masses of the component atoms. In 1 mole of juglone there are 10 moles of carbon atoms, 6 moles of hydrogen atoms, and 3 moles of oxygen atoms:

$$\begin{aligned}10 \text{ C: } 10 \times 12.01 \text{ g} &= 120.1 \text{ g} \\ 6 \text{ H: } 6 \times 1.008 \text{ g} &= 6.048 \text{ g} \\ 3 \text{ O: } 3 \times 16.00 \text{ g} &= 48.00 \text{ g} \\ \text{Mass of 1 mol } \text{C}_{10}\text{H}_6\text{O}_3 &= 174.1 \text{ g}\end{aligned}$$

The mass of 1 mole of juglone is 174.1 g, which is the molar mass.

- The mass of 1 mole of this compound is 174.1 g; thus 1.56×10^{-2} g is much less than a mole. The exact fraction of a mole can be determined as follows:

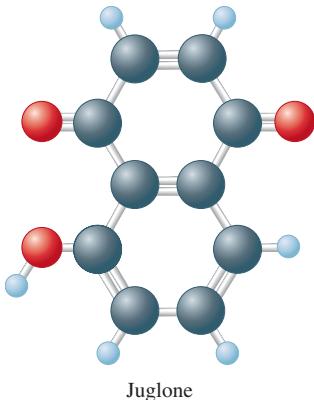
$$1.56 \times 10^{-2} \text{ g juglone} \times \frac{1 \text{ mol juglone}}{174.1 \text{ g juglone}} = 8.96 \times 10^{-5} \text{ mol juglone}$$

See Exercises 3.39 through 3.42.

Sample Exercise 3.7

Calculating Molar Mass II

Calcium carbonate (CaCO_3), also called *calcite*, is the principal mineral found in limestone, marble, chalk, pearls, and the shells of marine animals such as clams.





CHEMICAL IMPACT

Measuring the Masses of Large Molecules, or Making Elephants Fly

When a chemist produces a new molecule, one crucial property for making a positive identification is the molecule's mass. There are many ways to determine the molar mass of a compound, but one of the fastest and most accurate methods involves mass spectrometry. This method requires that the substance be put into the gas phase and ionized. The deflection that the resulting ion exhibits as it is accelerated through a magnetic field can be used to obtain a very precise value of its mass. One drawback of this method is that it is difficult to use with large molecules because they are difficult to vaporize. That is, substances that contain large molecules typically have very high boiling points, and these molecules are often damaged when they are vaporized at such high temperatures. A case in point involves proteins, an extremely important class of large biologic molecules that are quite fragile at high temperatures. Typical methods used to obtain the masses of protein molecules are slow and tedious.

Mass spectrometry has not been used previously to obtain protein masses because proteins decompose at the

temperatures necessary to vaporize them. However, a new technique called *matrix-assisted laser desorption* has been developed that allows mass spectrometric determination of protein molar masses. In this technique, the large "target" molecule is embedded in a matrix of smaller molecules. The matrix is then placed in a mass spectrometer and blasted with a laser beam, which causes its disintegration. Disintegration of the matrix frees the large target molecule, which is then swept into the mass spectrometer. One researcher involved in this project likened this method to an elephant on top of a tall building: "The elephant must fly if the building is suddenly turned into fine grains of sand."

This technique allows scientists to determine the mass of huge molecules. So far researchers have measured proteins with masses up to 350,000 daltons (1 dalton is the mass of a hydrogen atom). This method, which makes mass spectrometry a routine tool for the determination of protein masses, probably will be extended to even larger molecules such as DNA and could be a revolutionary development in the characterization of biomolecules.



Calcite crystals.

- Calculate the molar mass of calcium carbonate.
- A certain sample of calcium carbonate contains 4.86 moles. What is the mass in grams of this sample? What is the mass of the CO_3^{2-} ions present?

Solution

- Calcium carbonate is an ionic compound composed of Ca^{2+} and CO_3^{2-} ions. In 1 mole of calcium carbonate there are 1 mole of Ca^{2+} ions and 1 mole of CO_3^{2-} ions. The molar mass is calculated by summing the masses of the components:

$$1 \text{ Ca}^{2+}: 1 \times 40.08 \text{ g} = 40.08 \text{ g}$$

$$1 \text{ CO}_3^{2-}: \quad$$

$$1 \text{ C: } 1 \times 12.01 \text{ g} = 12.01 \text{ g}$$

$$3 \text{ O: } 3 \times 16.00 \text{ g} = \underline{\underline{48.00 \text{ g}}}$$

$$\text{Mass of 1 mol CaCO}_3 = 100.09 \text{ g}$$

Thus the mass of 1 mole of CaCO_3 (1 mol Ca^{2+} plus 1 mol CO_3^{2-}) is 100.09 g. This is the molar mass.

- The mass of 1 mole of CaCO_3 is 100.09 g. The sample contains nearly 5 moles, or close to 500 g. The exact amount is determined as follows:

$$4.86 \text{ mol CaCO}_3 \times \frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = 486 \text{ g CaCO}_3$$

To find the mass of carbonate ions (CO_3^{2-}) present in this sample, we must realize that 4.86 moles of CaCO_3 contains 4.86 moles of Ca^{2+} ions and 4.86 moles of CO_3^{2-} ions. The mass of 1 mole of CO_3^{2-} ions is

$$1 \text{ C: } 1 \times 12.01 = 12.01 \text{ g}$$

$$3 \text{ O: } 3 \times 16.00 = \underline{\underline{48.00 \text{ g}}}$$

$$\text{Mass of 1 mol } \text{CO}_3^{2-} = 60.01 \text{ g}$$

Thus the mass of 4.86 moles of CO_3^{2-} ions is

$$4.86 \text{ mol } \text{CO}_3^{2-} \times \frac{60.01 \text{ g } \text{CO}_3^{2-}}{1 \text{ mol } \text{CO}_3^{2-}} = 292 \text{ g } \text{CO}_3^{2-}$$

See Exercises 3.43 through 3.46.

Sample Exercise 3.8

Molar Mass and Numbers of Molecules

Isopentyl acetate ($\text{C}_7\text{H}_{14}\text{O}_2$) is the compound responsible for the scent of bananas. A molecular model of isopentyl acetate is shown in the margin below. Interestingly, bees release about $1 \mu\text{g}$ ($1 \times 10^{-6} \text{ g}$) of this compound when they sting. The resulting scent attracts other bees to join the attack. How many molecules of isopentyl acetate are released in a typical bee sting? How many atoms of carbon are present?

Solution

Since we are given a mass of isopentyl acetate and want to find the number of molecules, we must first compute the molar mass:

$$7 \text{ mol C} \times 12.01 \frac{\text{g}}{\text{mol}} = 84.07 \text{ g C}$$

$$14 \text{ mol H} \times 1.008 \frac{\text{g}}{\text{mol}} = 14.11 \text{ g H}$$

$$2 \text{ mol O} \times 16.00 \frac{\text{g}}{\text{mol}} = \frac{32.00 \text{ g O}}{130.18 \text{ g}}$$

This means that 1 mole of isopentyl acetate (6.022×10^{23} molecules) has a mass of 130.18 g.

To find the number of molecules released in a sting, we must first determine the number of moles of isopentyl acetate in $1 \times 10^{-6} \text{ g}$:

$$1 \times 10^{-6} \frac{\text{g } \text{C}_7\text{H}_{14}\text{O}_2}{\text{g } \text{C}_7\text{H}_{14}\text{O}_2} \times \frac{1 \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2}{130.18 \frac{\text{g }}{\text{mol } \text{C}_7\text{H}_{14}\text{O}_2}} = 8 \times 10^{-9} \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2$$

Since 1 mole is 6.022×10^{23} units, we can determine the number of molecules:

$$8 \times 10^{-9} \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2 \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol } \text{C}_7\text{H}_{14}\text{O}_2} = 5 \times 10^{15} \text{ molecules}$$

To determine the number of carbon atoms present, we must multiply the number of molecules by 7, since each molecule of isopentyl acetate contains seven carbon atoms:

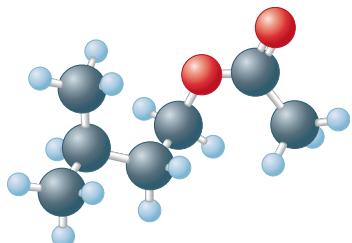
$$5 \times 10^{15} \text{ molecules} \times \frac{7 \text{ carbon atoms}}{\text{molecule}} = 4 \times 10^{16} \text{ carbon atoms}$$

Note: In keeping with our practice of always showing the correct number of significant figures, we have rounded after each step. However, if extra digits are carried throughout this problem, the final answer rounds to 3×10^{16} .

See Exercises 3.47 through 3.52.



Isopentyl acetate is released when a bee stings.



Carbon

Oxygen

Hydrogen

Isopentyl acetate

To show the correct number of significant figures in each calculation, we round after each step. In your calculations, always carry extra significant figures through to the end; then round.

3.5 Percent Composition of Compounds

There are two common ways of describing the composition of a compound: in terms of the numbers of its constituent atoms and in terms of the percentages (by mass) of its elements. We can obtain the mass percents of the elements from the formula of the compound by comparing the mass of each element present in 1 mole of the compound to the total mass of 1 mole of the compound.

For example, for ethanol, which has the formula C_2H_5OH , the mass of each element present and the molar mass are obtained as follows:

$$\text{Mass of C} = 2 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 24.02 \text{ g}$$

$$\text{Mass of H} = 6 \text{ mol} \times 1.008 \frac{\text{g}}{\text{mol}} = 6.048 \text{ g}$$

$$\text{Mass of O} = 1 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 16.00 \text{ g}$$

$$\text{Mass of 1 mol } C_2H_5OH = 46.07 \text{ g}$$

The **mass percent** (often called the *weight percent*) of carbon in ethanol can be computed by comparing the mass of carbon in 1 mole of ethanol to the total mass of 1 mole of ethanol and multiplying the result by 100:

$$\begin{aligned}\text{Mass percent of C} &= \frac{\text{mass of C in 1 mol } C_2H_5OH}{\text{mass of 1 mol } C_2H_5OH} \times 100\% \\ &= \frac{24.02 \text{ g}}{46.07 \text{ g}} \times 100\% = 52.14\%\end{aligned}$$

The mass percents of hydrogen and oxygen in ethanol are obtained in a similar manner:

$$\begin{aligned}\text{Mass percent of H} &= \frac{\text{mass of H in 1 mol } C_2H_5OH}{\text{mass of 1 mol } C_2H_5OH} \times 100\% \\ &= \frac{6.048 \text{ g}}{46.07 \text{ g}} \times 100\% = 13.13\% \\ \text{Mass percent of O} &= \frac{\text{mass of O in 1 mol } C_2H_5OH}{\text{mass of 1 mol } C_2H_5OH} \times 100\% \\ &= \frac{16.00 \text{ g}}{46.07 \text{ g}} \times 100\% = 34.73\%\end{aligned}$$

Reality Check: Notice that the percentages add up to 100.00%; this provides a check that the calculations are correct.

Sample Exercise 3.9

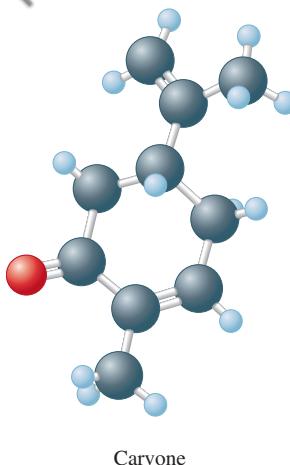
Calculating Mass Percent I

Carvone is a substance that occurs in two forms having different arrangements of the atoms but the same molecular formula ($C_{10}H_{14}O$) and mass. One type of carvone gives caraway seeds their characteristic smell, and the other type is responsible for the smell of spearmint oil. Compute the mass percent of each element in carvone.

Solution

The masses of the elements in 1 mole of carvone are

$$\text{Mass of C in 1 mol} = 10 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 120.1 \text{ g}$$



Carvone

$$\text{Mass of H in 1 mol} = 14 \text{ mol} \times 1.008 \frac{\text{g}}{\text{mol}} = 14.11 \text{ g}$$

$$\text{Mass of O in 1 mol} = 1 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 16.00 \text{ g}$$

$$\text{Mass of 1 mol } C_{10}H_{14}O = 150.2 \text{ g}$$

Next we find the fraction of the total mass contributed by each element and convert it to a percentage:

$$\text{Mass percent of C} = \frac{120.1 \text{ g C}}{150.2 \text{ g } C_{10}H_{14}O} \times 100\% = 79.96\%$$

$$\text{Mass percent of H} = \frac{14.11 \text{ g H}}{150.2 \text{ g } C_{10}H_{14}O} \times 100\% = 9.394\%$$

$$\text{Mass percent of O} = \frac{16.00 \text{ g O}}{150.2 \text{ g } C_{10}H_{14}O} \times 100\% = 10.65\%$$

Reality Check: Sum the individual mass percent values—they should total to 100% within round-off errors. In this case, the percentages add up to 100.00%.

See Exercises 3.59 and 3.60.

Sample Exercise 3.10

Although Fleming is commonly given credit for the discovery of penicillin, there is good evidence that penicillium mold extracts were used in the nineteenth century by Lord Joseph Lister to cure infections.

Calculating Mass Percent II

Penicillin, the first of a now large number of antibiotics (antibacterial agents), was discovered accidentally by the Scottish bacteriologist Alexander Fleming in 1928, but he was never able to isolate it as a pure compound. This and similar antibiotics have saved millions of lives that might have been lost to infections. Penicillin F has the formula $C_{14}H_{20}N_2SO_4$. Compute the mass percent of each element.

Solution

The molar mass of penicillin F is computed as follows:

$$\text{C: } 14 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 168.1 \text{ g}$$

$$\text{H: } 20 \text{ mol} \times 1.008 \frac{\text{g}}{\text{mol}} = 120.16 \text{ g}$$

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

$$\text{S: } 1 \text{ mol} \times 32.07 \frac{\text{g}}{\text{mol}} = 32.07 \text{ g}$$

$$\text{O: } 4 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 64.00 \text{ g}$$

$$\text{Mass of 1 mol } C_{14}H_{20}N_2SO_4 = 312.4 \text{ g}$$

$$\text{Mass percent of C} = \frac{168.1 \text{ g C}}{312.4 \text{ g } C_{14}H_{20}N_2SO_4} \times 100\% = 53.81\%$$

$$\text{Mass percent of H} = \frac{20.16 \text{ g H}}{312.4 \text{ g } C_{14}H_{20}N_2SO_4} \times 100\% = 6.453\%$$

$$\text{Mass percent of N} = \frac{28.02 \text{ g N}}{312.4 \text{ g } C_{14}H_{20}N_2SO_4} \times 100\% = 8.969\%$$

$$\text{Mass percent of S} = \frac{32.07 \text{ g S}}{312.4 \text{ g } C_{14}H_{20}N_2SO_4} \times 100\% = 10.27\%$$



Penicillin is isolated from a mold that can be grown in large quantities in fermentation tanks.

$$\text{Mass percent of O} = \frac{64.00 \text{ g O}}{312.4 \text{ g C}_{14}\text{H}_{20}\text{N}_2\text{SO}_4} \times 100\% = 20.49\%$$

Reality Check: The percentages add up to 99.99%.

See Exercises 3.61 and 3.62.

3.6 Determining the Formula of a Compound

When a new compound is prepared, one of the first items of interest is the formula of the compound. This is most often determined by taking a weighed sample of the compound and either decomposing it into its component elements or reacting it with oxygen to produce substances such as CO_2 , H_2O , and N_2 , which are then collected and weighed. A device for doing this type of analysis is shown in Fig. 3.5. The results of such analyses provide the mass of each type of element in the compound, which can be used to determine the mass percent of each element.

We will see how information of this type can be used to compute the formula of a compound. Suppose a substance has been prepared that is composed of carbon, hydrogen, and nitrogen. When 0.1156 gram of this compound is reacted with oxygen, 0.1638 gram of carbon dioxide (CO_2) and 0.1676 gram of water (H_2O) are collected. Assuming that all the carbon in the compound is converted to CO_2 , we can determine the mass of carbon originally present in the 0.1156-gram sample. To do this, we must use the fraction (by mass) of carbon in CO_2 . The molar mass of CO_2 is

$$\text{C: } 1 \text{ mol} \times 12.01 \frac{\text{g}}{\text{mol}} = 12.01 \text{ g}$$

$$\text{O: } 2 \text{ mol} \times 16.00 \frac{\text{g}}{\text{mol}} = 32.00 \text{ g}$$

$$\text{Molar mass of } \text{CO}_2 = 44.01 \text{ g/mol}$$

The fraction of carbon present by mass is

$$\frac{\text{Mass of C}}{\text{Total mass of } \text{CO}_2} = \frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2}$$

This factor can now be used to determine the mass of carbon in 0.1638 gram of CO_2 :

$$0.1638 \text{ g CO}_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2} = 0.04470 \text{ g C}$$

Remember that this carbon originally came from the 0.1156-gram sample of unknown compound. Thus the mass percent of carbon in this compound is

$$\frac{0.04470 \text{ g C}}{0.1156 \text{ g compound}} \times 100\% = 38.67\% \text{ C}$$

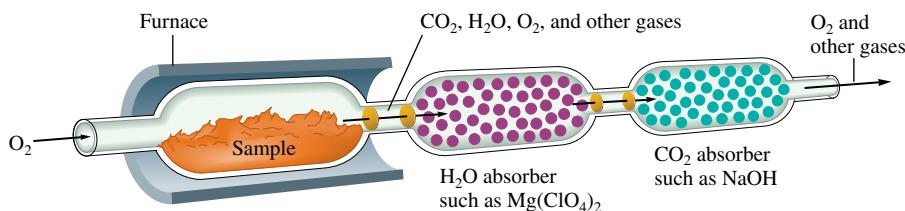
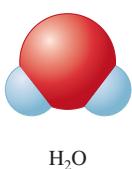
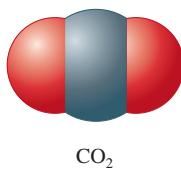


FIGURE 3.5

A schematic diagram of the combustion device used to analyze substances for carbon and hydrogen. The sample is burned in the presence of excess oxygen, which converts all its carbon to carbon dioxide and all its hydrogen to water. These products are collected by absorption using appropriate materials, and their amounts are determined by measuring the increase in masses of the absorbents.



The same procedure can be used to find the mass percent of hydrogen in the unknown compound. We assume that all the hydrogen present in the original 0.1156 gram of compound was converted to H₂O. The molar mass of H₂O is 18.02 grams, and the fraction of hydrogen by mass in H₂O is

$$\frac{\text{Mass of H}}{\text{Mass of H}_2\text{O}} = \frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}}$$

Therefore, the mass of hydrogen in 0.1676 gram of H₂O is

$$0.1676 \text{ g H}_2\text{O} \times \frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}} = 0.01875 \text{ g H}$$

The mass percent of hydrogen in the compound is

$$\frac{0.01875 \text{ g H}}{0.1156 \text{ g compound}} \times 100\% = 16.22\% \text{ H}$$

The unknown compound contains only carbon, hydrogen, and nitrogen. So far we have determined that it is 38.67% carbon and 16.22% hydrogen. The remainder must be nitrogen:

$$100.00\% - (38.67\% + 16.22\%) = 45.11\% \text{ N}$$

↑ ↑
% C % H

We have determined that the compound contains 38.67% carbon, 16.22% hydrogen, and 45.11% nitrogen. Next we use these data to obtain the formula.

Since the formula of a compound indicates the *numbers* of atoms in the compound, we must convert the masses of the elements to numbers of atoms. The easiest way to do this is to work with 100.00 grams of the compound. In the present case, 38.67% carbon by mass means 38.67 grams of carbon per 100.00 grams of compound; 16.22% hydrogen means 16.22 grams of hydrogen per 100.00 grams of compound; and so on. To determine the formula, we must calculate the number of carbon atoms in 38.67 grams of carbon, the number of hydrogen atoms in 16.22 grams of hydrogen, and the number of nitrogen atoms in 45.11 grams of nitrogen. We can do this as follows:

$$\begin{aligned} 38.67 \text{ g C} &\times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.220 \text{ mol C} \\ 16.22 \text{ g H} &\times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 16.09 \text{ mol H} \\ 45.11 \text{ g N} &\times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 3.219 \text{ mol N} \end{aligned}$$

Thus 100.00 grams of this compound contains 3.220 moles of carbon atoms, 16.09 moles of hydrogen atoms, and 3.219 moles of nitrogen atoms.

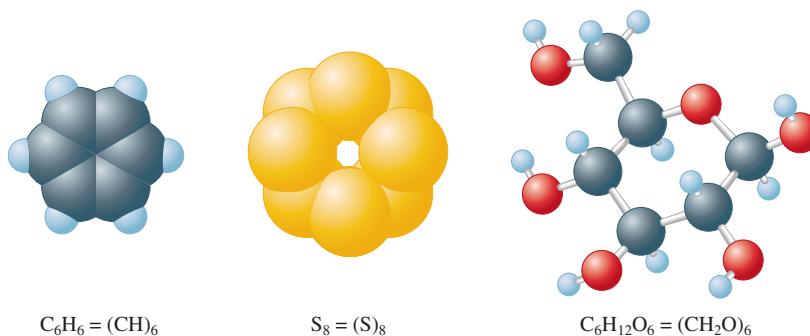
We can find the smallest *whole-number ratio* of atoms in this compound by dividing each of the mole values above by the smallest of the three:

$$\text{C: } \frac{3.220}{3.220} = 1.000 = 1$$

$$\text{H: } \frac{16.09}{3.220} = 4.997 = 5$$

$$\text{N: } \frac{3.219}{3.220} = 1.000 = 1$$

Thus the formula might well be CH₅N. However, it also could be C₂H₁₀N₂ or C₃H₁₅N₃, and so on—that is, some multiple of the smallest whole-number ratio. Each of these alternatives also has the correct relative numbers of atoms. That is, any molecule that can

**FIGURE 3.6**

Examples of substances whose empirical and molecular formulas differ. Notice that molecular formula = (empirical formula)_n, where n is an integer.

Molecular formula = (empirical formula)_n, where n is an integer.

be represented as $(\text{CH}_5\text{N})_n$, where n is an integer, has the **empirical formula** CH_5N . To be able to specify the exact formula of the molecule involved, the **molecular formula**, we must know the molar mass.

Suppose we know that this compound with empirical formula CH_5N has a molar mass of 31.06 g/mol. How do we determine which of the possible choices represents the molecular formula? Since the molecular formula is always a whole number multiple of the empirical formula, we must first find the empirical formula mass for CH_5N :

$$1 \text{ C: } 1 \times 12.01 \text{ g} = 12.01 \text{ g}$$

$$5 \text{ H: } 5 \times 1.008 \text{ g} = 5.040 \text{ g}$$

$$1 \text{ N: } 1 \times 14.01 \text{ g} = \underline{14.01 \text{ g}}$$

$$\text{Formula mass of } \text{CH}_5\text{N} = 31.06 \text{ g/mol}$$

This is the same as the known molar mass of the compound. Thus in this case the empirical formula and the molecular formula are the same; this substance consists of molecules with the formula CH_5N . It is quite common for the empirical and molecular formulas to be different; some examples where this is the case are shown in Fig. 3.6.

Sample Exercise 3.11

Determining Empirical and Molecular Formulas I

Determine the empirical and molecular formulas for a compound that gives the following percentages upon analysis (in mass percents):

$$71.65\% \text{ Cl} \quad 24.27\% \text{ C} \quad 4.07\% \text{ H}$$

The molar mass is known to be 98.96 g/mol.

Solution

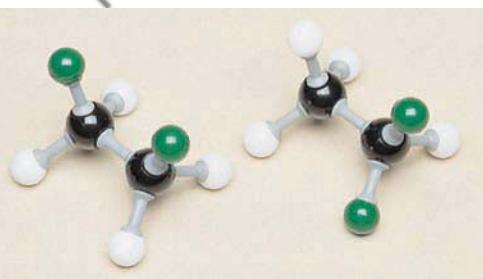
First, we convert the mass percents to masses in grams. In 100.00 g of this compound there are 71.65 g of chlorine, 24.27 g of carbon, and 4.07 g of hydrogen. We use these masses to compute the moles of atoms present:

$$71.65 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 2.021 \text{ mol Cl}$$

$$24.27 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.021 \text{ mol C}$$

$$4.07 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.04 \text{ mol H}$$

Dividing each mole value by 2.021 (the smallest number of moles present), we obtain the empirical formula ClCH_2 .

**FIGURE 3.7**

The two forms of dichloroethane.

To determine the molecular formula, we must compare the empirical formula mass with the molar mass. The empirical formula mass is 49.48 g/mol (confirm this). The molar mass is known to be 98.96 g/mol.

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{98.96 \text{ g/mol}}{49.48 \text{ g/mol}} = 2$$

$$\text{Molecular formula} = (\text{ClCH}_2)_2 = \text{Cl}_2\text{C}_2\text{H}_4$$

This substance is composed of molecules with the formula $\text{Cl}_2\text{C}_2\text{H}_4$.

Notice that the method we employ here allows us to determine the molecular formula of a compound but not its structural formula. The compound $\text{Cl}_2\text{C}_2\text{H}_4$ is called *dichloroethane*. There are two forms of this compound, shown in Fig. 3.7. The form on the right was formerly used as an additive in leaded gasoline.

See Exercises 3.57 and 3.58.

Sample Exercise 3.12

Determining Empirical and Molecular Formulas II

A white powder is analyzed and found to contain 43.64% phosphorus and 56.36% oxygen by mass. The compound has a molar mass of 283.88 g/mol. What are the compound's empirical and molecular formulas?

Solution

In 100.00 g of this compound there are 43.64 g of phosphorus and 56.36 g of oxygen. In terms of moles, in 100.00 g of the compound we have

$$43.64 \text{ g P} \times \frac{1 \text{ mol P}}{30.97 \text{ g P}} = 1.409 \text{ mol P}$$

$$56.36 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.523 \text{ mol O}$$

Dividing both mole values by the smaller one gives

$$\frac{1.409}{1.409} = 1 \text{ P} \quad \text{and} \quad \frac{3.523}{1.409} = 2.5 \text{ O}$$

This yields the formula $\text{PO}_{2.5}$. Since compounds must contain whole numbers of atoms, the empirical formula should contain only whole numbers. To obtain the simplest set of whole numbers, we multiply both numbers by 2 to give the empirical formula P_2O_5 .

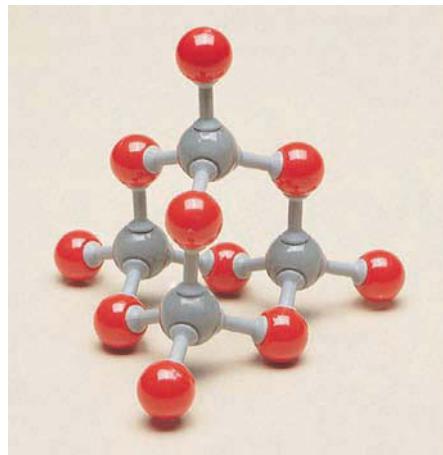
To obtain the molecular formula, we must compare the empirical formula mass to the molar mass. The empirical formula mass for P_2O_5 is 141.94.

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{283.88}{141.94} = 2$$

The molecular formula is $(\text{P}_2\text{O}_5)_2$, or P_4O_{10} .

The structural formula of this interesting compound is given in Fig. 3.8.

See Exercise 3.59.

**FIGURE 3.8**

The structure of P_4O_{10} . Note that some of the oxygen atoms act as "bridges" between the phosphorus atoms. This compound has a great affinity for water and is often used as a desiccant, or drying agent.

In Sample Exercises 3.11 and 3.12 we found the molecular formula by comparing the empirical formula mass with the molar mass. There is an alternate way to obtain the molecular formula. For example, in Sample Exercise 3.11 we know the molar mass of the compound is 98.96 g/mol. This means that 1 mole of the compound weighs 98.96 grams.

Since we also know the mass percentages of each element, we can compute the mass of each element present in 1 mole of compound:

$$\text{Chlorine: } \frac{71.65 \text{ g Cl}}{100.0 \text{ g compound}} \times \frac{98.96 \text{ g}}{\text{mol}} = \frac{70.90 \text{ g Cl}}{\text{mol compound}}$$

$$\text{Carbon: } \frac{24.27 \text{ g C}}{100.0 \text{ g compound}} \times \frac{98.96 \text{ g}}{\text{mol}} = \frac{24.02 \text{ g C}}{\text{mol compound}}$$

$$\text{Hydrogen: } \frac{4.07 \text{ g H}}{100.0 \text{ g compound}} \times \frac{98.96 \text{ g}}{\text{mol}} = \frac{4.03 \text{ g H}}{\text{mol compound}}$$

Now we can compute moles of atoms present per mole of compound:

$$\text{Chlorine: } \frac{70.90 \text{ g Cl}}{\text{mol compound}} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = \frac{2.000 \text{ mol Cl}}{\text{mol compound}}$$

$$\text{Carbon: } \frac{24.02 \text{ g C}}{\text{mol compound}} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = \frac{2.000 \text{ mol C}}{\text{mol compound}}$$

$$\text{Hydrogen: } \frac{4.03 \text{ g H}}{\text{mol compound}} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = \frac{4.00 \text{ mol H}}{\text{mol compound}}$$

Thus 1 mole of the compound contains 2 mol Cl atoms, 2 mol C atoms, and 4 mol H atoms, and the molecular formula is $\text{Cl}_2\text{C}_2\text{H}_4$, as obtained in Sample Exercise 3.11.

Sample Exercise 3.13

Determining a Molecular Formula

Caffeine, a stimulant found in coffee, tea, and chocolate, contains 49.48% carbon, 5.15% hydrogen, 28.87% nitrogen, and 16.49% oxygen by mass and has a molar mass of 194.2 g/mol. Determine the molecular formula of caffeine.

Solution

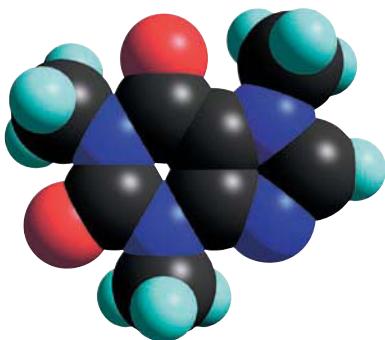
We will first determine the mass of each element in 1 mole (194.2 g) of caffeine:

$$\frac{49.48 \text{ g C}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{96.09 \text{ g C}}{\text{mol caffeine}}$$

$$\frac{5.15 \text{ g H}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{10.0 \text{ g H}}{\text{mol caffeine}}$$

$$\frac{28.87 \text{ g N}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{56.07 \text{ g N}}{\text{mol caffeine}}$$

$$\frac{16.49 \text{ g O}}{100.0 \text{ g caffeine}} \times \frac{194.2 \text{ g}}{\text{mol}} = \frac{32.02 \text{ g O}}{\text{mol caffeine}}$$



Computer-generated molecule of caffeine.

Now we will convert to moles:

$$\text{Carbon: } \frac{96.09 \text{ g C}}{\text{mol caffeine}} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = \frac{8.001 \text{ mol C}}{\text{mol caffeine}}$$

$$\text{Hydrogen: } \frac{10.0 \text{ g H}}{\text{mol caffeine}} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = \frac{9.92 \text{ mol H}}{\text{mol caffeine}}$$

$$\text{Nitrogen: } \frac{56.07 \text{ g N}}{\text{mol caffeine}} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = \frac{4.002 \text{ mol N}}{\text{mol caffeine}}$$

$$\text{Oxygen: } \frac{32.02 \text{ g O}}{\text{mol caffeine}} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = \frac{2.001 \text{ mol O}}{\text{mol caffeine}}$$

Rounding the numbers to integers gives the molecular formula for caffeine: $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$.

See Exercise 3.76.

The methods for obtaining empirical and molecular formulas are summarized as follows:

Empirical Formula Determination

- Since mass percentage gives the number of grams of a particular element per 100 grams of compound, base the calculation on 100 grams of compound. Each percent will then represent the mass in grams of that element.
- Determine the number of moles of each element present in 100 grams of compound using the atomic masses of the elements present.
- Divide each value of the number of moles by the smallest of the values. If each resulting number is a whole number (after appropriate rounding), these numbers represent the subscripts of the elements in the empirical formula.
- If the numbers obtained in the previous step are not whole numbers, multiply each number by an integer so that the results are all whole numbers.

Numbers very close to whole numbers, such as 9.92 and 1.08, should be rounded to whole numbers. Numbers such as 2.25, 4.33, and 2.72 should not be rounded to whole numbers.

Molecular Formula Determination

Method One

- Obtain the empirical formula.
- Compute the mass corresponding to the empirical formula.
- Calculate the ratio

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

- The integer from the previous step represents the number of empirical formula units in one molecule. When the empirical formula subscripts are multiplied by this integer, the molecular formula results. This procedure is summarized by the equation:

$$\text{Molecular formula} = (\text{empirical formula}) \times \frac{\text{molar mass}}{\text{empirical formula mass}}$$

Method Two

- Using the mass percentages and the molar mass, determine the mass of each element present in one mole of compound.
- Determine the number of moles of each element present in one mole of compound.
- The integers from the previous step represent the subscripts in the molecular formula.

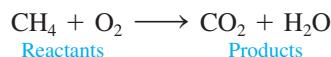
Note that method two assumes that the molar mass of the compound is known accurately.

3.7 Chemical Equations

Chemical Reactions

A chemical change involves a reorganization of the atoms in one or more substances. For example, when the methane (CH_4) in natural gas combines with oxygen (O_2) in the air and burns, carbon dioxide (CO_2) and water (H_2O) are formed. This process is represented

by a **chemical equation** with the **reactants** (here methane and oxygen) on the left side of an arrow and the **products** (carbon dioxide and water) on the right side:

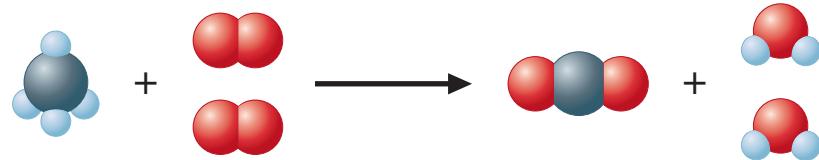


Notice that the atoms have been reorganized. *Bonds have been broken, and new ones have been formed.* It is important to recognize that *in a chemical reaction, atoms are neither created nor destroyed. All atoms present in the reactants must be accounted for among the products.* In other words, there must be the same number of each type of atom on the product side and on the reactant side of the arrow. Making sure that this rule is obeyed is called **balancing a chemical equation** for a reaction.

The equation (shown above) for the reaction between CH_4 and O_2 is not balanced. We can see this from the following representation of the reaction:

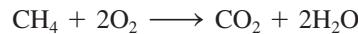


Notice that the number of oxygen atoms (in O_2) on the left of the arrow is two, while on the right there are three O atoms (in CO_2 and H_2O). Also, there are four hydrogen atoms (in CH_4) on the left and only two (in H_2O) on the right. Remember that a chemical reaction is simply a rearrangement of the atoms (a change in the way they are organized). Atoms are not created or destroyed in a chemical reaction. Thus the reactants and products must occur in numbers that give the same number of each type of atom among both the reactants and products. Simple trial and error will allow us to figure this out for the reaction of methane with oxygen. The needed numbers of molecules are

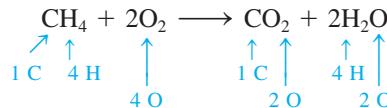


Notice that now we have the same number of each type of atom represented among the reactants and the products.

We can represent the preceding situation in a shorthand manner by the following chemical equation:



We can check that the equation is balanced by comparing the number of each type of atom on both sides:



To summarize, we have

Reactants	Products
1 C	1 C
4 H	4 H
4 O	4 O



Methane reacts with oxygen to produce the flame in a Bunsen burner.

TABLE 3.2 Information Conveyed by the Balanced Equation for the Combustion of Methane

Reactants		Products
$\text{CH}_4(g) + 2\text{O}_2(g)$	→	$\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
1 molecule + 2 molecules	→	1 molecule + 2 molecules
1 mole + 2 moles	→	1 mole + 2 moles
6.022×10^{23} molecules + 2 (6.022×10^{23} molecules)	→	6.022×10^{23} molecules + 2 (6.022×10^{23} molecules)
16 g + 2 (32 g)		44 g + 2 (18 g)
80 g reactants	→	80 g products

The Meaning of a Chemical Equation



Visualization: Oxygen, Hydrogen, Soap Bubbles, and Balloons

The chemical equation for a reaction gives two important types of information: the nature of the reactants and products and the relative numbers of each.

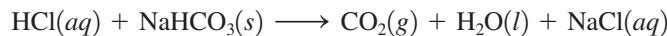
The reactants and products in a specific reaction must be identified by experiment. Besides specifying the compounds involved in the reaction, the equation often gives the *physical states* of the reactants and products:

State	Symbol
Solid	(s)
Liquid	(l)
Gas	(g)
Dissolved in water (in aqueous solution)	(aq)

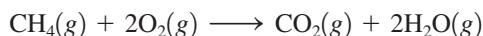


Hydrochloric acid reacts with solid sodium hydrogen carbonate to produce gaseous carbon dioxide.

For example, when hydrochloric acid in aqueous solution is added to solid sodium hydrogen carbonate, the products carbon dioxide gas, liquid water, and sodium chloride (which dissolves in the water) are formed:



The relative numbers of reactants and products in a reaction are indicated by the *coefficients* in the balanced equation. (The coefficients can be determined because we know that the same number of each type of atom must occur on both sides of the equation.) For example, the balanced equation



can be interpreted in several equivalent ways, as shown in Table 3.2. Note that the total mass is 80 grams for both reactants and products. We expect the mass to remain constant, since chemical reactions involve only a rearrangement of atoms. Atoms, and therefore mass, are conserved in a chemical reaction.

From this discussion you can see that a balanced chemical equation gives you a great deal of information.

3.8 Balancing Chemical Equations

An unbalanced chemical equation is of limited use. Whenever you see an equation, you should ask yourself whether it is balanced. The principle that lies at the heart of the balancing process is that atoms are conserved in a chemical reaction. The same number of each type of atom must be found among the reactants and products. It is also important to recognize that the identities of the reactants and products of a reaction are determined by experimental observation. For example, when liquid ethanol is burned in the presence of sufficient oxygen gas, the products are always carbon dioxide and water. When the equation for this reaction is

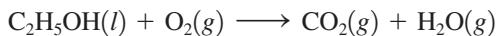


Visualization: Conservation of Mass and Balancing Equations

In balancing equations, start with the most complicated molecule.

balanced, the *identities* of the reactants and products must not be changed. *The formulas of the compounds must never be changed in balancing a chemical equation.* That is, the subscripts in a formula cannot be changed, nor can atoms be added or subtracted from a formula.

Most chemical equations can be balanced by inspection, that is, by trial and error. It is always best to start with the most complicated molecules (those containing the greatest number of atoms). For example, consider the reaction of ethanol with oxygen, given by the unbalanced equation

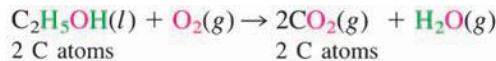


which can be represented by the following molecular models:

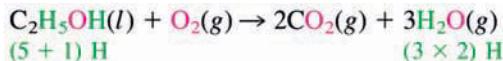


Notice that the carbon and hydrogen atoms are not balanced. There are two carbon atoms on the left and one on the right, and there are six hydrogens on the left and two on the right. We need to find the correct numbers of reactants and products so that we have the same number of all types of atoms among the reactants and products. We will balance the equation “by inspection” (a systematic trial-and-error procedure).

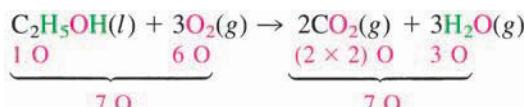
The most complicated molecule here is $\text{C}_2\text{H}_5\text{OH}$. We will begin by balancing the products that contain the atoms in $\text{C}_2\text{H}_5\text{OH}$. Since $\text{C}_2\text{H}_5\text{OH}$ contains two carbon atoms, we place the coefficient 2 before the CO_2 to balance the carbon atoms:



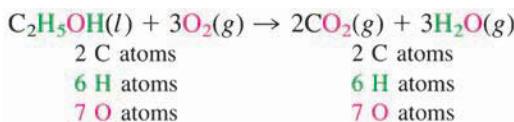
Since $\text{C}_2\text{H}_5\text{OH}$ contains six hydrogen atoms, the hydrogen atoms can be balanced by placing a 3 before the H_2O :



Last, we balance the oxygen atoms. Note that the right side of the preceding equation contains seven oxygen atoms, whereas the left side has only three. We can correct this by putting a 3 before the O_2 to produce the balanced equation:

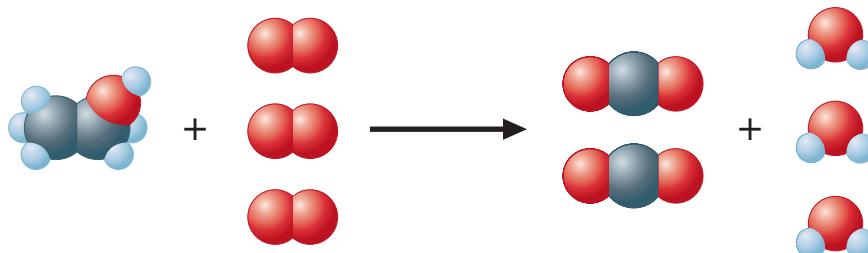


Now we check:



The equation is balanced.

The balanced equation can be represented as follows:



You can see that all the elements balance.

Writing and Balancing the Equation for a Chemical Reaction

- 1 Determine what reaction is occurring. What are the reactants, the products, and the physical states involved?
 - 2 Write the *unbalanced* equation that summarizes the reaction described in step 1.
 - 3 Balance the equation by inspection, starting with the most complicated molecule(s). Determine what coefficients are necessary so that the same number of each type of atom appears on both reactant and product sides. Do not change the identities (formulas) of any of the reactants or products.

Sample Exercise 3.14

Balancing a Chemical Equation I

Chromate and dichromate compounds are carcinogens (cancer-inducing agents) and should be handled very carefully.

Chromium compounds exhibit a variety of bright colors. When solid ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, a vivid orange compound, is ignited, a spectacular reaction occurs, as shown in the two photographs on the next page. Although the reaction is actually somewhat more complex, let's assume here that the products are solid chromium(III) oxide, nitrogen gas (consisting of N_2 molecules), and water vapor. Balance the equation for this reaction.

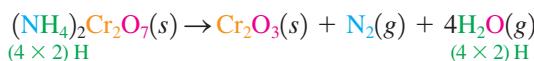
Solution

- 1 From the description given, the reactant is solid ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s)$, and the products are nitrogen gas, $\text{N}_2(g)$, water vapor, $\text{H}_2\text{O}(g)$, and solid chromium(III) oxide, $\text{Cr}_2\text{O}_3(s)$. The formula for chromium(III) oxide can be determined by recognizing that the Roman numeral III means that Cr^{3+} ions are present. For a neutral compound, the formula must then be Cr_2O_3 , since each oxide ion is O^{2-} .

- 2 The unbalanced equation is

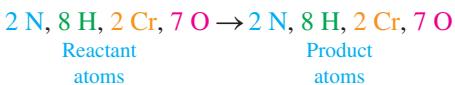


- 3 Note that nitrogen and chromium are balanced (two nitrogen atoms and two chromium atoms on each side), but hydrogen and oxygen are not. A coefficient of 4 for H_2O balances the hydrogen atoms:



Note that in balancing the hydrogen we also have balanced the oxygen, since there are seven oxygen atoms in the reactants and in the products.

Reality Check:



The equation is balanced.

See Exercises 3.81 and 3.82.



Decomposition of ammonium dichromate.

**Sample Exercise 3.15****Balancing a Chemical Equation II**

The Ostwald process is described in Section 20.2.

At 1000°C, ammonia gas, $\text{NH}_3(g)$, reacts with oxygen gas to form gaseous nitric oxide, $\text{NO}(g)$, and water vapor. This reaction is the first step in the commercial production of nitric acid by the Ostwald process. Balance the equation for this reaction.

Solution

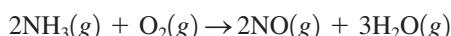
The unbalanced equation for the reaction is



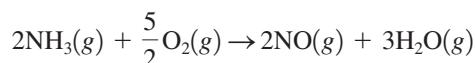
Because all the molecules in this equation are of about equal complexity, where we start in balancing it is rather arbitrary. Let's begin by balancing the hydrogen. A coefficient of 2 for NH_3 and a coefficient of 3 for H_2O give six atoms of hydrogen on both sides:



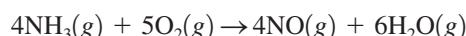
The nitrogen can be balanced with a coefficient of 2 for NO :



Finally, note that there are two atoms of oxygen on the left and five on the right. The oxygen can be balanced with a coefficient of $\frac{5}{2}$ for O_2 :

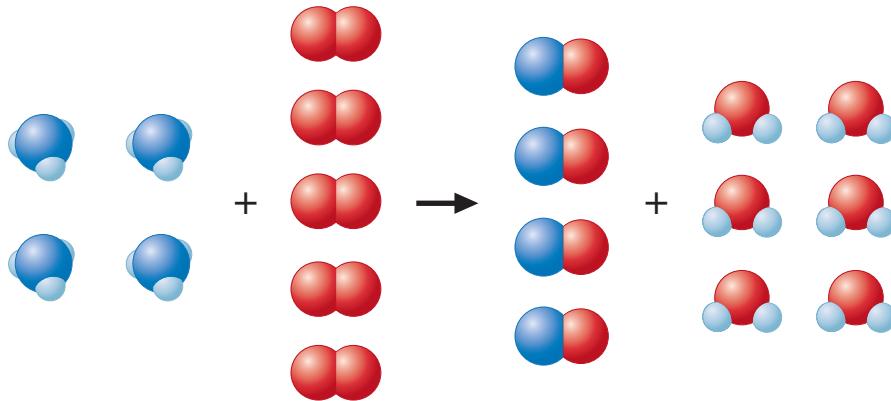


However, the usual custom is to have whole-number coefficients. We simply multiply the entire equation by 2.



Reality Check: There are 4 N, 12 H, and 10 O on both sides, so the equation is balanced.

We can represent this balanced equation visually as

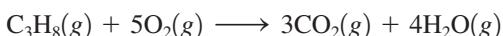


See Exercises 3.83 through 3.88.

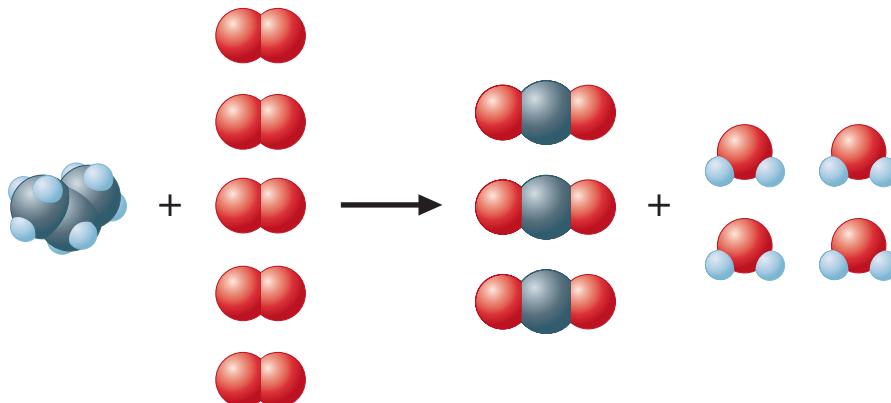
3.9 Stoichiometric Calculations: Amounts of Reactants and Products

As we have seen in previous sections of this chapter, the coefficients in chemical equations represent *numbers* of molecules, not masses of molecules. However, when a reaction is to be run in a laboratory or chemical plant, the amounts of substances needed cannot be determined by counting molecules directly. Counting is always done by weighing. In this section we will see how chemical equations can be used to determine the *masses* of reacting chemicals.

To develop the principles for dealing with the stoichiometry of reactions, we will consider the reaction of propane with oxygen to produce carbon dioxide and water. We will consider the question: “*What mass of oxygen will react with 96.1 grams of propane?*” In doing stoichiometry, the first thing we must do is *write the balanced chemical equation* for the reaction. In this case the balanced equation is



which can be visualized as



This equation means that 1 mole of C_3H_8 reacts with 5 moles of O_2 to produce 3 moles of CO_2 and 4 moles of H_2O . To use this equation to find the masses of reactants and products, we must be able to convert between masses and moles of substances. Thus we must first ask: “*How many moles of propane are present in 96.1 grams of propane?*” The molar



CHEMICAL IMPACT

High Mountains—Low Octane

The next time that you visit a gas station, take a moment to note the octane rating that accompanies the grade of gasoline that you are purchasing. The gasoline is priced according to its octane rating—a measure of the fuel’s antiknock properties. In a conventional internal combustion engine, gasoline vapors and air are drawn into the combustion cylinder on the downward stroke of the piston. This air–fuel mixture is compressed on the upward piston stroke (compression stroke), and a spark from the sparkplug ignites the mix. The rhythmic combustion of the air–fuel mix occurring sequentially in several cylinders furnishes the power to propel the vehicle down the road. Excessive heat and pressure (or poor-quality fuel) within the cylinder may cause the premature combustion of the mixture—commonly known as engine “knock” or “ping.” Over time, this engine knock can damage the engine, resulting in inefficient performance and costly repairs.

A consumer typically is faced with three choices of gasoline, with octane ratings of 87 (regular), 89 (midgrade), and 93 (premium). But if you happen to travel or live in the

higher elevations of the Rocky Mountain states, you might be surprised to find different octane ratings at the gasoline pumps. The reason for this provides a lesson in stoichiometry. At higher elevations the air is less dense—the volume of oxygen per unit volume of air is smaller. Most engines are designed to achieve a 14:1 oxygen-to-fuel ratio in the cylinder prior to combustion. If less oxygen is available, then less fuel is required to achieve this optimal ratio. In turn, the lower volumes of oxygen and fuel result in a lower pressure in the cylinder. Because high pressure tends to promote knocking, the lower pressure within engine cylinders at higher elevations promotes a more controlled combustion of the air–fuel mixture, and therefore, octane requirements are lower. While consumers in the Rocky Mountain states can purchase three grades of gasoline, the octane ratings of these fuel blends are different from those in the rest of the United States. In Denver, Colorado, regular gasoline is 85 octane, midgrade is 87 octane, and premium is 91 octane—2 points lower than gasoline sold in most of the rest of the country.

mass of propane to three significant figures is 44.1 (that is, $3 \times 12.01 + 8 \times 1.008$). The moles of propane can be calculated as follows:

$$96.1 \text{ g } \text{C}_3\text{H}_8 \times \frac{1 \text{ mol } \text{C}_3\text{H}_8}{44.1 \text{ g } \text{C}_3\text{H}_8} = 2.18 \text{ mol } \text{C}_3\text{H}_8$$

Next we must take into account the fact that each mole of propane reacts with 5 moles of oxygen. The best way to do this is to use the balanced equation to construct a **mole ratio**. In this case we want to convert from moles of propane to moles of oxygen. From the balanced equation we see that 5 moles of O₂ is required for each mole of C₃H₈, so the appropriate ratio is

$$\frac{5 \text{ mol O}_2}{1 \text{ mol } \text{C}_3\text{H}_8}$$

Multiplying the number of moles of C₃H₈ by this factor gives the number of moles of O₂ required:

$$2.18 \text{ mol } \text{C}_3\text{H}_8 \times \frac{5 \text{ mol O}_2}{1 \text{ mol } \text{C}_3\text{H}_8} = 10.9 \text{ mol O}_2$$

Notice that the mole ratio is set up so that the moles of C₃H₈ cancel out, and the units that result are moles of O₂.

Since the original question asked for the mass of oxygen needed to react with 96.1 grams of propane, the 10.9 moles of O₂ must be converted to *grams*. Since the molar mass of O₂ is 32.0 g/mol,

$$10.9 \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 349 \text{ g O}_2$$

Therefore, 349 grams of oxygen is required to burn 96.1 grams of propane.

This example can be extended by asking: “*What mass of carbon dioxide is produced when 96.1 grams of propane is combusted with oxygen?*” In this case we must convert between moles of propane and moles of carbon dioxide. This can be accomplished by looking at the balanced equation, which shows that 3 moles of CO₂ is produced for each mole of C₃H₈ reacted. The mole ratio needed to convert from moles of propane to moles of carbon dioxide is

$$\frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8}$$

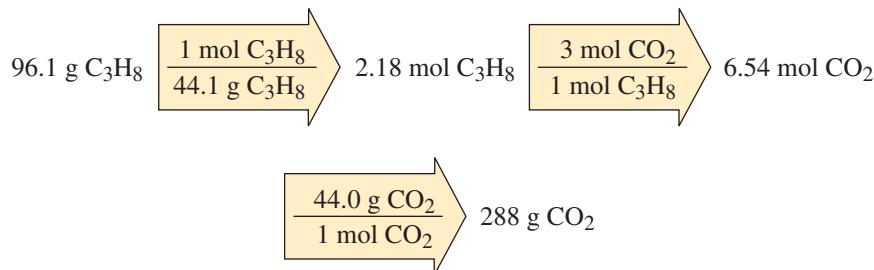
The conversion is

$$2.18 \text{ mol C}_3\text{H}_8 \times \frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} = 6.54 \text{ mol CO}_2$$

Then, using the molar mass of CO₂ (44.0 g/mol), we calculate the mass of CO₂ produced:

$$6.54 \text{ mol CO}_2 \times \frac{44.0 \text{ g CO}_2}{1 \text{ mol CO}_2} = 288 \text{ g CO}_2$$

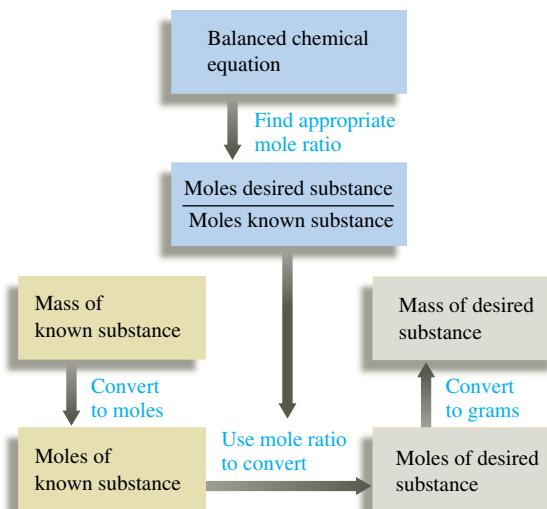
We will now summarize the sequence of steps needed to carry out stoichiometric calculations.



Calculating Masses of Reactants and Products in Chemical Reactions

- 1 Balance the equation for the reaction.
- 2 Convert the known mass of the reactant or product to moles of that substance.
- 3 Use the balanced equation to set up the appropriate mole ratios.
- 4 Use the appropriate mole ratios to calculate the number of moles of the desired reactant or product.
- 5 Convert from moles back to grams if required by the problem.

These steps are summarized by the following diagram:



Sample Exercise 3.16**Chemical Stoichiometry I**

Solid lithium hydroxide is used in space vehicles to remove exhaled carbon dioxide from the living environment by forming solid lithium carbonate and liquid water. What mass of gaseous carbon dioxide can be absorbed by 1.00 kg of lithium hydroxide?

Solution

→ 1 Using the description of the reaction, we can write the unbalanced equation:



The balanced equation is



→ 2 We convert the given mass of LiOH to moles, using the molar mass of LiOH ($6.941 + 16.00 + 1.008 = 23.95$ g/mol):

$$1.00 \text{ kg LiOH} \times \frac{1000 \text{ g LiOH}}{1 \text{ kg LiOH}} \times \frac{1 \text{ mol LiOH}}{23.95 \text{ g LiOH}} = 41.8 \text{ mol LiOH}$$

→ 3 Since we want to determine the amount of CO_2 that reacts with the given amount of LiOH, the appropriate mole ratio is

$$\frac{1 \text{ mol CO}_2}{2 \text{ mol LiOH}}$$

→ 4 We calculate the moles of CO_2 needed to react with the given mass of LiOH using this mole ratio:

$$41.8 \text{ mol LiOH} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol LiOH}} = 20.9 \text{ mol CO}_2$$

→ 5 Next we calculate the mass of CO_2 , using its molar mass (44.0 g/mol):

$$20.9 \text{ mol CO}_2 \times \frac{44.0 \text{ g CO}_2}{1 \text{ mol CO}_2} = 9.20 \times 10^2 \text{ g CO}_2$$

Thus 920. g of $\text{CO}_2(g)$ will be absorbed by 1.00 kg of $\text{LiOH}(s)$.

See Exercises 3.89 and 3.90.

Sample Exercise 3.17**Chemical Stoichiometry II**

Baking soda (NaHCO_3) is often used as an antacid. It neutralizes excess hydrochloric acid secreted by the stomach:



Milk of magnesia, which is an aqueous suspension of magnesium hydroxide, is also used as an antacid:

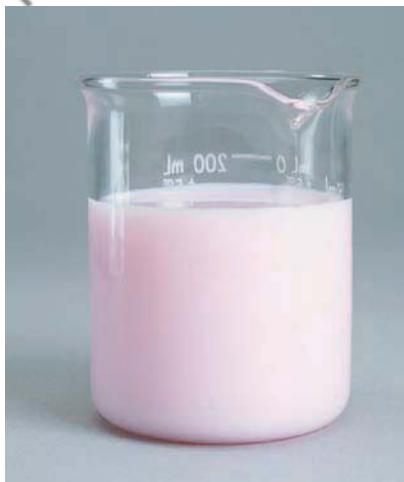


Which is the more effective antacid per gram, NaHCO_3 or Mg(OH)_2 ?

Solution

To answer the question, we must determine the amount of HCl neutralized per gram of NaHCO_3 and per gram of Mg(OH)_2 . Using the molar mass of NaHCO_3 (84.01 g/mol), we can determine the moles of NaHCO_3 in 1.00 g of NaHCO_3 :

$$1.00 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} = 1.19 \times 10^{-2} \text{ mol NaHCO}_3$$



Milk of magnesia contains a suspension of $\text{Mg}(\text{OH})_2(s)$.

The details of the Haber process are discussed in Section 19.2.



Visualization: Limiting Reactant

Next we determine the moles of HCl using the mole ratio 1 mol HCl/1 mol NaHCO_3 :

$$1.19 \times 10^{-2} \text{ mol NaHCO}_3 \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaHCO}_3} = 1.19 \times 10^{-2} \text{ mol HCl}$$

Thus 1.00 g of NaHCO_3 will neutralize 1.19×10^{-2} mol HCl.

Using the molar mass of $\text{Mg}(\text{OH})_2$ (58.32 g/mol), we determine the moles of $\text{Mg}(\text{OH})_2$ in 1.00 g:

$$1.00 \text{ g Mg(OH)}_2 \times \frac{1 \text{ mol Mg(OH)}_2}{58.32 \text{ g Mg(OH)}_2} = 1.71 \times 10^{-2} \text{ mol Mg(OH)}_2$$

To determine the moles of HCl that will react with this amount of $\text{Mg}(\text{OH})_2$, we use the mole ratio 2 mol HCl/1 mol $\text{Mg}(\text{OH})_2$:

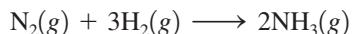
$$1.71 \times 10^{-2} \text{ mol Mg(OH)}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Mg(OH)}_2} = 3.42 \times 10^{-2} \text{ mol HCl}$$

Thus 1.00 g of $\text{Mg}(\text{OH})_2$ will neutralize 3.42×10^{-2} mol HCl. It is a better antacid per gram than NaHCO_3 .

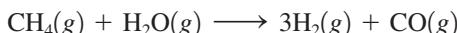
See Exercises 3.91 and 3.92.

3.10 Calculations Involving a Limiting Reactant

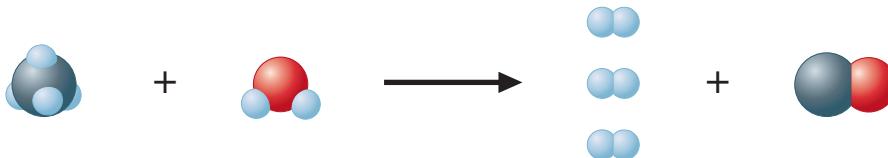
When chemicals are mixed together to undergo a reaction, they are often mixed in **stoichiometric quantities**, that is, in exactly the correct amounts so that all reactants “run out” (are used up) at the same time. To clarify this concept, let’s consider the production of hydrogen for use in the manufacture of ammonia by the **Haber process**. Ammonia, a very important fertilizer itself and a starting material for other fertilizers, is made by combining nitrogen (from the air) with hydrogen according to the equation



Hydrogen can be obtained from the reaction of methane with water vapor:



We can illustrate what we mean by stoichiometric quantities by first visualizing the balanced equation as follows:



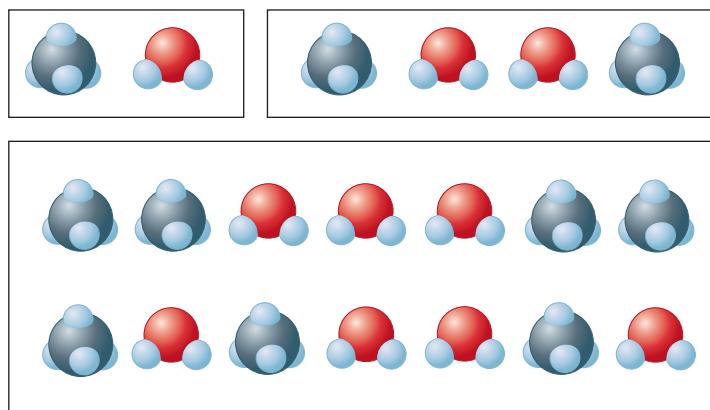
Since this reaction involves one molecule of methane reacting with one molecule of water, to have stoichiometric amounts of methane and water we must have equal numbers of them, as shown in Fig. 3.9, where several stoichiometric mixtures are shown.

Suppose we want to calculate the mass of water required to react *exactly* with 2.50×10^3 kilograms of methane. That is, how much water will just consume all the 2.50×10^3 kilograms of methane, leaving no methane or water remaining?

To do this calculation, we need to recognize that we need equal numbers of methane and water molecules. Therefore, we first need to find the number of moles of methane molecules in 2.50×10^3 kg (2.50×10^6 g) of methane:

$$2.50 \times 10^6 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} = 1.56 \times 10^5 \text{ mol CH}_4 \text{ molecules}$$

↑
molar mass of CH₄

**FIGURE 3.9**

Three different stoichiometric mixtures of methane and water, which react one-to-one.

This same number of water molecules has a mass determined as follows:

$$1.56 \times 10^5 \text{ mol H}_2\text{O} \times \frac{18.02 \text{ g}}{\text{mol H}_2\text{O}} = 2.81 \times 10^6 \text{ g H}_2\text{O} = 2.81 \times 10^3 \text{ kg H}_2\text{O}$$

Thus, if 2.50×10^3 kilograms of methane is mixed with 2.81×10^3 kilograms of water, both reactants will “run out” at the same time. The reactants have been mixed in stoichiometric quantities.

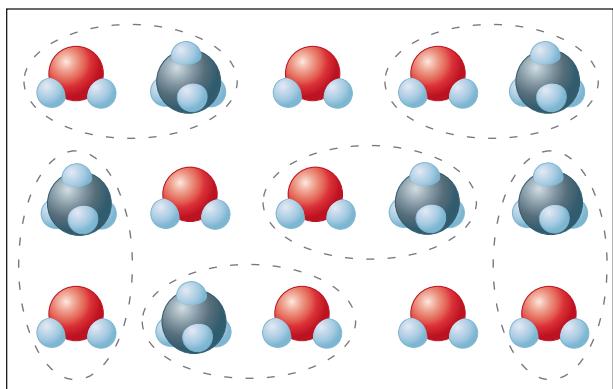
If, on the other hand, 2.50×10^3 kilograms of methane is mixed with 3.00×10^3 kilograms of water, the methane will be consumed before the water runs out. The water will be in *excess*; that is, there will be more water molecules than methane molecules in the reaction mixture. What is the implication of this with respect to the number of product molecules that can form?

To answer this question, consider the situation on a smaller scale. Assume we mix 10 CH₄ molecules and 17 H₂O molecules and let them react. How many H₂ and CO molecules can form?

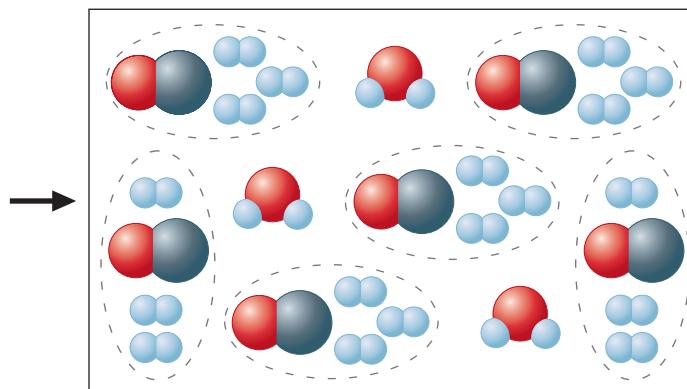
First picture the mixture of CH₄ and H₂O molecules as shown in Fig. 3.10.

Then imagine that groups consisting of one CH₄ molecule and one H₂O molecule (Fig. 3.10) will react to form three H₂ and one CO molecules (Fig. 3.11).

Notice that products can form only when both CH₄ and H₂O are available to react. Once the 10 CH₄ molecules are used up by reacting with 10 H₂O molecules, the remaining water

**FIGURE 3.10**

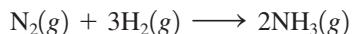
A mixture of CH₄ and H₂O molecules.

**FIGURE 3.11**

Methane and water have reacted to form products according to the equation CH₄ + H₂O \longrightarrow 3H₂ + CO.

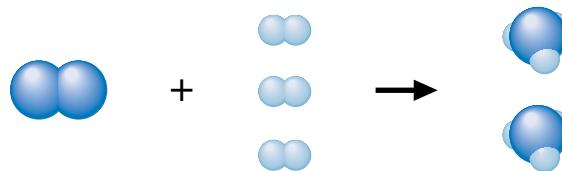
molecules cannot react. They are in excess. Thus the number of products that can form is *limited* by the methane. Once the methane is consumed, no more products can be formed, even though some water still remains. In this situation the amount of methane *limits* the amount of products that can be formed. This brings us to the concept of the **limiting reactant** (or **limiting reagent**), which is the reactant that is consumed first and that therefore limits the amounts of products that can be formed. In any stoichiometry calculation involving a chemical reaction, it is essential to determine which reactant is limiting so as to calculate correctly the amounts of products that will be formed.

To further explore the idea of a limiting reactant, consider the ammonia synthesis reaction:



Ammonia is dissolved in irrigation water to provide fertilizer for a field of corn.

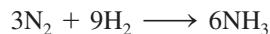
Assume that 5 N₂ molecules and 9 H₂ molecules are placed in a flask. Is this a stoichiometric mixture of reactants, or will one of them be consumed before the other runs out? From the balanced equation we know that each N₂ molecule requires 3 H₂ molecules for the reaction to occur:



Thus the required H₂/N₂ ratio is 3H₂/1N₂. In our experiment we have 9 H₂ and 5 N₂, or a ratio of 9H₂/5N₂ = 1.8H₂/1N₂.

Since the actual ratio (1.8:1) of H₂/N₂ is less than the ratio required by the balanced equation (3:1), there is not enough hydrogen to react with all the nitrogen. That is, the hydrogen will run out first, leaving some unreacted N₂ molecules. We can visualize this as shown in Fig. 3.12.

Figure 3.12 shows that 3 of the N₂ molecules react with the 9 H₂ molecules to produce 6 NH₃ molecules:



This leaves 2 N₂ molecules unreacted—the nitrogen is in excess.

What we have shown here is that in this experiment the hydrogen is the limiting reactant. The amount of H₂ initially present determines the amount of NH₃ that can form. The reaction was not able to use up all the N₂ molecules because the H₂ molecules were all consumed by the first 3 N₂ molecules to react.

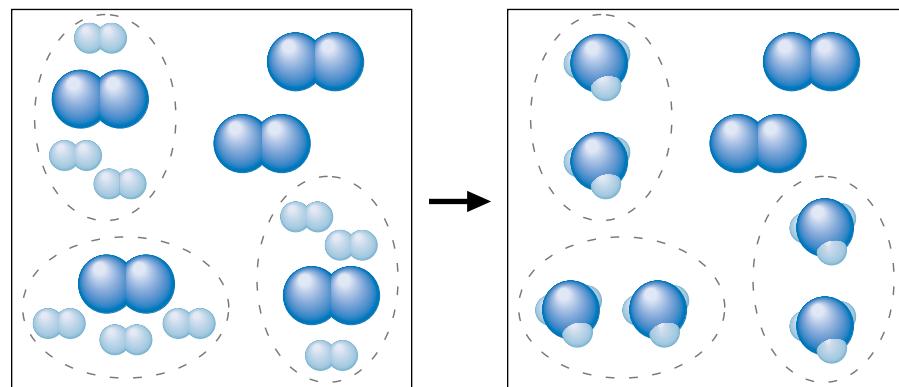
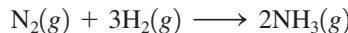


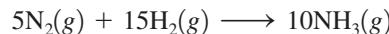
FIGURE 3.12

Hydrogen and nitrogen react to form ammonia according to the equation
 $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

Another way to look at this is to determine how much H₂ would be required by 5 N₂ molecules. Multiplying the balanced equation

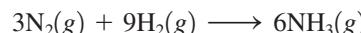


by 5 gives

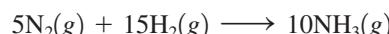


Thus 5 N₂ molecules would require 15 H₂ molecules and we have only 9. This tells us the same thing we learned earlier—the hydrogen is limiting.

The most important point here is this: *The limiting reactant limits the amount of product that can form.* The reaction that actually occurred was



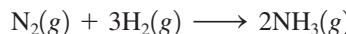
not



Thus 6 NH₃ were formed, not 10 NH₃, because the H₂, not the N₂, was limiting.

In the laboratory or chemical plant we work with much larger quantities than the few molecules of the preceding example. Therefore, we must learn to deal with limiting reactants using moles. The ideas are exactly the same, except that we are using moles of molecules instead of individual molecules. For example, suppose 25.0 kilograms of nitrogen and 5.00 kilograms of hydrogen are mixed and reacted to form ammonia. How do we calculate the mass of ammonia produced when this reaction is run to completion (until one of the reactants is completely consumed)?

As in the preceding example, we must use the balanced equation



to determine whether nitrogen or hydrogen is the limiting reactant and then to determine the amount of ammonia that is formed. We first calculate the moles of reactants present:

$$\begin{aligned} 25.0 \text{ kg N}_2 &\times \frac{1000 \text{ g N}_2}{1 \text{ kg N}_2} \times \frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} = 8.93 \times 10^2 \text{ mol N}_2 \\ 5.00 \text{ kg H}_2 &\times \frac{1000 \text{ g H}_2}{1 \text{ kg H}_2} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 2.48 \times 10^3 \text{ mol H}_2 \end{aligned}$$

Since 1 mol N₂ reacts with 3 mol H₂, the number of moles of H₂ that will react exactly with 8.93×10^2 mol N₂ is

$$8.93 \times 10^2 \text{ mol N}_2 \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} = 2.68 \times 10^3 \text{ mol H}_2$$

Thus 8.93×10^2 mol N₂ requires 2.68×10^3 mol H₂ to react completely. However, in this case, only 2.48×10^3 mol H₂ is present. This means that the hydrogen will be consumed before the nitrogen. Thus hydrogen is the *limiting reactant* in this particular situation, and we must use the amount of hydrogen to compute the quantity of ammonia formed:

$$2.48 \times 10^3 \text{ mol H}_2 \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} = 1.65 \times 10^3 \text{ mol NH}_3$$

Converting moles to kilograms gives

$$1.65 \times 10^3 \text{ mol NH}_3 \times \frac{17.0 \text{ g NH}_3}{1 \text{ mol NH}_3} = 2.80 \times 10^4 \text{ g NH}_3 = 28.0 \text{ kg NH}_3$$

Always determine which reactant is limiting.

Note that to determine the limiting reactant, we could have started instead with the given amount of hydrogen and calculated the moles of nitrogen required:

$$2.48 \times 10^3 \text{ mol H}_2 \times \frac{1 \text{ mol N}_2}{3 \text{ mol H}_2} = 8.27 \times 10^2 \text{ mol N}_2$$

Thus 2.48×10^3 mol H₂ requires 8.27×10^2 mol N₂. Since 8.93×10^2 mol N₂ is actually present, the nitrogen is in excess. The hydrogen will run out first, and thus again we find that hydrogen limits the amount of ammonia formed.

A related but simpler way to determine which reactant is limiting is to compare the mole ratio of the substances required by the balanced equation with the mole ratio of reactants actually present. For example, in this case the mole ratio of H₂ to N₂ required by the balanced equation is

$$\frac{3 \text{ mol H}_2}{1 \text{ mol N}_2}$$

That is,

$$\frac{\text{mol H}_2}{\text{mol N}_2} (\text{required}) = \frac{3}{1} = 3$$

In this experiment we have 2.48×10^3 mol H₂ and 8.93×10^2 mol N₂. Thus the ratio

$$\frac{\text{mol H}_2}{\text{mol N}_2} (\text{actual}) = \frac{2.48 \times 10^3}{8.93 \times 10^2} = 2.78$$

Since 2.78 is less than 3, the actual mole ratio of H₂ to N₂ is too small, and H₂ must be limiting. If the actual H₂ to N₂ mole ratio had been greater than 3, then the H₂ would have been in excess and the N₂ would be limiting.

Sample Exercise 3.18

Stoichiometry: Limiting Reactant

Nitrogen gas can be prepared by passing gaseous ammonia over solid copper(II) oxide at high temperatures. The other products of the reaction are solid copper and water vapor. If a sample containing 18.1 g of NH₃ is reacted with 90.4 g of CuO, which is the limiting reactant? How many grams of N₂ will be formed?

Solution

From the description of the problem, we can obtain the following balanced equation:



Next we must compute the moles of NH₃ (molar mass = 17.03 g/mol) and of CuO (molar mass = 79.55 g/mol):

$$18.1 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} = 1.06 \text{ mol NH}_3$$

$$90.4 \text{ g CuO} \times \frac{1 \text{ mol CuO}}{79.55 \text{ g CuO}} = 1.14 \text{ mol CuO}$$

To determine the limiting reactant, we use the mole ratio for CuO and NH₃:

$$1.06 \text{ mol NH}_3 \times \frac{3 \text{ mol CuO}}{2 \text{ mol NH}_3} = 1.59 \text{ mol CuO}$$

Thus 1.59 mol CuO is required to react with 1.06 mol NH₃. Since only 1.14 mol CuO is actually present, the amount of CuO is limiting; CuO will run out before NH₃ does. We

can verify this conclusion by comparing the mole ratio of CuO and NH₃ required by the balanced equation

$$\frac{\text{mol CuO}}{\text{mol NH}_3} \text{ (required)} = \frac{3}{2} = 1.5$$

with the mole ratio actually present

$$\frac{\text{mol CuO}}{\text{mol NH}_3} \text{ (actual)} = \frac{1.14}{1.06} = 1.08$$

Since the actual ratio is too small (smaller than 1.5), CuO is the limiting reactant.

Because CuO is the limiting reactant, we must use the amount of CuO to calculate the amount of N₂ formed. From the balanced equation, the mole ratio between CuO and N₂ is

$$\frac{1 \text{ mol N}_2}{3 \text{ mol CuO}} \\ 1.14 \text{ mol CuO} \times \frac{1 \text{ mol N}_2}{3 \text{ mol CuO}} = 0.380 \text{ mol N}_2$$

Using the molar mass of N₂ (28.0 g/mol), we can calculate the mass of N₂ produced:

$$0.380 \text{ mol N}_2 \times \frac{28.0 \text{ g N}_2}{1 \text{ mol N}_2} = 10.6 \text{ g N}_2$$

See Exercises 3.99 through 3.101.

The amount of a product formed when the limiting reactant is completely consumed is called the **theoretical yield** of that product. In Sample Exercise 3.18, 10.6 grams of nitrogen represents the theoretical yield. This is the *maximum amount* of nitrogen that can be produced from the quantities of reactants used. Actually, the amount of product predicted by the theoretical yield is seldom obtained because of side reactions (other reactions that involve one or more of the reactants or products) and other complications. The *actual yield* of product is often given as a percentage of the theoretical yield. This is called the **percent yield**:

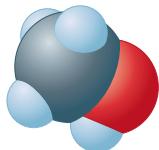
$$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\% = \text{percent yield}$$

For example, if the reaction considered in Sample Exercise 3.18 actually gave 6.63 grams of nitrogen instead of the predicted 10.6 grams, the percent yield of nitrogen would be

$$\frac{6.63 \text{ g N}_2}{10.6 \text{ g N}_2} \times 100\% = 62.5\%$$

Sample Exercise 3.19

Calculating Percent Yield

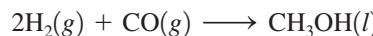


Methanol

Methanol (CH₃OH), also called *methyl alcohol*, is the simplest alcohol. It is used as a fuel in race cars and is a potential replacement for gasoline. Methanol can be manufactured by combination of gaseous carbon monoxide and hydrogen. Suppose 68.5 kg CO(g) is reacted with 8.60 kg H₂(g). Calculate the theoretical yield of methanol. If 3.57 × 10⁴ g CH₃OH is actually produced, what is the percent yield of methanol?

Solution

First, we must find out which reactant is limiting. The balanced equation is



Next we must calculate the moles of reactants:

$$68.5 \text{ kg CO} \times \frac{1000 \text{ g CO}}{1 \text{ kg CO}} \times \frac{1 \text{ mol CO}}{28.02 \text{ g CO}} = 2.44 \times 10^3 \text{ mol CO}$$

$$8.60 \text{ kg H}_2 \times \frac{1000 \text{ g H}_2}{1 \text{ kg H}_2} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 4.27 \times 10^3 \text{ mol H}_2$$

To determine which reactant is limiting, we compare the mole ratio of H₂ and CO required by the balanced equation

$$\frac{\text{mol H}_2}{\text{mol CO}} (\text{required}) = \frac{2}{1} = 2$$

with the actual mole ratio

$$\frac{\text{mol H}_2}{\text{mol CO}} (\text{actual}) = \frac{4.27 \times 10^3}{2.44 \times 10^3} = 1.75$$

Since the actual mole ratio of H₂ to CO is smaller than the required ratio, H₂ is *limiting*. We therefore must use the amount of H₂ and the mole ratio between H₂ and CH₃OH to determine the maximum amount of methanol that can be produced:

$$4.27 \times 10^3 \text{ mol H}_2 \times \frac{1 \text{ mol CH}_3\text{OH}}{2 \text{ mol H}_2} = 2.14 \times 10^3 \text{ mol CH}_3\text{OH}$$

Using the molar mass of CH₃OH (32.04 g/mol), we can calculate the theoretical yield in grams:

$$2.14 \times 10^3 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} = 6.86 \times 10^4 \text{ g CH}_3\text{OH}$$

Thus, from the amount of reactants given, the maximum amount of CH₃OH that can be formed is 6.86 × 10⁴ g. This is the *theoretical yield*.

The percent yield is

$$\frac{\text{Actual yield (grams)}}{\text{Theoretical yield (grams)}} \times 100 = \frac{3.57 \times 10^4 \text{ g CH}_3\text{OH}}{6.86 \times 10^4 \text{ g CH}_3\text{OH}} \times 100\% = 52.0\%$$

See Exercises 3.103 and 3.104.

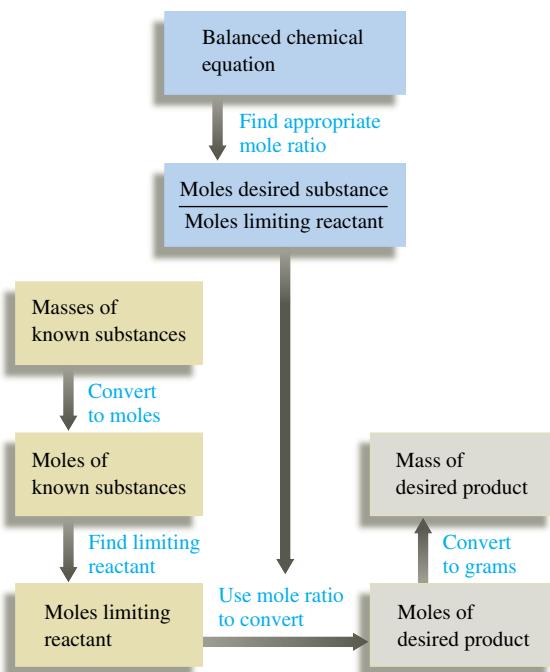


Methanol is used as a fuel in Indianapolis-type racing cars.

Solving a Stoichiometry Problem Involving Masses of Reactants and Products

- 1 Write and balance the equation for the reaction.
- 2 Convert the known masses of substances to moles.
- 3 Determine which reactant is limiting.
- 4 Using the amount of the limiting reactant and the appropriate mole ratios, compute the number of moles of the desired product.
- 5 Convert from moles to grams, using the molar mass.

This process is summarized in the diagram below:



Key Terms

chemical stoichiometry

Section 3.2

mass spectrometer
average atomic mass

Section 3.3

mole
Avogadro's number

Section 3.4

molar mass

Section 3.5

mass percent

Section 3.6

empirical formula
molecular formula

For Review

Stoichiometry

- Deals with the amounts of substances consumed and/or produced in a chemical reaction.
- We count atoms by measuring the mass of the sample.
- To relate mass and the number of atoms, the average atomic mass is required.

Mole

- The amount of carbon atoms in exactly 12 g of pure ^{12}C
- 6.022×10^{23} units of a substance
- The mass of one mole of an element = the atomic mass in grams

Molar mass

- Mass (g) of one mole of a compound or element
- Obtained for a compound by finding the sum of the average masses of its constituent atoms

Section 3.7

chemical equation
reactants
products
balancing a chemical equation

Section 3.9

mole ratio

Section 3.10

stoichiometric quantities
Haber process
limiting reactant (reagent)
theoretical yield
percent yield

Percent composition

- The mass percent of each element in a compound
- $\text{Mass percent} = \frac{\text{mass of element in 1 mole of substance}}{\text{mass of 1 mole of substance}} \times 100\%$

Empirical formula

- The simplest whole-number ratio of the various types of atoms in a compound
- Can be obtained from the mass percent of elements in a compound

Molecular formula

- For molecular substances:
 - The formula of the constituent molecules
 - Always an integer multiple of the empirical formula
- For ionic substances:
 - The same as the empirical formula

Chemical reactions

- Reactants are turned into products.
- Atoms are neither created nor destroyed.
- All of the atoms present in the reactants must also be present in the products.

Characteristics of a chemical equation

- Represents a chemical reaction
- Reactants on the left side of the arrow, products on the right side
- When balanced, gives the relative numbers of reactant and product molecules or ions

Stoichiometry calculations

- Amounts of reactants consumed and products formed can be determined from the balanced chemical equation.
- The limiting reactant is the one consumed first, thus limiting the amount of product that can form.

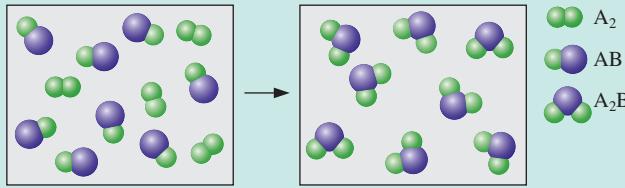
Yield

- The theoretical yield is the maximum amount that can be produced from a given amount of the limiting reactant.
- The actual yield, the amount of product actually obtained, is always less than the theoretical yield.
- $\text{Percent yield} = \frac{\text{actual yield (g)}}{\text{theoretical yield (g)}} \times 100\%$

REVIEW QUESTIONS

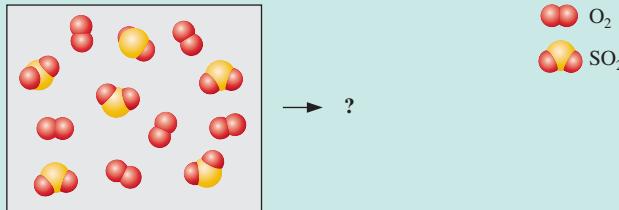
- Explain the concept of “counting by weighing” using marbles as your example.
- Atomic masses are relative masses. What does this mean?
- The atomic mass of boron (B) is given in the periodic table as 10.81, yet no single atom of boron has a mass of 10.81 amu. Explain.
- What three conversion factors and in what order would you use them to convert the mass of a compound into atoms of a particular element in that compound—for example, from 1.00 g aspirin ($C_9H_8O_4$) to number of hydrogen atoms in the 1.00-g sample?
- Figure 3.5 illustrates a schematic diagram of a combustion device used to analyze organic compounds. Given that a certain amount of a compound containing carbon, hydrogen, and oxygen is combusted in this device, explain how the data relating to the mass of CO_2 produced and the mass of H_2O produced can be manipulated to determine the empirical formula.

6. What is the difference between the empirical and molecular formulas of a compound? Can they ever be the same? Explain.
7. Consider the hypothetical reaction between A_2 and AB pictured below.



What is the balanced equation? If 2.50 mol A_2 is reacted with excess AB, what amount (moles) of product will form? If the mass of AB is 30.0 amu and the mass of A_2 is 40.0 amu, what is the mass of the product? If 15.0 g of AB is reacted, what mass of A_2 is required to react with all of the AB, and what mass of product is formed?

8. What is a limiting reactant problem? Explain two different strategies that can be used to solve limiting reactant problems.
9. Consider the following mixture of $SO_2(g)$ and $O_2(g)$.



If $SO_2(g)$ and $O_2(g)$ react to form $SO_3(g)$, draw a representation of the product mixture assuming the reaction goes to completion. What is the limiting reactant in the reaction? If 96.0 g of SO_2 reacts with 32.0 g O_2 , what mass of product will form?

10. Why is the actual yield of a reaction often less than the theoretical yield?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- The following are actual student responses to the question: Why is it necessary to balance chemical equations?
 - The chemicals will not react until you have added the correct mole ratios.
- The correct products will not be formed unless the right amount of reactants have been added.
- A certain number of products cannot be formed without a certain number of reactants.
- The balanced equation tells you how much reactant you need and allows you to predict how much product you'll make.
- A mole-to-mole ratio must be established for the reaction to occur as written.

Justify the best choice, and for choices you did not pick, explain what is wrong with them.

- What information do we get from a formula? From an equation?

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3. You are making cookies and are missing a key ingredient—eggs. You have most of the other ingredients needed to make the cookies, except you have only 1.33 cups of butter and no eggs. You note that the recipe calls for 2 cups of butter and 3 eggs (plus the other ingredients) to make 6 dozen cookies. You call a friend and have him bring you some eggs.

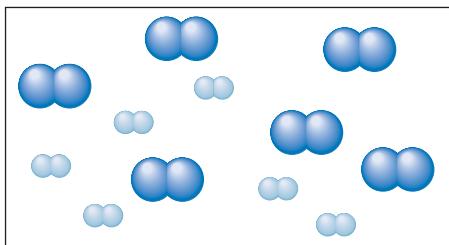
- What number of eggs do you need?
- If you use all the butter (and get enough eggs), what number of cookies will you make?

Unfortunately, your friend hangs up before you tell him how many eggs you need. When he arrives, he has a surprise for you—to save time, he has broken them all in a bowl for you. You ask him how many he brought, and he replies, “I can’t remember.” You weigh the eggs and find that they weigh 62.1 g. Assuming that an average egg weighs 34.21 g,

- What quantity of butter is needed to react with all the eggs?
- What number of cookies can you make?
- Which will you have left over, eggs or butter?
- What quantity is left over?

4. Nitrogen (N_2) and hydrogen (H_2) react to form ammonia (NH_3).

Consider the mixture of N_2 () and H_2 () in a closed container as illustrated below:



Assuming the reaction goes to completion, draw a representation of the product mixture. Explain how you arrived at this representation.

5. For the preceding question, which of the following equations best represents the reaction?

- $6N_2 + 6H_2 \longrightarrow 4NH_3 + 4N_2$
- $N_2 + H_2 \longrightarrow NH_3$
- $N + 3H \longrightarrow NH_3$
- $N_2 + 3H_2 \longrightarrow 2NH_3$
- $2N_2 + 6H_2 \longrightarrow 4NH_3$

Justify your choice, and for choices you did not pick, explain what is wrong with them.

6. You know that chemical A reacts with chemical B. You react 10.0 g A with 10.0 g B. What information do you need to determine the amount of product that will be produced? Explain.

7. A new grill has a mass of 30.0 kg. You put 3.0 kg of charcoal in the grill. You burn all the charcoal and the grill has a mass of 30.0 kg. What is the mass of the gases given off? Explain.

8. Consider an iron bar on a balance as shown.



As the iron bar rusts, which of the following is true? Explain your answer.

- The balance will read less than 75.0 g.
- The balance will read 75.0 g.
- The balance will read greater than 75.0 g.
- The balance will read greater than 75.0 g, but if the bar is removed, the rust is scraped off, and the bar replaced, the balance will read 75.0 g.

9. You may have noticed that water sometimes drips from the exhaust of a car as it is running. Is this evidence that there is at least a small amount of water originally present in the gasoline? Explain.

Questions 10 and 11 deal with the following situation: You react chemical A with chemical B to make one product. It takes 100 g of A to react completely with 20 g B.

10. What is the mass of the product?

- less than 10 g
- between 20 and 100 g
- between 100 and 120 g
- exactly 120 g
- more than 120 g

11. What is true about the chemical properties of the product?

- The properties are more like chemical A.
- The properties are more like chemical B.
- The properties are an average of those of chemical A and chemical B.
- The properties are not necessarily like either chemical A or chemical B.
- The properties are more like chemical A or more like chemical B, but more information is needed.

Justify your choice, and for choices you did not pick, explain what is wrong with them.

12. Is there a difference between a homogeneous mixture of hydrogen and oxygen in a 2:1 mole ratio and a sample of water vapor? Explain.

13. Chlorine exists mainly as two isotopes, ^{37}Cl and ^{35}Cl . Which is more abundant? How do you know?

14. The average mass of a carbon atom is 12.011. Assuming you could pick up one carbon atom, estimate the chance that you would randomly get one with a mass of 12.011. Support your answer.

15. Can the subscripts in a chemical formula be fractions? Explain. Can the coefficients in a balanced chemical equation be fractions? Explain. Changing the subscripts of chemicals can balance the equations mathematically. Why is this unacceptable?

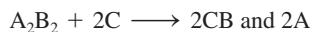
16. Consider the equation $2A + B \longrightarrow A_2B$. If you mix 1.0 mol of A with 1.0 mol of B, what amount (moles) of A_2B can be produced?

17. According to the law of conservation of mass, mass cannot be gained or destroyed in a chemical reaction. Why can't you simply add the masses of two reactants to determine the total mass of product?
18. Which of the following pairs of compounds have the same *empirical formula*?
- acetylene, C₂H₂, and benzene, C₆H₆
 - ethane, C₂H₆, and butane, C₄H₁₀
 - nitrogen dioxide, NO₂, and dinitrogen tetroxide, N₂O₄
 - diphenyl ether, C₁₂H₁₀O, and phenol, C₆H₅OH

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the *Solutions Guide*.

Questions

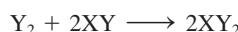
19. Reference section 3.2 to find the atomic masses of ¹²C and ¹³C, the relative abundance of ¹²C and ¹³C in natural carbon, and the average mass (in amu) of a carbon atom. If you had a sample of natural carbon containing exactly 10,000 atoms, determine the number of ¹²C and ¹³C atoms present. What would be the average mass (in amu) and the total mass (in amu) of the carbon atoms in this 10,000-atom sample? If you had a sample of natural carbon containing 6.0221×10^{23} atoms, determine the number of ¹²C and ¹³C atoms present. What would be the average mass (in amu) and the total mass (in amu) of this 6.0221×10^{23} atom sample? Given that 1 g = 6.0221×10^{23} amu, what is the total mass of 1 mol of natural carbon in units of grams?
20. Avogadro's number, molar mass, and the chemical formula of a compound are three useful conversion factors. What unit conversions can be accomplished using these conversion factors?
21. If you had a mol of U.S. dollar bills and equally distributed the money to all of the people of the world, how rich would every person be? Assume a world population of 6 billion.
22. What is the difference between the molar mass and the empirical formula mass of a compound? When are these masses the same and when are they different? When different, how is the molar mass related to the empirical formula mass?
23. How is the mass percent of elements in a compound different for a 1.0-g sample versus a 100.-g sample versus a 1-mol sample of the compound?
24. A balanced chemical equation contains a large amount of information. What information is given in a balanced equation?
25. Consider the following generic reaction:



What steps and information are necessary to perform the following determinations assuming that 1.00×10^4 molecules of A₂B₂ are reacted with excess C?

- mass of CB produced
- atoms of A produced
- mol of C reacted
- percent yield of CB

26. Consider the following generic reaction:



In a limiting reactant problem, a certain quantity of each reactant is given and you are usually asked to calculate the mass of product formed. If 10.0 g of Y₂ is reacted with 10.0 g of XY, outline two methods you could use to determine which reactant is limiting (runs out first) and thus determines the mass of product formed. A method sometimes used to solve limiting reactant problems is to assume each reactant is limiting and then calculate the mass of product formed from each given quantity of reactant. How does this method work in determining which reactant is limiting?

Exercises

In this section similar exercises are paired.

Atomic Masses and the Mass Spectrometer

27. An element consists of 1.40% of an isotope with mass 203.973 amu, 24.10% of an isotope with mass 205.9745 amu, 22.10% of an isotope with mass 206.9759 amu, and 52.40% of an isotope with mass 207.9766 amu. Calculate the average atomic mass and identify the element.
28. An element "X" has five major isotopes, which are listed below along with their abundances. What is the element?

Isotope	Percent Natural Abundance	Atomic Mass
⁴⁶ X	8.00%	45.95269
⁴⁷ X	7.30%	46.951764
⁴⁸ X	73.80%	47.947947
⁴⁹ X	5.50%	48.947841
⁵⁰ X	5.40%	49.944792

29. The element rhenium (Re) has two naturally occurring isotopes, ¹⁸⁵Re and ¹⁸⁷Re, with an average atomic mass of 186.207 amu. Rhenium is 62.60% ¹⁸⁷Re, and the atomic mass of ¹⁸⁷Re is 186.956 amu. Calculate the mass of ¹⁸⁵Re.
30. Assume silicon has three major isotopes in nature as shown in the table below. Fill in the missing information.

Isotope	Mass (amu)	Abundance
²⁸ Si	27.98	
²⁹ Si		4.70%
³² Si	29.97	3.09%

31. The mass spectrum of bromine (Br₂) consists of three peaks with the following characteristics:

Mass (amu)	Relative Size
157.84	0.2534
159.84	0.5000
161.84	0.2466

How do you interpret these data?

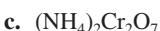
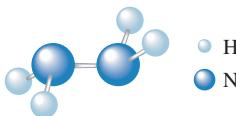
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32. Gallium arsenide, GaAs, has gained widespread use in semiconductor devices that convert light and electrical signals in fiber-optic communications systems. Gallium consists of 60% ^{69}Ga and 40% ^{71}Ga . Arsenic has only one naturally occurring isotope, ^{75}As . Gallium arsenide is a polymeric material, but its mass spectrum shows fragments with the formulas GaAs and Ga_2As_2 . What would the distribution of peaks look like for these two fragments?

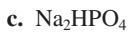
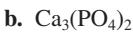
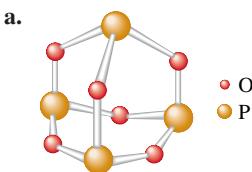
Moles and Molar Masses

- 33.** Calculate the mass of 500. atoms of iron (Fe).
- 34.** What number of Fe atoms and what amount (moles) of Fe atoms are in 500.0 g of iron?
- 35.** Diamond is a natural form of pure carbon. What number of atoms of carbon are in a 1.00-carat diamond (1.00 carat = 0.200 g)?
- 36.** A diamond contains 5.0×10^{21} atoms of carbon. What amount (moles) of carbon and what mass (grams) of carbon are in this diamond?
- 37.** Aluminum metal is produced by passing an electric current through a solution of aluminum oxide (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6). Calculate the molar masses of Al_2O_3 and Na_3AlF_6 .
- 38.** The Freons are a class of compounds containing carbon, chlorine, and fluorine. While they have many valuable uses, they have been shown to be responsible for depletion of the ozone in the upper atmosphere. In 1991, two replacement compounds for Freons went into production: HFC-134a (CH_2FCF_3) and HCFC-124 (CHClFCF_3). Calculate the molar masses of these two compounds.

- 39.** Calculate the molar mass of the following substances.



- 40.** Calculate the molar mass of the following substances.



- 41.** What amount (moles) of compound is present in 1.00 g of each of the compounds in Exercise 39?
- 42.** What amount (moles) of compound is present in 1.00 g of each of the compounds in Exercise 40?
- 43.** What mass of compound is present in 5.00 mol of each of the compounds in Exercise 39?
- 44.** What mass of compound is present in 5.00 mol of each of the compounds in Exercise 40?

45. What mass of nitrogen is present in 5.00 mol of each of the compounds in Exercise 39?

46. What mass of phosphorus is present in 5.00 mol of each of the compounds in Exercise 40?

47. What number of molecules (or formula units) are present in 1.00 g of each of the compounds in Exercise 39?

48. What number of molecules (or formula units) are present in 1.00 g of each of the compounds in Exercise 40?

49. What number of atoms of nitrogen are present in 1.00 g of each of the compounds in Exercise 39?

50. What number of atoms of phosphorus are present in 1.00 g of each of the compounds in Exercise 40?

51. Ascorbic acid, or vitamin C ($\text{C}_6\text{H}_8\text{O}_6$), is an essential vitamin. It cannot be stored by the body and must be present in the diet. What is the molar mass of ascorbic acid? Vitamin C tablets are taken as a dietary supplement. If a typical tablet contains 500.0 mg of vitamin C, what amount (moles) and what number of molecules of vitamin C does it contain?

52. The molecular formula of acetylsalicylic acid (aspirin), one of the most commonly used pain relievers, is $\text{C}_9\text{H}_8\text{O}_4$.

a. Calculate the molar mass of aspirin.

b. A typical aspirin tablet contains 500. mg of $\text{C}_9\text{H}_8\text{O}_4$. What amount (moles) of $\text{C}_9\text{H}_8\text{O}_4$ molecules and what number of molecules of acetylsalicylic acid are in a 500.-mg tablet?

53. What amount (moles) are represented by each of these samples?

- a. 150.0 g Fe_2O_3 c. 1.5×10^{16} molecules of BF_3
b. 10.0 mg NO_2

54. What amount (moles) is represented by each of these samples?

- a. 20.0 mg caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
b. 2.72×10^{21} molecules of ethanol, $\text{C}_2\text{H}_5\text{OH}$
c. 1.50 g of dry ice, CO_2

55. What number of atoms of nitrogen are present in 5.00 g of each of the following?

- a. glycine, $\text{C}_2\text{H}_5\text{O}_2\text{N}$ c. calcium nitrate
b. magnesium nitride d. dinitrogen tetroxide

56. Complete the following table.

Mass of Sample	Moles of Sample	Molecules in Sample	Total Atoms in Sample
4.24 g C_6H_6	_____	_____	_____
_____	0.224 mol H_2O	_____	_____
_____	_____	2.71×10^{22} molecules CO_2	_____
_____	_____	_____	3.35×10^{22} total atoms in CH_3OH sample

57. Aspartame is an artificial sweetener that is 160 times sweeter than sucrose (table sugar) when dissolved in water. It is marketed

as Nutra-Sweet. The molecular formula of aspartame is $C_{14}H_{18}N_2O_5$.

- Calculate the molar mass of aspartame.
 - What amount (moles) of molecules are present in 10.0 g aspartame?
 - Calculate the mass in grams of 1.56 mol aspartame.
 - What number of molecules are in 5.0 mg aspartame?
 - What number of atoms of nitrogen are in 1.2 g aspartame?
 - What is the mass in grams of 1.0×10^9 molecules of aspartame?
 - What is the mass in grams of one molecule of aspartame?
- 58.** Chloral hydrate ($C_2H_3Cl_3O_2$) is a drug formerly used as a sedative and hypnotic. It is the compound used to make "Mickey Finns" in detective stories.
- Calculate the molar mass of chloral hydrate.
 - What amount (moles) of $C_2H_3Cl_3O_2$ molecules are in 500.0 g chloral hydrate?
 - What is the mass in grams of 2.0×10^{-2} mol chloral hydrate?
 - What number of chlorine atoms are in 5.0 g chloral hydrate?
 - What mass of chloral hydrate would contain 1.0 g Cl?
 - What is the mass of exactly 500 molecules of chloral hydrate?

Percent Composition

- 59.** Calculate the percent composition by mass of the following compounds that are important starting materials for synthetic polymers:
- $C_3H_4O_2$ (acrylic acid, from which acrylic plastics are made)
 - $C_4H_6O_2$ (methyl acrylate, from which Plexiglas is made)
 - C_3H_3N (acrylonitrile, from which Orlon is made)
- 60.** Anabolic steroids are performance enhancement drugs whose use has been banned from most major sporting activities. One anabolic steroid is fluoxymesterone ($C_{20}H_{29}FO_3$). Calculate the percent composition by mass of fluoxymesterone.
- 61.** Several important compounds contain only nitrogen and oxygen. Place the following compounds in order of increasing mass percent of nitrogen.
- NO, a gas formed by the reaction of N_2 with O_2 in internal combustion engines
 - NO_2 , a brown gas mainly responsible for the brownish color of photochemical smog
 - N_2O_4 , a colorless liquid used as fuel in space shuttles
 - N_2O , a colorless gas sometimes used as an anesthetic by dentists (known as laughing gas)
- 62.** Arrange the following substances in order of increasing mass percent of carbon.
- caffeine, $C_8H_{10}N_4O_2$
 - sucrose, $C_{12}H_{22}O_{11}$
 - ethanol, C_2H_5OH

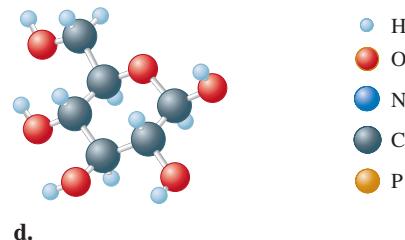
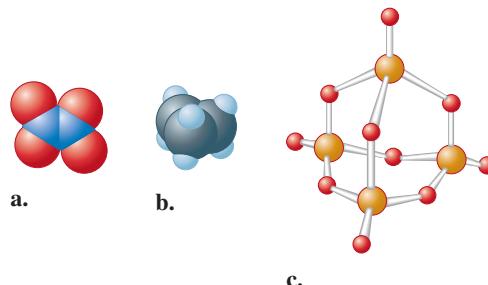
- 63.** Vitamin B_{12} , cyanocobalamin, is essential for human nutrition. It is concentrated in animal tissue but not in higher plants. Although nutritional requirements for the vitamin are quite low, people who abstain completely from animal products may develop a deficiency anemia. Cyanocobalamin is the form used in vitamin supplements. It contains 4.34% cobalt by mass. Calculate the molar mass of cyanocobalamin, assuming that there is one atom of cobalt in every molecule of cyanocobalamin.

- 64.** Fungal laccase, a blue protein found in wood-rotting fungi, is 0.390% Cu by mass. If a fungal laccase molecule contains 4 copper atoms, what is the molar mass of fungal laccase?

Empirical and Molecular Formulas

- 65.** Express the composition of each of the following compounds as the mass percents of its elements.
- formaldehyde, CH_2O
 - glucose, $C_6H_{12}O_6$
 - acetic acid, $HC_2H_3O_2$
- 66.** Considering your answer to Exercise 65, which type of formula, empirical or molecular, can be obtained from elemental analysis that gives percent composition?

- 67.** Give the empirical formula for each of the compounds represented below.



d.

- H
- O
- N
- C
- P

- 68.** Determine the molecular formulas to which the following empirical formulas and molar masses pertain.
- SNH (188.35 g/mol)
 - $NPCL_2$ (347.64 g/mol)
 - CoC_4O_4 (341.94 g/mol)
 - SN (184.32 g/mol)
- 69.** The compound adrenaline contains 56.79% C, 6.56% H, 28.37% O, and 8.28% N by mass. What is the empirical formula for adrenaline?
- 70.** The most common form of nylon (nylon-6) is 63.68% carbon, 12.38% nitrogen, 9.80% hydrogen, and 14.14% oxygen. Calculate the empirical formula for nylon-6.
- 71.** There are two binary compounds of mercury and oxygen. Heating either of them results in the decomposition of the compound, with oxygen gas escaping into the atmosphere while leaving a residue of pure mercury. Heating 0.6498 g of one of the compounds leaves a residue of 0.6018 g. Heating 0.4172 g of the other compound results in a mass loss of 0.016 g. Determine the empirical formula of each compound.

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72. A sample of urea contains 1.121 g N, 0.161 g H, 0.480 g C, and 0.640 g O. What is the empirical formula of urea?

73. A compound containing only sulfur and nitrogen is 69.6% S by mass; the molar mass is 184 g/mol. What are the empirical and molecular formulas of the compound?

74. Determine the molecular formula of a compound that contains 26.7% P, 12.1% N, and 61.2% Cl, and has a molar mass of 580 g/mol.

75. Adipic acid is an organic compound composed of 49.31% C, 43.79% O, and the rest hydrogen. If the molar mass of adipic acid is 146.1 g/mol, what are the empirical and molecular formulas for adipic acid?

76. Maleic acid is an organic compound composed of 41.39% C, 3.47% H, and the rest oxygen. If 0.129 mol of maleic acid has a mass of 15.0 g, what are the empirical and molecular formulas of maleic acid?

77. Many homes in rural America are heated by propane gas, a compound that contains only carbon and hydrogen. Complete combustion of a sample of propane produced 2.641 g of carbon dioxide and 1.442 g of water as the only products. Find the empirical formula of propane.

78. A compound contains only C, H, and N. Combustion of 35.0 mg of the compound produces 33.5 mg CO₂ and 41.1 mg H₂O. What is the empirical formula of the compound?

79. Cumene is a compound containing only carbon and hydrogen that is used in the production of acetone and phenol in the chemical industry. Combustion of 47.6 mg cumene produces some CO₂ and 42.8 mg water. The molar mass of cumene is between 115 and 125 g/mol. Determine the empirical and molecular formulas.

80. A compound contains only carbon, hydrogen, and oxygen. Combustion of 10.68 mg of the compound yields 16.01 mg CO₂ and 4.37 mg H₂O. The molar mass of the compound is 176.1 g/mol. What are the empirical and molecular formulas of the compound?

Balancing Chemical Equations

81. Give the balanced equation for each of the following chemical reactions:

- a. Glucose (C₆H₁₂O₆) reacts with oxygen gas to produce gaseous carbon dioxide and water vapor.
- b. Solid iron(III) sulfide reacts with gaseous hydrogen chloride to form solid iron(III) chloride and hydrogen sulfide gas.
- c. Carbon disulfide liquid reacts with ammonia gas to produce hydrogen sulfide gas and solid ammonium thiocyanate (NH₄SCN).

82. Give the balanced equation for each of the following.

- a. The combustion of ethanol (C₂H₅OH) forms carbon dioxide and water vapor. A combustion reaction refers to a reaction of a substance with oxygen gas.
- b. Aqueous solutions of lead(II) nitrate and sodium phosphate are mixed, resulting in the precipitate formation of lead(II) phosphate with aqueous sodium nitrate as the other product.

c. Solid zinc reacts with aqueous HCl to form aqueous zinc chloride and hydrogen gas.

d. Aqueous strontium hydroxide reacts with aqueous hydrobromic acid to produce water and aqueous strontium bromide.

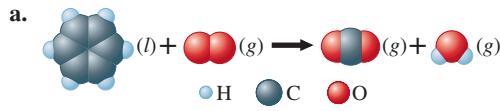
83. Balance the following equations:

- a. Ca(OH)₂(aq) + H₃PO₄(aq) → H₂O(l) + Ca₃(PO₄)₂(s)
- b. Al(OH)₃(s) + HCl(aq) → AlCl₃(aq) + H₂O(l)
- c. AgNO₃(aq) + H₂SO₄(aq) → Ag₂SO₄(s) + HNO₃(aq)

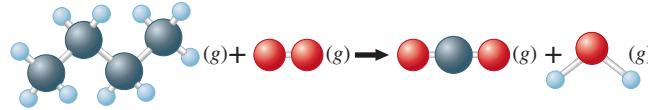
84. Balance each of the following chemical equations.

- a. KO₂(s) + H₂O(l) → KOH(aq) + O₂(g) + H₂O₂(aq)
- b. Fe₂O₃(s) + HNO₃(aq) → Fe(NO₃)₃(aq) + H₂O(l)
- c. NH₃(g) + O₂(g) → NO(g) + H₂O(g)
- d. PCl₅(l) + H₂O(l) → H₃PO₄(aq) + HCl(g)
- e. CaO(s) + C(s) → CaC₂(s) + CO₂(g)
- f. MoS₂(s) + O₂(g) → MoO₃(s) + SO₂(g)
- g. FeCO₃(s) + H₂CO₃(aq) → Fe(HCO₃)₂(aq)

85. Balance the following equations representing combustion reactions:



b.



- c. C₁₂H₂₂O₁₁(s) + O₂(g) → CO₂(g) + H₂O(g)
- d. Fe(s) + O₂(g) → Fe₂O₃(s)
- e. FeO(s) + O₂(g) → Fe₂O₃(s)

86. Balance the following equations:

- a. Cr(s) + S₈(s) → Cr₂S₃(s)
- b. NaHCO₃(s) $\xrightarrow{\text{Heat}}$ Na₂CO₃(s) + CO₂(g) + H₂O(g)
- c. KClO₃(s) $\xrightarrow{\text{Heat}}$ KCl(s) + O₂(g)
- d. Eu(s) + HF(g) → EuF₃(s) + H₂(g)

87. Silicon is produced for the chemical and electronics industries by the following reactions. Give the balanced equation for each reaction.

- a. SiO₂(s) + C(s) $\xrightarrow[\text{arc furnace}]{\text{Electric}}$ Si(s) + CO(g)
- b. Silicon tetrachloride is reacted with very pure magnesium, producing silicon and magnesium chloride.
- c. Na₂SiF₆(s) + Na(s) → Si(s) + NaF(s)

88. Glass is a mixture of several compounds, but a major constituent of most glass is calcium silicate, CaSiO₃. Glass can be etched by treatment with hydrofluoric acid; HF attacks the calcium silicate of the glass, producing gaseous and water-soluble products (which can be removed by washing the glass). For example, the volumetric glassware in chemistry laboratories is often graduated by using this process. Balance the following equation for the reaction of hydrofluoric acid with calcium silicate.



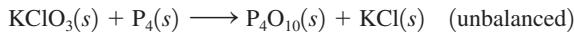
Reaction Stoichiometry

- 89.** Over the years, the thermite reaction has been used for welding railroad rails, in incendiary bombs, and to ignite solid-fuel rocket motors. The reaction is

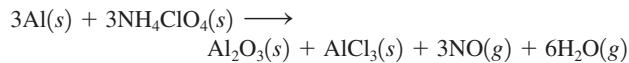


What masses of iron(III) oxide and aluminum must be used to produce 15.0 g iron? What is the maximum mass of aluminum oxide that could be produced?

- 90.** The reaction between potassium chlorate and red phosphorus takes place when you strike a match on a matchbox. If you were to react 52.9 g of potassium chlorate (KClO_3) with excess red phosphorus, what mass of tetraphosphorus decaoxide (P_4O_{10}) would be produced?

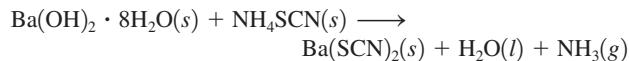


- 91.** The reusable booster rockets of the U.S. space shuttle employ a mixture of aluminum and ammonium perchlorate for fuel. A possible equation for this reaction is



What mass of NH_4ClO_4 should be used in the fuel mixture for every kilogram of Al?

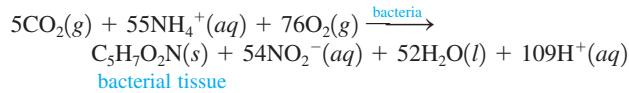
- 92.** One of relatively few reactions that takes place directly between two solids at room temperature is



In this equation, the $\cdot 8\text{H}_2\text{O}$ in $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ indicates the presence of eight water molecules. This compound is called barium hydroxide octahydrate.

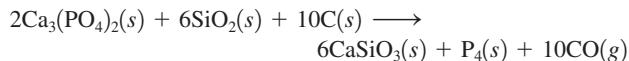
- Balance the equation.
- What mass of ammonium thiocyanate (NH_4SCN) must be used if it is to react completely with 6.5 g barium hydroxide octahydrate?

- 93.** Bacterial digestion is an economical method of sewage treatment. The reaction



is an intermediate step in the conversion of the nitrogen in organic compounds into nitrate ions. What mass of bacterial tissue is produced in a treatment plant for every 1.0×10^4 kg of wastewater containing 3.0% NH_4^+ ions by mass? Assume that 95% of the ammonium ions are consumed by the bacteria.

- 94.** Phosphorus can be prepared from calcium phosphate by the following reaction:



Phosphorite is a mineral that contains $\text{Ca}_3(\text{PO}_4)_2$ plus other non-phosphorus-containing compounds. What is the maximum amount of P_4 that can be produced from 1.0 kg of phosphorite if the phosphorite sample is 75% $\text{Ca}_3(\text{PO}_4)_2$ by mass? Assume an excess of the other reactants.

- 95.** Aspirin ($\text{C}_9\text{H}_8\text{O}_4$) is synthesized by reacting salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) with acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$). The balanced equation is

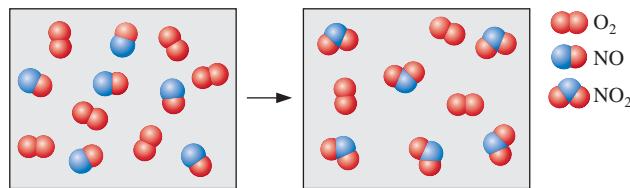


- What mass of acetic anhydride is needed to completely consume 1.00×10^2 g salicylic acid?
- What is the maximum mass of aspirin (the theoretical yield) that could be produced in this reaction?

- 96.** The space shuttle environmental control system handles excess CO_2 (which the astronauts breathe out; it is 4.0% by mass of exhaled air) by reacting it with lithium hydroxide, LiOH , pellets to form lithium carbonate, Li_2CO_3 , and water. If there are 7 astronauts on board the shuttle, and each exhales 20. L of air per minute, how long could clean air be generated if there were 25,000 g of LiOH pellets available for each shuttle mission? Assume the density of air is 0.0010 g/mL.

Limiting Reactants and Percent Yield

- 97.** Consider the reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ represented below.



What is the balanced equation for this reaction and what is the limiting reactant?

- 98.** Consider the following reaction:



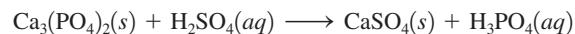
If a container were to have 10 molecules of O_2 and 10 molecules of NH_3 initially, how many total molecules (reactants plus products) would be present in the container after this reaction goes to completion?

- 99.** Hydrogen peroxide is used as a cleaning agent in the treatment of cuts and abrasions for several reasons. It is an oxidizing agent that can directly kill many microorganisms; it decomposes upon contact with blood, releasing elemental oxygen gas (which inhibits the growth of anaerobic microorganisms); and it foams upon contact with blood, which provides a cleansing action. In the laboratory, small quantities of hydrogen peroxide can be prepared by the action of an acid on an alkaline earth metal peroxide, such as barium peroxide:



What mass of hydrogen peroxide should result when 1.50 g of barium peroxide is treated with 25.0 mL of hydrochloric acid solution containing 0.0272 g of HCl per mL? What mass of which reagent is left unreacted?

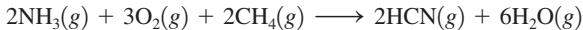
- 100.** Consider the following unbalanced equation:



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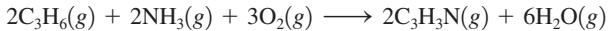
What masses of calcium sulfate and phosphoric acid can be produced from the reaction of 1.0 kg calcium phosphate with 1.0 kg concentrated sulfuric acid (98% H₂SO₄ by mass)?

- 101.** Hydrogen cyanide is produced industrially from the reaction of gaseous ammonia, oxygen, and methane:



If 5.00×10^3 kg each of NH₃, O₂, and CH₄ are reacted, what mass of HCN and of H₂O will be produced, assuming 100% yield?

- 102.** Acrylonitrile (C₃H₃N) is the starting material for many synthetic carpets and fabrics. It is produced by the following reaction.



If 15.0 g C₃H₆, 10.0 g O₂, and 5.00 g NH₃ are reacted, what mass of acrylonitrile can be produced, assuming 100% yield?

- 103.** A student prepared aspirin in a laboratory experiment using the reaction in Exercise 95. The student reacted 1.50 g salicylic acid with 2.00 g acetic anhydride. The yield was 1.50 g aspirin. Calculate the theoretical yield and the percent yield for this experiment.

- 104.** DDT, an insecticide harmful to fish, birds, and humans, is produced by the following reaction:



In a government lab, 1142 g of chlorobenzene is reacted with 485 g of chloral.

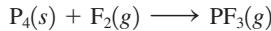
- a. What mass of DDT is formed?
- b. Which reactant is limiting? Which is in excess?
- c. What mass of the excess reactant is left over?
- d. If the actual yield of DDT is 200.0 g, what is the percent yield?

- 105.** Bornite (Cu₃FeS₃) is a copper ore used in the production of copper. When heated, the following reaction occurs:



If 2.50 metric tons of bornite is reacted with excess O₂ and the process has an 86.3% yield of copper, what mass of copper is produced?

- 106.** Consider the following unbalanced reaction:



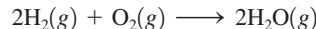
What mass of F₂ is needed to produce 120. g of PF₃ if the reaction has a 78.1% yield?

Additional Exercises

- 107.** A given sample of a xenon fluoride compound contains molecules of the type XeF_n, where n is some whole number. Given that 9.03×10^{20} molecules of XeF_n weighs 0.368 g, determine the value for n in the formula.
- 108.** Many cereals are made with high moisture content so that the cereal can be formed into various shapes before it is dried. A cereal product containing 58% H₂O by mass is produced at the rate

of 1000. kg/h. What mass of water must be evaporated per hour if the final product contains only 20% water?

- 109.** Consider the reaction



Identify the limiting reagent in each of the reaction mixtures given below:

- a. 50 molecules of H₂ and 25 molecules of O₂
- b. 100 molecules of H₂ and 40 molecules of O₂
- c. 100 molecules of H₂ and 100 molecules of O₂
- d. 0.50 mol H₂ and 0.75 mol O₂
- e. 0.80 mol H₂ and 0.75 mol O₂
- f. 1.0 g H₂ and 0.25 mol O₂
- g. 5.00 g H₂ and 56.00 g O₂

- 110.** Some bismuth tablets, a medication used to treat upset stomachs, contain 262 mg of bismuth subsalicylate, C₇H₅BiO₄, per tablet. Assuming two tablets are digested, calculate the mass of bismuth consumed.

- 111.** The empirical formula of styrene is CH; the molar mass of styrene is 104.14 g/mol. What number of H atoms are present in a 2.00-g sample of styrene?

- 112.** Terephthalic acid is an important chemical used in the manufacture of polyesters and plasticizers. It contains only C, H, and O. Combustion of 19.81 mg terephthalic acid produces 41.98 mg CO₂ and 6.45 mg H₂O. If 0.250 mol of terephthalic acid has a mass of 41.5 g, determine the molecular formula for terephthalic acid.

- 113.** A sample of a hydrocarbon (a compound consisting of only carbon and hydrogen) contains 2.59×10^{23} atoms of hydrogen and is 17.3% hydrogen by mass. If the molar mass of the hydrocarbon is between 55 and 65 g/mol, what amount (moles) of compound are present, and what is the mass of the sample?

- 114.** A binary compound between an unknown element E and hydrogen contains 91.27% E and 8.73% H by mass. If the formula of the compound is E₃H₈, calculate the atomic mass of E.

- 115.** A 0.755-g sample of hydrated copper(II) sulfate



was heated carefully until it had changed completely to anhydrous copper(II) sulfate (CuSO₄) with a mass of 0.483 g. Determine the value of x. [This number is called the *number of waters of hydration* of copper(II) sulfate. It specifies the number of water molecules per formula unit of CuSO₄ in the hydrated crystal.]

- 116.** ABS plastic is a tough, hard plastic used in applications requiring shock resistance. The polymer consists of three monomer units: acrylonitrile (C₃H₃N), butadiene (C₄H₆), and styrene (C₈H₈).

- a. A sample of ABS plastic contains 8.80% N by mass. It took 0.605 g of Br₂ to react completely with a 1.20-g sample of ABS plastic. Bromine reacts 1:1 (by moles) with the butadiene molecules in the polymer and nothing else. What is the percent by mass of acrylonitrile and butadiene in this polymer?
- b. What are the relative numbers of each of the monomer units in this polymer?

- 117.** A sample of LSD (d-lysergic acid diethylamide, C₂₄H₃₀N₃O) is added to some table salt (sodium chloride) to form a mixture. Given that a 1.00-g sample of the mixture undergoes combustion

to produce 1.20 g of CO_2 , what is the mass percentage of LSD in the mixture?

- 118.** Methane (CH_4) is the main component of marsh gas. Heating methane in the presence of sulfur produces carbon disulfide and hydrogen sulfide as the only products.

- Write the balanced chemical equation for the reaction of methane and sulfur.
- Calculate the theoretical yield of carbon disulfide when 120. g of methane is reacted with an equal mass of sulfur.

- 119.** A potential fuel for rockets is a combination of B_5H_9 and O_2 . The two react according to the following balanced equation:



If one tank in a rocket holds 126 g of B_5H_9 and another tank holds 192 g of O_2 , what mass of water can be produced when the entire contents of each tank react together?

- 120.** Silver sulfadiazine burn-treating cream creates a barrier against bacterial invasion and releases antimicrobial agents directly into the wound. If 25.0 g of Ag_2O is reacted with 50.0 g of $\text{C}_{10}\text{H}_{10}\text{N}_4\text{SO}_2$, what mass of silver sulfadiazine, $\text{AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2$, can be produced, assuming 100% yield?

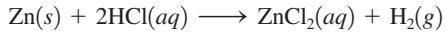


- 121.** An iron ore sample contains Fe_2O_3 plus other impurities. A 752-g sample of impure iron ore is heated with excess carbon, producing 453 g of pure iron by the following reaction:



What is the mass percent of Fe_2O_3 in the impure iron ore sample? Assume that Fe_2O_3 is the only source of iron and that the reaction is 100% efficient.

- 122.** Commercial brass, an alloy of Zn and Cu, reacts with hydrochloric acid as follows:



(Cu does not react with HCl.) When 0.5065 g of a certain brass alloy is reacted with excess HCl, 0.0985 g ZnCl_2 is eventually isolated.

- What is the composition of the brass by mass?
 - How could this result be checked without changing the above procedure?
- 123.** Vitamin A has a molar mass of 286.4 g/mol and a general molecular formula of $\text{C}_x\text{H}_y\text{E}$, where E is an unknown element. If vitamin A is 83.86% C and 10.56% H by mass, what is the molecular formula of vitamin A?

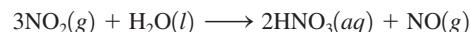
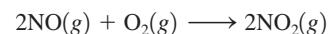
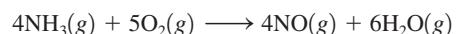
Challenge Problems

- 124.** Natural rubidium has the average mass of 85.4678 and is composed of isotopes ^{85}Rb (mass = 84.9117) and ^{87}Rb . The ratio of atoms $^{85}\text{Rb}/^{87}\text{Rb}$ in natural rubidium is 2.591. Calculate the mass of ^{87}Rb .

- 125.** A compound contains only carbon, hydrogen, nitrogen, and oxygen. Combustion of 0.157 g of the compound produced 0.213 g CO_2 and 0.0310 g H_2O . In another experiment, it is found that 0.103 g of the compound produces 0.0230 g NH_3 . What is the

empirical formula of the compound? Hint: Combustion involves reacting with excess O_2 . Assume that all the carbon ends up in CO_2 and all the hydrogen ends up in H_2O . Also assume that all the nitrogen ends up in the NH_3 in the second experiment.

- 126.** Nitric acid is produced commercially by the Ostwald process, represented by the following equations:



What mass of NH_3 must be used to produce 1.0×10^6 kg HNO_3 by the Ostwald process? Assume 100% yield in each reaction and assume that the NO produced in the third step is not recycled.

- 127.** Consider a 5.430-g mixture of FeO and Fe_3O_4 . You react this mixture with an excess of oxygen to form 5.779 g Fe_2O_3 . Calculate the percent by mass of FeO in the original mixture.

- 128.** A 9.780-g gaseous mixture contains ethane (C_2H_6) and propane (C_3H_8). Complete combustion to form carbon dioxide and water requires 1.120 mol of oxygen. Calculate the mass percent of ethane in the original mixture.

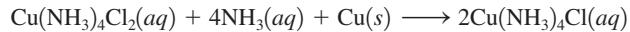
- 129.** Zinc and magnesium metal each react with hydrochloric acid to make chloride salts of the respective metals, and hydrogen gas. A 10.00-g mixture of zinc and magnesium produces 0.5171 g of hydrogen gas upon being mixed with an excess of hydrochloric acid. Determine the percent magnesium by mass in the original mixture.

- 130.** A 2.077-g sample of an element, which has an atomic mass between 40 and 55, reacts with oxygen to form 3.708 g of an oxide. Determine the formula of the oxide (and identify the element).

- 131.** Consider a gaseous binary compound with a molar mass of 62.09 g/mol. When 1.39 g of this compound is completely burned in excess oxygen, 1.21 g of water is formed. Determine the formula of the compound. Assume water is the only product that contains hydrogen.

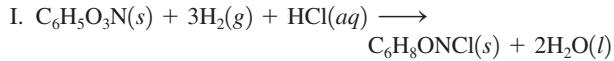
- 132.** A 2.25-g sample of scandium metal is reacted with excess hydrochloric acid to produce 0.1502 g hydrogen gas. What is the formula of the scandium chloride produced in the reaction?

- 133.** In the production of printed circuit boards for the electronics industry, a 0.60-mm layer of copper is laminated onto an insulating plastic board. Next, a circuit pattern made of a chemically resistant polymer is printed on the board. The unwanted copper is removed by chemical etching, and the protective polymer is finally removed by solvents. One etching reaction is

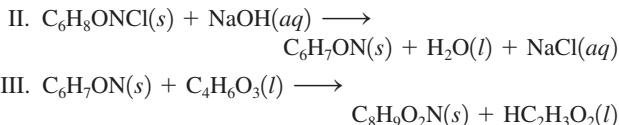


A plant needs to manufacture 10,000 printed circuit boards, each 8.0×16.0 cm in area. An average of 80.0% of the copper is removed from each board (density of copper = 8.96 g/cm³). What masses of $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ and NH_3 are needed to do this? Assume 100% yield.

- 134.** The aspirin substitute, acetaminophen ($\text{C}_8\text{H}_8\text{O}_2\text{N}$), is produced by the following three-step synthesis:



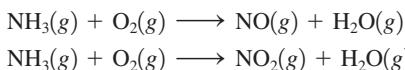
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The first two reactions have percent yields of 87% and 98% by mass, respectively. The overall reaction yields 3 mol of acetaminophen product for every 4 mol of $\text{C}_6\text{H}_5\text{O}_3\text{N}$ reacted.

- What is the percent yield by mass for the overall process?
- What is the percent yield by mass of step III?

135. An element X forms both a dichloride (XCl_2) and a tetrachloride (XCl_4). Treatment of 10.00 g XCl_2 with excess chlorine forms 12.55 g XCl_4 . Calculate the atomic mass of X, and identify X.
136. When $\text{M}_2\text{S}_3(s)$ is heated in air, it is converted to $\text{MO}_2(s)$. A 4.000-g sample of $\text{M}_2\text{S}_3(s)$ shows a decrease in mass of 0.277 g when it is heated in air. What is the average atomic mass of M?
137. When aluminum metal is heated with an element from Group 6A of the periodic table, an ionic compound forms. When the experiment is performed with an unknown Group 6A element, the product is 18.56% Al by mass. What is the formula of the compound?
138. A sample of a mixture containing only sodium chloride and potassium chloride has a mass of 4.000 g. When this sample is dissolved in water and excess silver nitrate is added, a white solid (silver chloride) forms. After filtration and drying, the solid silver chloride has the mass 8.5904 g. Calculate the mass percent of each mixture component.
139. Ammonia reacts with O_2 to form either $\text{NO}(g)$ or $\text{NO}_2(g)$ according to these unbalanced equations:



In a certain experiment 2.00 mol of $\text{NH}_3(g)$ and 10.00 mol of $\text{O}_2(g)$ are contained in a closed flask. After the reaction is complete, 6.75 mol of $\text{O}_2(g)$ remains. Calculate the number of moles of $\text{NO}(g)$ in the product mixture: (Hint: You cannot do this problem by adding the balanced equations, because you cannot assume that the two reactions will occur with equal probability.)

140. You take 1.00 g of an aspirin tablet (a compound consisting solely of carbon, hydrogen, and oxygen), burn it in air, and collect 2.20 g CO_2 and 0.400 g H_2O . You know that the molar mass of aspirin is between 170 and 190 g/mol. Reacting 1 mole of salicylic acid with 1 mole of acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$) gives you 1 mole of aspirin and 1 mole of acetic acid ($\text{C}_2\text{H}_4\text{O}_2$). Use this information to determine the molecular formula of salicylic acid.

Integrative Problems

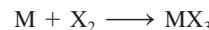
These problems require the integration of multiple concepts to find the solutions.

141. With the advent of techniques such as scanning tunneling microscopy, it is now possible to “write” with individual atoms by manipulating and arranging atoms on an atomic surface.
- If an image is prepared by manipulating iron atoms and their total mass is 1.05×10^{-20} g, what number of iron atoms were used?

- If the image is prepared on a platinum surface that is exactly 20 platinum atoms high and 14 platinum atoms wide, what is the mass (grams) of the atomic surface?

- If the atomic surface were changed to ruthenium atoms and the same surface mass as determined in part b is used, what number of ruthenium atoms is needed to construct the surface?

142. Tetrodotoxin is a toxic chemical found in fugu pufferfish, a popular but rare delicacy in Japan. This compound has a LD_{50} (the amount of substance that is lethal to 50% of a population sample) of 10. μg per kg of body mass. Tetrodotoxin is 41.38% carbon by mass, 13.16% nitrogen by mass, and 5.37% hydrogen by mass, with the remaining amount consisting of oxygen. What is the empirical formula of tetrodotoxin? If three molecules of tetrodotoxin has a mass of 1.59×10^{-21} g, what is the molecular formula of tetrodotoxin? What number of molecules of tetrodotoxin would be the LD_{50} dosage for a person weighing 165 lb?
143. An ionic compound MX_3 is prepared according to the following unbalanced chemical equation.



A 0.105-g sample of X_2 contains 8.92×10^{20} molecules. The compound MX_3 consists of 54.47% X by mass. What are the identities of M and X, and what is the correct name for MX_3 ? Starting with 1.00 g each of M and X_2 , what mass of MX_3 can be prepared?

144. The compound As_2I_4 is synthesized by reaction of arsenic metal with arsenic triiodide. If a solid cubic block of arsenic ($d = 5.72 \text{ g/cm}^3$) that is 3.00 cm on edge is allowed to react with 1.01×10^{24} molecules of arsenic triiodide, how much As_2I_4 can be prepared? If the percent yield of As_2I_4 was 75.6%, what mass of As_2I_4 was actually isolated?

Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

- *145. From the information below, determine the mass of substance C that will be formed if 45.0 grams of substance A reacts with 23.0 grams of substance B. (Assume that the reaction between A and B goes to completion.)
- Substance A is a gray solid that consists of an alkaline earth metal and carbon (37.5% by mass). It reacts with substance B to produce substances C and D. Forty million trillion formula units of A have a mass of 4.26 milligrams.
 - 47.9 grams of substance B contains 5.36 grams of hydrogen and 42.5 grams of oxygen.
 - When 10.0 grams of C is burned in excess oxygen, 33.8 grams of carbon dioxide and 6.92 grams of water are produced. A mass spectrum of substance C shows a parent molecular ion with a mass-to-charge ratio of 26.
 - Substance D is the hydroxide of the metal in substance A.

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146. Consider the following balanced chemical equation:



- a. Equal masses of A and B are reacted. Complete each of the following with either “A is the limiting reactant because _____”; “B is the limiting reactant because _____”; or “we cannot determine the limiting reactant because _____”.
- If the molar mass of A is greater than the molar mass of B, then
 - If the molar mass of B is greater than the molar mass of A, then

b. The products of the reaction are carbon dioxide (C) and water (D). Compound A has the same molar mass as carbon dioxide. Compound B is a diatomic molecule. Identify compound B and support your answer.

c. Compound A is a hydrocarbon that is 81.71% carbon by mass. Determine its empirical and molecular formulas.

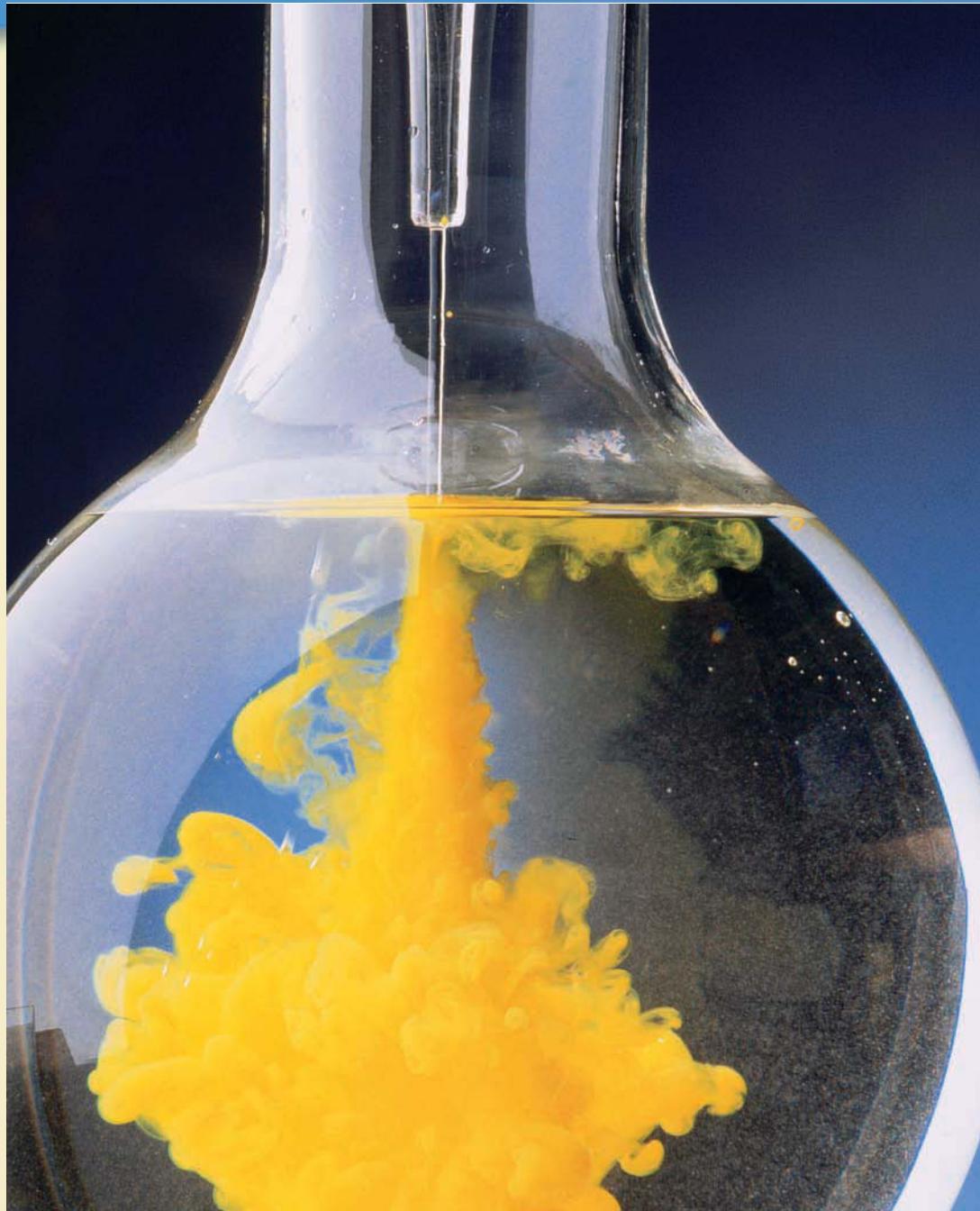


Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmcoc.com/PIC/zumdahl7e.

4 Types of Chemical Reactions and Solution Stoichiometry

Contents

- 4.1 Water, the Common Solvent
- 4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes
 - Strong Electrolytes
 - Weak Electrolytes
 - Nonelectrolytes
- 4.3 The Composition of Solutions
 - Dilution
- 4.4 Types of Chemical Reactions
- 4.5 Precipitation Reactions
- 4.6 Describing Reactions in Solution
- 4.7 Stoichiometry of Precipitation Reactions
- 4.8 Acid–Base Reactions
 - Acid–Base Titrations
- 4.9 Oxidation–Reduction Reactions
 - Oxidation States
 - The Characteristics of Oxidation–Reduction Reactions
- 4.10 Balancing Oxidation–Reduction Equations
 - The Half-Reaction Method for Balancing Oxidation–Reduction Reactions in Aqueous Solutions



Yellow lead(II) iodide is produced when lead(II) nitrate is mixed with potassium iodide.

M

uch of the chemistry that affects each of us occurs among substances dissolved in water. For example, virtually all the chemistry that makes life possible occurs in an aqueous environment. Also, various medical tests involve aqueous reactions, depending heavily on analyses of blood and other body fluids. In addition to the common tests for sugar, cholesterol, and iron, analyses for specific chemical markers allow detection of many diseases before obvious symptoms occur.

Aqueous chemistry is also important in our environment. In recent years, contamination of the groundwater by substances such as chloroform and nitrates has been widely publicized. Water is essential for life, and the maintenance of an ample supply of clean water is crucial to all civilization.

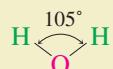
To understand the chemistry that occurs in such diverse places as the human body, the atmosphere, the groundwater, the oceans, the local water treatment plant, your hair as you shampoo it, and so on, we must understand how substances dissolved in water react with each other.

However, before we can understand solution reactions, we need to discuss the nature of solutions in which water is the dissolving medium, or *solvent*. These solutions are called **aqueous solutions**. In this chapter we will study the nature of materials after they are dissolved in water and various types of reactions that occur among these substances. You will see that the procedures developed in Chapter 3 to deal with chemical reactions work very well for reactions that take place in aqueous solutions. To understand the types of reactions that occur in aqueous solutions, we must first explore the types of species present. This requires an understanding of the nature of water.

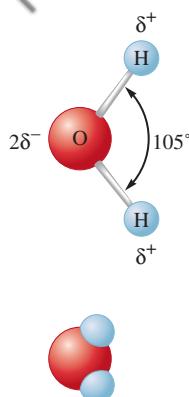
4.1 Water, the Common Solvent

Water is one of the most important substances on earth. It is essential for sustaining the reactions that keep us alive, but it also affects our lives in many indirect ways. Water helps moderate the earth's temperature; it cools automobile engines, nuclear power plants, and many industrial processes; it provides a means of transportation on the earth's surface and a medium for the growth of a myriad of creatures we use as food; and much more.

One of the most valuable properties of water is its ability to dissolve many different substances. For example, salt “disappears” when you sprinkle it into the water used to cook vegetables, as does sugar when you add it to your iced tea. In each case the “disappearing” substance is obviously still present—you can taste it. What happens when a solid dissolves? To understand this process, we need to consider the nature of water. Liquid water consists of a collection of H_2O molecules. An individual H_2O molecule is “bent” or V-shaped, with an H—O—H angle of approximately 105 degrees:



The O—H bonds in the water molecule are covalent bonds formed by electron sharing between the oxygen and hydrogen atoms. However, the electrons of the bond are not shared equally between these atoms. For reasons we will discuss in later chapters, oxygen has a greater attraction for electrons than does hydrogen. If the electrons were shared equally between the two atoms, both would be electrically neutral because, on average, the number of electrons around each would equal the number of protons in that nucleus.

**FIGURE 4.1**

(top) The water molecule is polar. (bottom) A space-filling model of the water molecule.

However, because the oxygen atom has a greater attraction for electrons, the shared electrons tend to spend more time close to the oxygen than to either of the hydrogens. Thus the oxygen atom gains a slight excess of negative charge, and the hydrogen atoms become slightly positive. This is shown in Fig. 4.1, where δ (delta) indicates a *partial* charge (*less than one unit of charge*). Because of this unequal charge distribution, water is said to be a **polar molecule**. It is this polarity that gives water its great ability to dissolve compounds.

A schematic of an ionic solid dissolving in water is shown in Fig. 4.2. Note that the “positive ends” of the water molecules are attracted to the negatively charged anions and that the “negative ends” are attracted to the positively charged cations. This process is called **hydration**. The hydration of its ions tends to cause a salt to “fall apart” in the water, or to dissolve. The strong forces present among the positive and negative ions of the solid are replaced by strong water–ion interactions.

It is very important to recognize that when ionic substances (salts) dissolve in water, they break up into the *individual* cations and anions. For instance, when ammonium nitrate (NH_4NO_3) dissolves in water, the resulting solution contains NH_4^+ and NO_3^- ions moving around independently. This process can be represented as

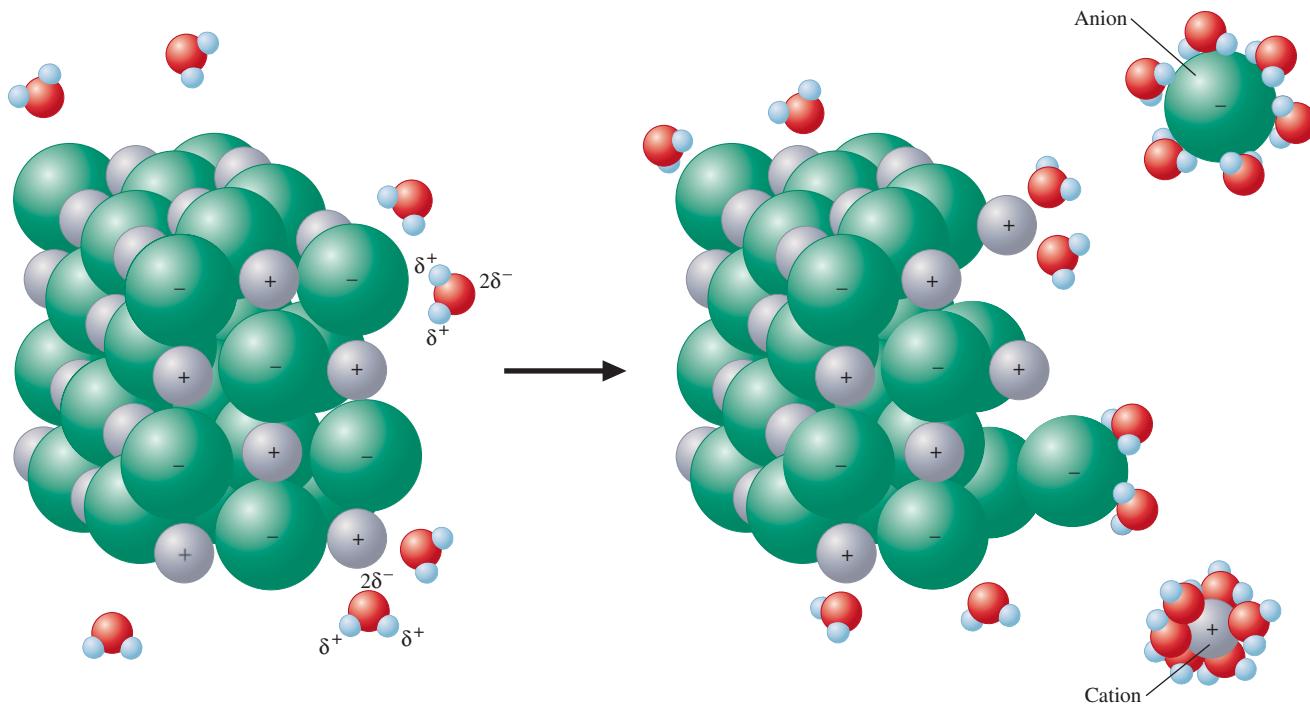


where (aq) designates that the ions are hydrated by unspecified numbers of water molecules.

The **solubility** of ionic substances in water varies greatly. For example, sodium chloride is quite soluble in water, whereas silver chloride (contains Ag^+ and Cl^- ions) is only very slightly soluble. The differences in the solubilities of ionic compounds in water typically depend on the relative attractions of the ions for each other (these forces hold the solid together) and the attractions of the ions for water molecules (which cause the solid to disperse [dissolve] in water). Solubility is a complex topic that we will explore in much more detail in Chapter 11. However, the most important thing to remember at



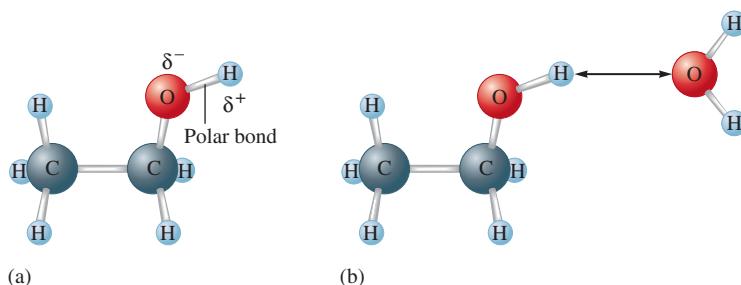
Visualization: The Dissolution of a Solid in a Liquid

**FIGURE 4.2**

Polar water molecules interact with the positive and negative ions of a salt, assisting in the dissolving process.

FIGURE 4.3

(a) The ethanol molecule contains a polar O—H bond similar to those in the water molecule. (b) The polar water molecule interacts strongly with the polar O—H bond in ethanol. This is a case of “like dissolves like.”



this point is that when an ionic solid does dissolve in water, the ions become hydrated and are dispersed (move around independently).

Water also dissolves many nonionic substances. Ethanol (C_2H_5OH), for example, is very soluble in water. Wine, beer, and mixed drinks are aqueous solutions of ethanol and other substances. Why is ethanol so soluble in water? The answer lies in the structure of the alcohol molecules, which is shown in Fig. 4.3(a). The molecule contains a polar O—H bond like those in water, which makes it very compatible with water. The interaction of water with ethanol is represented in Fig. 4.3(b).

Many substances do not dissolve in water. Pure water will not, for example, dissolve animal fat, because fat molecules are nonpolar and do not interact effectively with polar water molecules. In general, polar and ionic substances are expected to be more soluble in water than nonpolar substances. “Like dissolves like” is a useful rule for predicting solubility. We will explore the basis for this generalization when we discuss the details of solution formation in Chapter 11.

4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes

As we discussed in Chapter 2, a solution is a homogeneous mixture. It is the same throughout (the first sip of a cup of coffee is the same as the last), but its composition can be varied by changing the amount of dissolved substances (one can make weak or strong coffee). In this section we will consider what happens when a substance, the **solute**, is dissolved in liquid water, the **solvent**.

One useful property for characterizing a solution is its **electrical conductivity**, its ability to conduct an electric current. This characteristic can be checked conveniently by using an apparatus like the ones shown in Figure 4.4. If the solution in the container conducts electricity, the bulb lights. Pure water is not an electrical conductor. However, some aqueous solutions conduct current very efficiently, and the bulb shines very brightly; these solutions contain **strong electrolytes**. Other solutions conduct only a small current, and the bulb glows dimly; these solutions contain **weak electrolytes**. Some solutions permit no current to flow, and the bulb remains unlit; these solutions contain **nonelectrolytes**.

The basis for the conductivity properties of solutions was first correctly identified by Svante Arrhenius (1859–1927), then a Swedish graduate student in physics, who carried out research on the nature of solutions at the University of Uppsala in the early 1880s. Arrhenius came to believe that the conductivity of solutions arose from the presence of ions, an idea that was at first scorned by the majority of the scientific establishment. However, in the late 1890s when atoms were found to contain charged particles, the ionic theory suddenly made sense and became widely accepted.

As Arrhenius postulated, the extent to which a solution can conduct an electric current depends directly on the number of ions present. Some materials, such as sodium chloride, readily produce ions in aqueous solution and thus are strong electrolytes. Other substances,

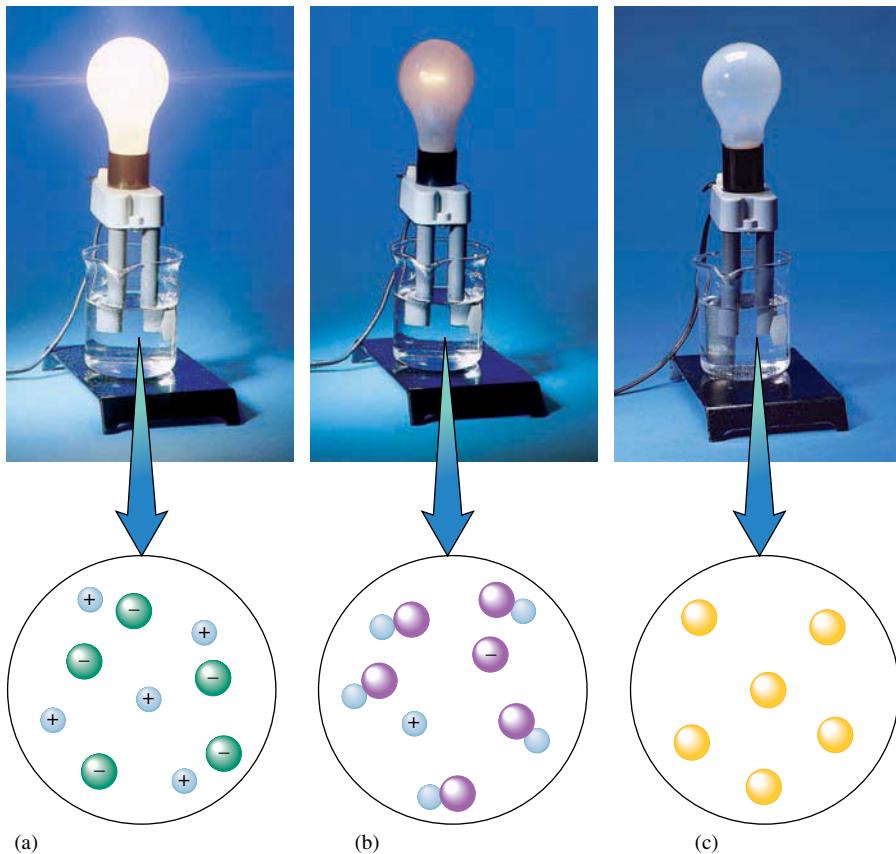


Visualization: Electrolytes

An **electrolyte** is a substance that when dissolved in water produces a solution that can conduct electricity.



Visualization: Electrolyte Behavior



such as acetic acid, produce relatively few ions when dissolved in water and are weak electrolytes. A third class of materials, such as sugar, form virtually no ions when dissolved in water and are nonelectrolytes.

Strong Electrolytes

Strong electrolytes are substances that are completely ionized when they are dissolved in water, as represented in Fig. 4.4(a). We will consider several classes of strong electrolytes: (1) soluble salts, (2) strong acids, and (3) strong bases.

As shown in Fig. 4.2, a salt consists of an array of cations and anions that separate and become hydrated when the salt dissolves. For example, when NaCl dissolves in water, it produces hydrated Na^+ and Cl^- ions in the solution (see Fig. 4.5). Virtually no NaCl

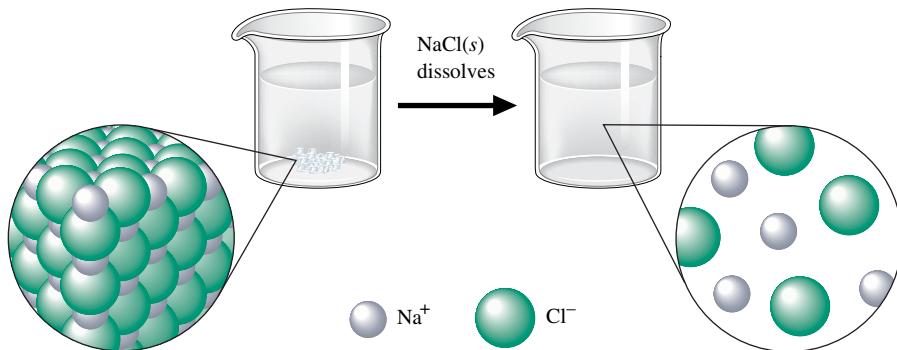


FIGURE 4.5

When solid NaCl dissolves, the Na^+ and Cl^- ions are randomly dispersed in the water.

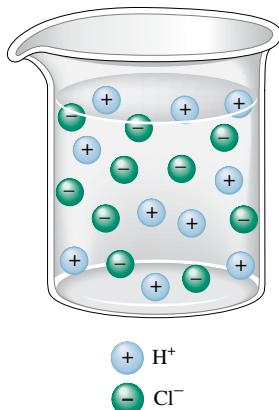


FIGURE 4.6
HCl(aq) is completely ionized.

The Arrhenius definition of an acid is a substance that produces H⁺ ions in solution.

Strong electrolytes dissociate (ionize) completely in aqueous solution.

Perchloric acid, HClO₄(aq), is another strong acid.

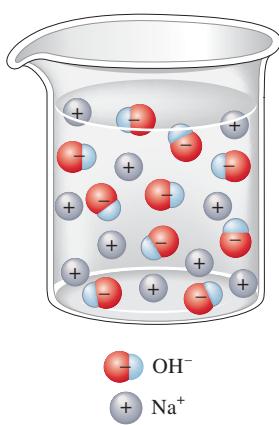


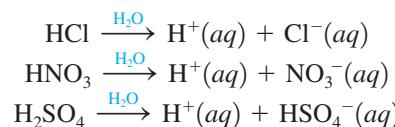
FIGURE 4.7
An aqueous solution of sodium hydroxide.

Weak electrolytes dissociate (ionize) only to a small extent in aqueous solution.

units are present. Thus NaCl is a strong electrolyte. It is important to recognize that these aqueous solutions contain millions of water molecules that we will not include in our molecular-level drawings.

One of Arrhenius's most important discoveries concerned the nature of acids. Acidity was first associated with the sour taste of citrus fruits. In fact, the word *acid* comes directly from the Latin word *acidus*, meaning “sour.” The mineral acids sulfuric acid (H₂SO₄) and nitric acid (HNO₃), so named because they were originally obtained by the treatment of minerals, were discovered around 1300.

Although acids were known for hundreds of years before the time of Arrhenius, no one had recognized their essential nature. In his studies of solutions, Arrhenius found that when the substances HCl, HNO₃, and H₂SO₄ were dissolved in water, they behaved as strong electrolytes. He postulated that this was the result of ionization reactions in water, for example:



Thus Arrhenius proposed that an *acid* is a substance that produces H⁺ ions (protons) when it is dissolved in water.

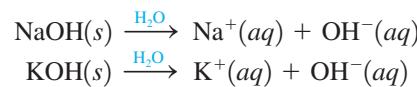
Studies of conductivity show that when HCl, HNO₃, and H₂SO₄ are placed in water, virtually every molecule ionizes. These substances are strong electrolytes and are thus called **strong acids**. All three are very important chemicals, and much more will be said about them as we proceed. However, at this point the following facts are important:

Sulfuric acid, nitric acid, and hydrochloric acid are aqueous solutions and should be written in chemical equations as H₂SO₄(aq), HNO₃(aq), and HCl(aq), respectively, although they often appear without the (aq) symbol.

A strong acid is one that completely dissociates into its ions. Thus, if 100 molecules of HCl are dissolved in water, 100 H⁺ ions and 100 Cl⁻ ions are produced. Virtually no HCl molecules exist in aqueous solutions (see Fig. 4.6).

Sulfuric acid is a special case. The formula H₂SO₄ indicates that this acid can produce two H⁺ ions per molecule when dissolved in water. However, only the first H⁺ ion is completely dissociated. The second H⁺ ion can be pulled off under certain conditions, which we will discuss later. Thus an aqueous solution of H₂SO₄ contains mostly H⁺ ions and SO₄²⁻ ions.

Another important class of strong electrolytes consists of the **strong bases**, soluble ionic compounds containing the hydroxide ion (OH⁻). When these compounds are dissolved in water, the cations and OH⁻ ions separate and move independently. Solutions containing bases have a bitter taste and a slippery feel. The most common basic solutions are those produced when solid sodium hydroxide (NaOH) or potassium hydroxide (KOH) is dissolved in water to produce ions, as follows (see Fig. 4.7):



Weak Electrolytes

Weak electrolytes are substances that exhibit a small degree of ionization in water. That is, they produce relatively few ions when dissolved in water, as shown in Fig. 4.4(b). The most common weak electrolytes are weak acids and weak bases.



CHEMICAL IMPACT

Arrhenius: A Man with Solutions

Science is a human endeavor, subject to human frailties and governed by personalities, politics, and prejudices. One of the best illustrations of the often bumpy path of the advancement of scientific knowledge is the story of Swedish chemist Svante Arrhenius.

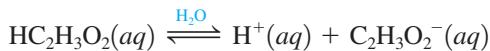
When Arrhenius began studies toward his doctorate at the University of Uppsala around 1880, he chose to investigate the passage of electricity through solutions, a mystery that had baffled scientists for a century. The first experiments had been done in the 1770s by Cavendish, who compared the conductivity of salt solution with that of rain water using his own physiologic reaction to the electric shocks he received! Arrhenius had an array of instruments to measure electric current, but the process of carefully weighing, measuring, and recording data from a multitude of experiments was a tedious one.

After his long series of experiments was performed, Arrhenius quit his laboratory bench and returned to his country



Svante August Arrhenius.

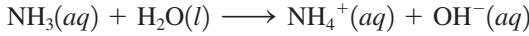
The main acidic component of vinegar is acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$). The formula is written to indicate that acetic acid has two chemically distinct types of hydrogen atoms. Formulas for acids are often written with the acidic hydrogen atom or atoms (any that will produce H^+ ions in solution) listed first. If any nonacidic hydrogens are present, they are written later in the formula. Thus the formula $\text{HC}_2\text{H}_3\text{O}_2$ indicates one acidic and three nonacidic hydrogen atoms. The dissociation reaction for acetic acid in water can be written as follows:



Acetic acid is very different from the strong acids because only about 1% of its molecules dissociate in aqueous solutions at typical concentrations. For example, in a solution containing 0.1 mole of $\text{HC}_2\text{H}_3\text{O}_2$ per liter, for every 100 molecules of $\text{HC}_2\text{H}_3\text{O}_2$ originally dissolved in water, approximately 99 molecules of $\text{HC}_2\text{H}_3\text{O}_2$ remain intact (see Fig. 4.8). That is, only one molecule out of every 100 dissociates (to produce one H^+ ion and one $\text{C}_2\text{H}_3\text{O}_2^-$ ion).

Because acetic acid is a weak electrolyte, it is called a **weak acid**. Any acid, such as acetic acid, that *dissociates (ionizes) only to a slight extent in aqueous solutions* is called a weak acid. In Chapter 14 we will explore the subject of weak acids in detail.

The most common weak base is ammonia (NH_3). When ammonia is dissolved in water, it reacts as follows:



The solution is *basic* because OH^- ions are produced. Ammonia is called a **weak base** because *the resulting solution is a weak electrolyte*; that is, very few ions are formed. In fact, in a solution containing 0.1 mole of NH_3 per liter, for every 100 molecules of NH_3

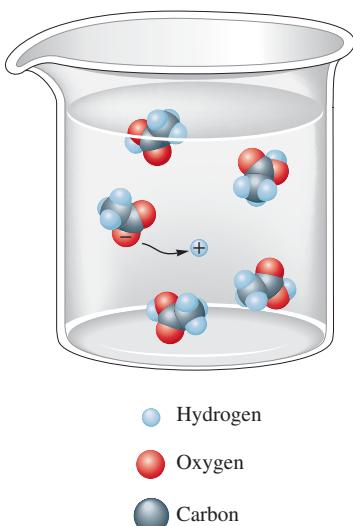


FIGURE 4.8

Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) exists in water mostly as undissociated molecules. Only a small percentage of the molecules are ionized.

home to try to formulate a model that could account for his data. He wrote, “I got the idea in the night of the 17th of May in the year 1883, and I could not sleep that night until I had worked through the whole problem.” His idea was that ions were responsible for conducting electricity through a solution.

Back at Uppsala, Arrhenius took his doctoral dissertation containing the new theory to his advisor, Professor Cleve, an eminent chemist and the discoverer of the elements holmium and thulium. Cleve’s uninterested response was what Arrhenius had expected. It was in keeping with Cleve’s resistance to new ideas—he had not even accepted Mendeleev’s periodic table, introduced 10 years earlier.

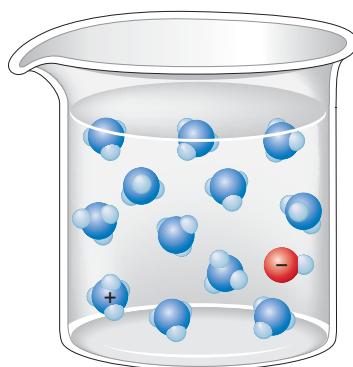
It is a long-standing custom that before a doctoral degree is granted, the dissertation must be defended before a panel of professors. Although this procedure is still followed at most universities today, the problems are usually worked out in private with the evaluating professors before the actual defense. However, when Arrhenius did it, the dissertation defense was an open debate, which could be rancorous and humiliating. Knowing that it would be unwise to antagonize his professors, Arrhenius downplayed his convictions about

his new theory as he defended his dissertation. His diplomacy paid off: He was awarded his degree, albeit reluctantly, because the professors still did not believe his model and considered him to be a marginal scientist, at best.

Such a setback could have ended his scientific career, but Arrhenius was a crusader; he was determined to see his theory triumph. He promptly embarked on a political campaign, enlisting the aid of several prominent scientists, to get his theory accepted.

Ultimately, the ionic theory triumphed. Arrhenius’s fame spread, and honors were heaped on him, culminating in the Nobel Prize in chemistry in 1903. Not one to rest on his laurels, Arrhenius turned to new fields, including astronomy; he formulated a new theory that the solar system may have come into being through the collision of stars. His exceptional versatility led him to study the use of serums to fight disease, energy resources and conservation, and the origin of life.

Additional insight on Arrhenius and his scientific career can be obtained from his address on receiving the Willard Gibbs Award. See *Journal of the American Chemical Society* 36 (1912): 353.



- Hydrogen
- Oxygen
- Nitrogen

FIGURE 4.9
The reaction of NH_3 in water.

originally dissolved, only one NH_4^+ ion and one OH^- ion are produced; 99 molecules of NH_3 remain unreacted (see Fig. 4.9).

Nonelectrolytes

Nonelectrolytes are substances that dissolve in water but do not produce any ions, as shown in Fig. 4.4(c). An example of a nonelectrolyte is ethanol (see Fig. 4.3 for the structural formula). When ethanol dissolves, entire $\text{C}_2\text{H}_5\text{OH}$ molecules are dispersed in the water. Since the molecules do not break up into ions, the resulting solution does not conduct an electric current. Another common nonelectrolyte is table sugar (sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$), which is very soluble in water but which produces no ions when it dissolves. The sucrose molecules remain intact.

4.3 The Composition of Solutions

Chemical reactions often take place when two solutions are mixed. To perform stoichiometric calculations in such cases, we must know two things: (1) the *nature of the reaction*, which depends on the exact forms the chemicals take when dissolved, and (2) the *amounts of chemicals* present in the solutions, usually expressed as concentrations.

The concentration of a solution can be described in many different ways, as we will see in Chapter 11. At this point we will consider only the most commonly used expression of concentration, **molarity** (M), which is defined as *moles of solute per volume of solution in liters*:

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

A solution that is 1.0 molar (written as $1.0 M$) contains 1.0 mole of solute per liter of solution.

Sample Exercise 4.1**Calculation of Molarity I**

Calculate the molarity of a solution prepared by dissolving 11.5 g of solid NaOH in enough water to make 1.50 L of solution.

Solution

To find the molarity of the solution, we first compute the number of moles of solute using the molar mass of NaOH (40.00 g/mol):

$$11.5 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 0.288 \text{ mol NaOH}$$

Then we divide by the volume of the solution in liters:

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.288 \text{ mol NaOH}}{1.50 \text{ L solution}} = 0.192 \text{ M NaOH}$$

See Exercises 4.21 and 4.22.

Sample Exercise 4.2**Calculation of Molarity II**

Calculate the molarity of a solution prepared by dissolving 1.56 g of gaseous HCl in enough water to make 26.8 mL of solution.

Solution

First we calculate the number of moles of HCl (molar mass = 36.46 g/mol):

$$1.56 \text{ g HCl} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 4.28 \times 10^{-2} \text{ mol HCl}$$

Next we must change the volume of the solution to liters:

$$26.8 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.68 \times 10^{-2} \text{ L}$$

Finally, we divide the moles of solution by the liters of solution:

$$\text{Molarity} = \frac{4.28 \times 10^{-2} \text{ mol HCl}}{2.68 \times 10^{-2} \text{ L solution}} = 1.60 \text{ M HCl}$$

See Exercises 4.21 and 4.22.

It is important to realize that the conventional description of a solution's concentration may not accurately reflect the true composition of the solution. Solution concentration is always given in terms of the form of the solute *before* it dissolves. For example, when a solution is described as being 1.0 M NaCl, this means that the solution was prepared by dissolving 1.0 mole of solid NaCl in enough water to make 1.0 liter of solution; it does not mean that the solution contains 1.0 mole of NaCl units. Actually, the solution contains 1.0 mole of Na⁺ ions and 1.0 mole of Cl⁻ ions. This situation is further illustrated in Sample Exercise 4.3.

Sample Exercise 4.3**Concentrations of Ions I**

Give the concentration of each type of ion in the following solutions:

- a. 0.50 M Co(NO₃)₂
- b. 1 M Fe(ClO₄)₃

An aqueous solution of $\text{Co}(\text{NO}_3)_2$.

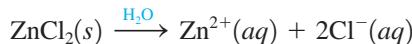
$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Sample Exercise 4.4

Calculate the number of moles of Cl^- ions in 1.75 L of $1.0 \times 10^{-3} M \text{ ZnCl}_2$.

Solution

When solid ZnCl_2 dissolves, it produces ions as follows:



Thus a $1.0 \times 10^{-3} M \text{ ZnCl}_2$ solution contains $1.0 \times 10^{-3} M \text{ Zn}^{2+}$ ions and $2.0 \times 10^{-3} M \text{ Cl}^-$ ions. To calculate the moles of Cl^- ions in 1.75 L of the $1.0 \times 10^{-3} M \text{ ZnCl}_2$ solution, we must multiply the volume times the molarity:

$$1.75 \text{ L solution} \times 2.0 \times 10^{-3} M \text{ Cl}^- = 1.75 \text{ L solution} \times \frac{2.0 \times 10^{-3} \text{ mol Cl}^-}{\text{L solution}} \\ = 3.5 \times 10^{-3} \text{ mol Cl}^-$$

See Exercise 4.25.

Sample Exercise 4.5**Concentration and Volume**

Typical blood serum is about $0.14 M \text{ NaCl}$. What volume of blood contains 1.0 mg NaCl ?

Solution

We must first determine the number of moles represented by 1.0 mg NaCl (molar mass = 58.45 g/mol):

$$1.0 \text{ mg NaCl} \times \frac{1 \text{ g NaCl}}{1000 \text{ mg NaCl}} \times \frac{1 \text{ mol NaCl}}{58.45 \text{ g NaCl}} = 1.7 \times 10^{-5} \text{ mol NaCl}$$

Next, we must determine what volume of 0.14 M NaCl solution contains 1.7×10^{-5} mol NaCl. There is some volume, call it V , that when multiplied by the molarity of this solution will yield 1.7×10^{-5} mol NaCl. That is:

$$V \times \frac{0.14 \text{ mol NaCl}}{\text{L solution}} = 1.7 \times 10^{-5} \text{ mol NaCl}$$

We want to solve for the volume:

$$V = \frac{1.7 \times 10^{-5} \text{ mol NaCl}}{\frac{0.14 \text{ mol NaCl}}{\text{L solution}}} = 1.2 \times 10^{-4} \text{ L solution}$$

Thus 0.12 mL of blood contains 1.7×10^{-5} mol NaCl or 1.0 mg NaCl.

See Exercises 4.27 and 4.28.

A **standard solution** is a *solution whose concentration is accurately known*. Standard solutions, often used in chemical analysis, can be prepared as shown in Fig. 4.10 and in Sample Exercise 4.6.

Sample Exercise 4.6

Solutions of Known Concentration

To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$ (potassium dichromate) solution. How much solid $\text{K}_2\text{Cr}_2\text{O}_7$ must be weighed out to make this solution?

Solution

We must first determine the moles of $\text{K}_2\text{Cr}_2\text{O}_7$ required:

$$1.00 \text{ L solution} \times \frac{0.200 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7}{\text{L solution}} = 0.200 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7$$

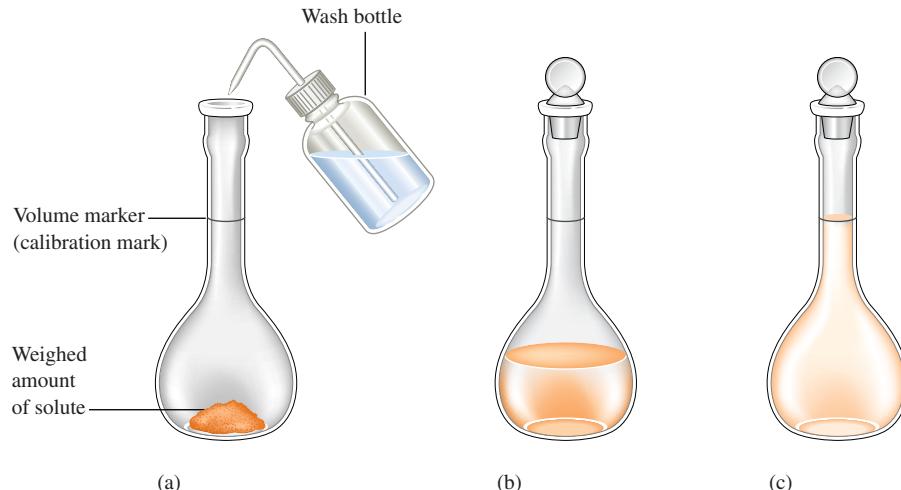


FIGURE 4.10

Steps involved in the preparation of a standard aqueous solution. (a) Put a weighed amount of a substance (the solute) into the volumetric flask, and add a small quantity of water. (b) Dissolve the solid in the water by gently swirling the flask (*with the stopper in place*). (c) Add more water (with gentle swirling) until the level of the solution just reaches the mark etched on the neck of the flask. Then mix the solution thoroughly by inverting the flask several times.

This amount can be converted to grams using the molar mass of $\text{K}_2\text{Cr}_2\text{O}_7$ (294.18 g/mol).

$$0.200 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.20 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7}{\text{mol } \text{K}_2\text{Cr}_2\text{O}_7} = 58.8 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7$$

Thus, to make 1.00 L of 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$, the chemist must weigh out 58.8 g $\text{K}_2\text{Cr}_2\text{O}_7$, transfer it to a 1.00-L volumetric flask, and add distilled water to the mark on the flask.

See Exercises 4.29a and c and 4.30c and e.



Visualization: Dilution

Dilution with water does not alter the numbers of moles of solute present.

Dilution

To save time and space in the laboratory, routinely used solutions are often purchased or prepared in concentrated form (called *stock solutions*). Water is then added to achieve the molarity desired for a particular solution. This process is called **dilution**. For example, the common acids are purchased as concentrated solutions and diluted as needed. A typical dilution calculation involves determining how much water must be added to an amount of stock solution to achieve a solution of the desired concentration. The key to doing these calculations is to remember that

$$\text{Moles of solute after dilution} = \text{moles of solute before dilution}$$

because only water (no solute) is added to accomplish the dilution.

For example, suppose we need to prepare 500. mL of 1.00 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) from a 17.4 M stock solution of acetic acid. What volume of the stock solution is required? The first step is to determine the number of moles of acetic acid in the final solution by multiplying the volume by the molarity (remembering that the volume must be changed to liters):

$$500. \text{ mL solution} \times \frac{1 \text{ L solution}}{1000 \text{ mL solution}} \times \frac{1.00 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2}{\text{L solution}} = 0.500 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2$$

Thus we need to use a volume of 17.4 M acetic acid that contains 0.500 mol $\text{HC}_2\text{H}_3\text{O}_2$. That is,

$$V \times \frac{17.4 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2}{\text{L solution}} = 0.500 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2$$

Solving for V gives

$$V = \frac{0.500 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2}{\frac{17.4 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2}{\text{L solution}}} = 0.0287 \text{ L or } 28.7 \text{ mL solution}$$

Thus, to make 500 mL of a 1.00 M acetic acid solution, we can take 28.7 mL of 17.4 M acetic acid and dilute it to a total volume of 500 mL with distilled water.

A dilution procedure typically involves two types of glassware: a pipet and a volumetric flask. A *pipet* is a device for accurately measuring and transferring a given volume of solution. There are two common types of pipets: *volumetric (or transfer) pipets* and *measuring pipets*, as shown in Fig. 4.11. Volumetric pipets come in specific sizes, such as 5 mL, 10 mL, 25 mL, and so on. Measuring pipets are used to measure volumes for which a volumetric pipet is not available. For example, we would use a measuring pipet as shown in Fig. 4.12 on page 139 to deliver 28.7 mL of 17.4 M acetic acid into a 500-mL volumetric flask and then add water to the mark to perform the dilution described above.

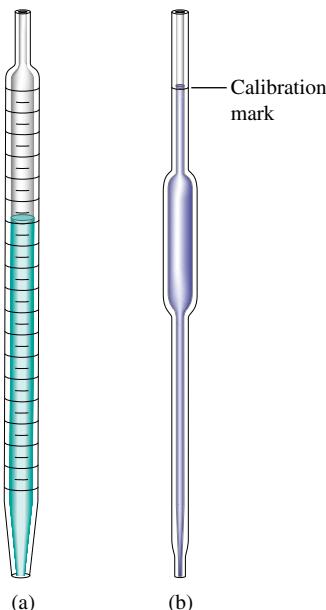


FIGURE 4.11

(a) A measuring pipet is graduated and can be used to measure various volumes of liquid accurately. (b) A volumetric (transfer) pipet is designed to measure one volume accurately. When filled to the mark, it delivers the volume indicated on the pipet.



CHEMICAL IMPACT

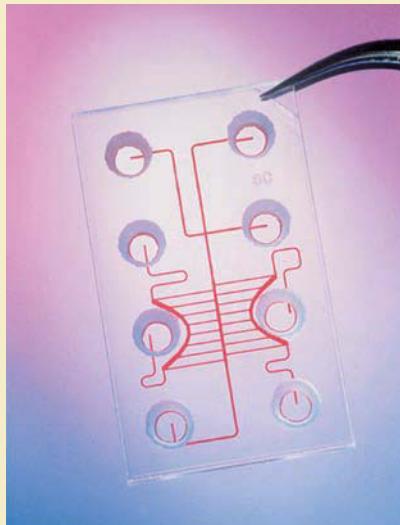
Tiny Laboratories

One of the major impacts of modern technology is to make things smaller. The best example is the computer. Calculations that 30 years ago required a machine the size of a large room now can be carried out on a hand-held calculator. This tendency toward miniaturization is also having a major impact on the science of chemical analysis. Using the techniques of computer chip makers, researchers are now constructing minuscule laboratories on the surface of a tiny chip made of silicon, glass, or plastic (see photo). Instead of electrons, 10^{-6} to 10^{-9} L of liquids moves between reaction chambers on the chip through tiny capillaries. The chips typically contain no moving parts. Instead of conventional pumps, the chip-based laboratories use voltage differences to move liquids that contain ions from one reaction chamber to another.

Microchip laboratories have many advantages. They require only tiny amounts of sample. This is especially advantageous for expensive, difficult-to-prepare materials or in cases such as criminal investigations, where only small amounts of evidence may exist. The chip laboratories also minimize contamination because they represent a “closed system” once the material has been introduced to the chip. In addition, the chips can be made to be disposable to prevent cross-contamination of different samples.

The chip laboratories present some difficulties not found in macroscopic laboratories. The main problem concerns the large surface area of the capillaries and reaction chambers relative to the sample volume. Molecules or biological cells in the sample solution encounter so much “wall” that they may undergo unwanted reactions with the wall materials. Glass seems to present the least of these problems, and the walls of silicon chip laboratories can be protected by formation of relatively inert silicon dioxide. Because plastic is inexpensive, it seems a good choice for disposable chips, but plastic also is the most reactive with the samples and the least durable of the available materials.

Caliper Technologies Corporation, of Palo Alto, California, is working toward creating a miniature chemistry laboratory about the size of a toaster that can be used with “plug-in” chip-based laboratories. Various chips would be furnished with the unit that would be appropriate for different types of analyses. The entire unit would be connected to a computer to collect and analyze the data. There is even the possibility that these “laboratories” could be used in the home to perform analyses such as blood sugar and blood cholesterol and to check for the presence of bacteria such as *E. coli* and many others. This would revolutionize the health care industry.



Plastic chips such as this one made by Caliper Technologies are being used to perform laboratory procedures traditionally done with test tubes.

Adapted from “The Incredible Shrinking Laboratory,” by Corinna Wu, as appeared in *Science News*, Vol. 154, August 15, 1998, p. 104.

Sample Exercise 4.7

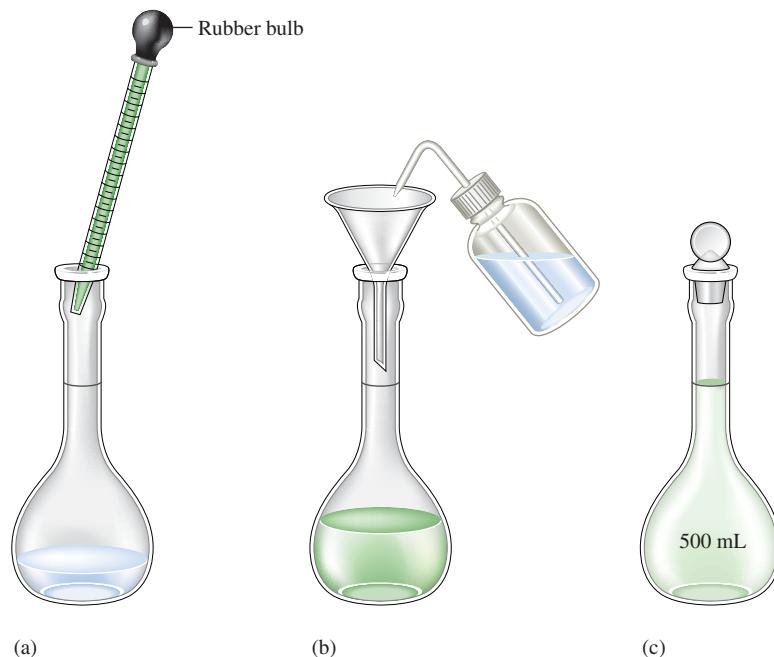
Concentration and Volume

What volume of 16 M sulfuric acid must be used to prepare 1.5 L of a 0.10 M H₂SO₄ solution?

Solution

We must first determine the moles of H₂SO₄ in 1.5 L of 0.10 M H₂SO₄:

$$1.5 \text{ L}_{\text{solution}} \times \frac{0.10 \text{ mol H}_2\text{SO}_4}{\text{L}_{\text{solution}}} = 0.15 \text{ mol H}_2\text{SO}_4$$

**FIGURE 4.12**

(a) A measuring pipet is used to transfer 28.7 mL of 17.4 M acetic acid solution to a volumetric flask. (b) Water is added to the flask to the calibration mark. (c) The resulting solution is 1.00 M acetic acid.

Next we must find the volume of 16 M H₂SO₄ that contains 0.15 mol H₂SO₄:

$$V \times \frac{16 \text{ mol H}_2\text{SO}_4}{\text{L solution}} = 0.15 \text{ mol H}_2\text{SO}_4$$

Solving for V gives

$$V = \frac{0.15 \text{ mol H}_2\text{SO}_4}{\frac{16 \text{ mol H}_2\text{SO}_4}{1 \text{ L solution}}} = 9.4 \times 10^{-3} \text{ L or } 9.4 \text{ mL solution}$$

In diluting an acid, “Do what you oughta, always add acid to water.”

Thus, to make 1.5 L of 0.10 M H₂SO₄ using 16 M H₂SO₄, we must take 9.4 mL of the concentrated acid and dilute it with water to 1.5 L. The correct way to do this is to add the 9.4 mL of acid to about 1 L of distilled water and then dilute to 1.5 L by adding more water.

See Exercises 4.29b and d and 4.30a, b, and d.

As noted earlier, the central idea in performing the calculations associated with dilutions is to recognize that the moles of solute are not changed by the dilution. Another way to express this condition is by the following equation:

$$M_1 V_1 = M_2 V_2$$

where M_1 and V_1 represent the molarity and volume of the original solution (before dilution) and M_2 and V_2 represent the molarity and volume of the diluted solution. This equation makes sense because

$$\begin{aligned} M_1 \times V_1 &= \text{mol solute before dilution} \\ &= \text{mol solute after dilution} = M_2 \times V_2 \end{aligned}$$

Repeat Sample Exercise 4.7 using the equation $M_1V_1 = M_2V_2$. Note that in doing so

$$M_1 = 16 \text{ M} \quad M_2 = 0.10 \text{ M} \quad V_2 = 1.5 \text{ L}$$

and V_1 is the unknown quantity sought. The equation $M_1V_1 = M_2V_2$ always holds for a dilution. This equation will be easy for you to remember if you understand where it comes from.

4.4 Types of Chemical Reactions

Although we have considered many reactions so far in this text, we have examined only a tiny fraction of the millions of possible chemical reactions. To make sense of all these reactions, we need some system for grouping reactions into classes. Although there are many different ways to do this, we will use the system most commonly used by practicing chemists:

Types of Solution Reactions

- Precipitation reactions
- Acid–base reactions
- Oxidation–reduction reactions

Virtually all reactions can be put into one of these classes. We will define and illustrate each type in the following sections.

4.5 Precipitation Reactions

When two solutions are mixed, an insoluble substance sometimes forms; that is, a solid forms and separates from the solution. Such a reaction is called a **precipitation reaction**, and the solid that forms is called a **precipitate**. For example, a precipitation reaction occurs when an aqueous solution of potassium chromate, $\text{K}_2\text{CrO}_4(aq)$, which is yellow, is added to a colorless aqueous solution containing barium nitrate, $\text{Ba}(\text{NO}_3)_2(aq)$. As shown in Fig. 4.13, when these solutions are mixed, a yellow solid forms. What is the equation that describes this chemical change? To write the equation, we must know the identities of the reactants and products. The reactants have already been described: $\text{K}_2\text{CrO}_4(aq)$ and $\text{Ba}(\text{NO}_3)_2(aq)$. Is there some way we can predict the identities of the products? In particular, what is the yellow solid?

The best way to predict the identity of this solid is to think carefully about what products are possible. To do this, we need to know what species are present in the solution after the two reactant solutions are mixed. First, let's think about the nature of each reactant solution. The designation $\text{Ba}(\text{NO}_3)_2(aq)$ means that barium nitrate (a white solid) has been dissolved in water. Notice that barium nitrate contains the Ba^{2+} and NO_3^- ions. *Remember: In virtually every case, when a solid containing ions dissolves in water, the ions separate and move around independently.* That is, $\text{Ba}(\text{NO}_3)_2(aq)$ does not contain $\text{Ba}(\text{NO}_3)_2$ units; it contains separated Ba^{2+} and NO_3^- ions. See Fig. 4.14(a).

Similarly, since solid potassium chromate contains the K^+ and CrO_4^{2-} ions, an aqueous solution of potassium chromate (which is prepared by dissolving solid K_2CrO_4 in water) contains these separated ions, as shown in Fig. 4.14(b).

We can represent the mixing of $\text{K}_2\text{CrO}_4(aq)$ and $\text{Ba}(\text{NO}_3)_2(aq)$ in two ways. First, we can write

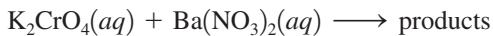


FIGURE 4.13

When yellow aqueous potassium chromate is added to a colorless barium nitrate solution, yellow barium chromate precipitates.

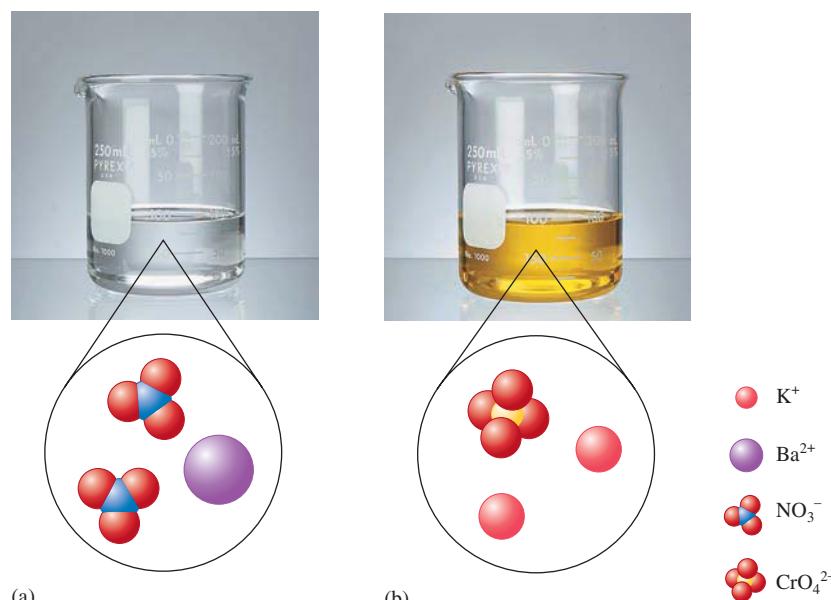
A *precipitation reaction* also can be called a *double displacement reaction*.



Visualization: Precipitation Reactions

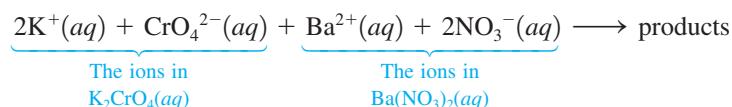
The quantitative aspects of precipitation reactions are covered in Chapter 15.

When ionic compounds dissolve in water, the resulting solution contains the separated ions.

**FIGURE 4.14**

Reactant solutions: (a) Ba(NO₃)₂(aq) and (b) K₂CrO₄(aq).

However, a much more accurate representation is

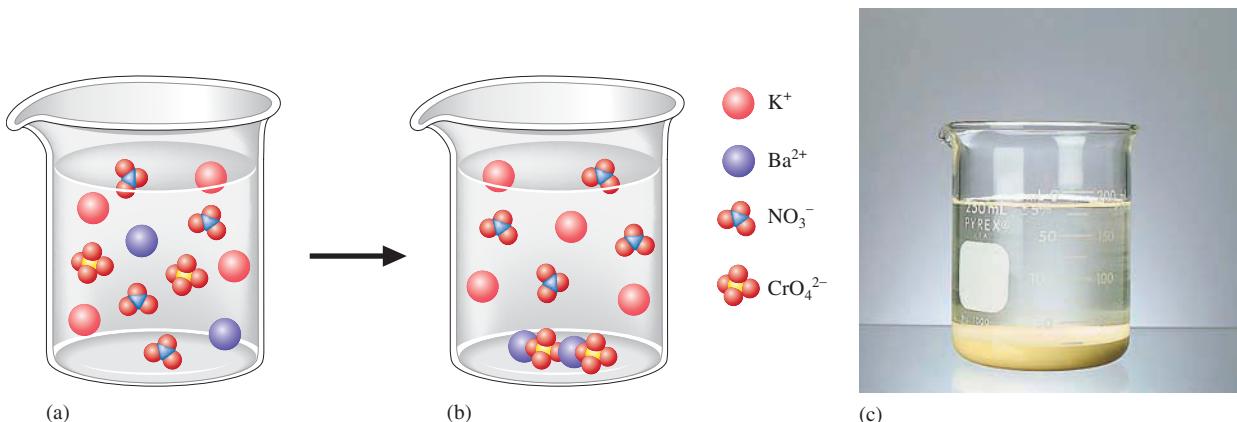


Thus the mixed solution contains the ions:



as illustrated in Fig. 4.15(a).

How can some or all of these ions combine to form a yellow solid? This is not an easy question to answer. In fact, predicting the products of a chemical reaction is one of the hardest things a beginning chemistry student is asked to do. Even an experienced chemist, when confronted with a new reaction, is often not sure what will happen. The chemist tries to think of the various possibilities, considers the likelihood of each

**FIGURE 4.15**

The reaction of K₂CrO₄(aq) and Ba(NO₃)₂(aq). (a) The molecular-level “picture” of the mixed solution before any reaction has occurred. (b) The molecular-level “picture” of the solution after the reaction has occurred to form BaCrO₄(s). Note: BaCrO₄(s) is not molecular. It actually contains Ba²⁺ and CrO₄²⁻ ions packed together in a lattice. (c) A photo of the solution after the reaction has occurred, showing the solid BaCrO₄ on the bottom.

possibility, and then makes a prediction (an educated guess). Only after identifying each product *experimentally* is the chemist sure what reaction has taken place. However, an educated guess is very useful because it provides a place to start. It tells us what kinds of products we are most likely to find. We already know some things that will help us predict the products of the above reaction.

- When ions form a solid compound, the compound must have a zero net charge. Thus the products of this reaction must contain *both anions and cations*. For example, K^+ and Ba^{2+} could not combine to form the solid, nor could CrO_4^{2-} and NO_3^- .
- Most ionic materials contain only two types of ions: one type of cation and one type of anion (for example, $NaCl$, KOH , Na_2SO_4 , K_2CrO_4 , $Co(NO_3)_2$, NH_4Cl , Na_2CO_3).

The possible combinations of a given cation and a given anion from the list of ions K^+ , CrO_4^{2-} , Ba^{2+} , and NO_3^- are

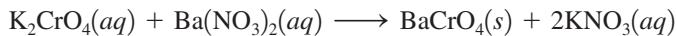


Which of these possibilities is most likely to represent the yellow solid? We know it's not K_2CrO_4 or $Ba(NO_3)_2$. They are the reactants. They were present (dissolved) in the separate solutions that were mixed. The only real possibilities for the solid that formed are



To decide which of these most likely represents the yellow solid, we need more facts. An experienced chemist knows that the K^+ ion and the NO_3^- ion are both colorless. Thus, if the solid is KNO_3 , it should be white, not yellow. On the other hand, the CrO_4^{2-} ion is yellow (note in Fig. 4.14 that $K_2CrO_4(aq)$ is yellow). Thus the yellow solid is almost certainly $BaCrO_4$. Further tests show that this is the case.

So far we have determined that one product of the reaction between $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$ is $BaCrO_4(s)$, but what happened to the K^+ and NO_3^- ions? The answer is that these ions are left dissolved in the solution; KNO_3 does not form a solid when the K^+ and NO_3^- ions are present in this much water. In other words, if we took solid KNO_3 and put it in the same quantity of water as is present in the mixed solution, it would dissolve. Thus, when we mix $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$, $BaCrO_4(s)$ forms, but KNO_3 is left behind in solution (we write it as $KNO_3(aq)$). Thus the overall equation for this precipitation reaction using the formulas of the reactants and products is

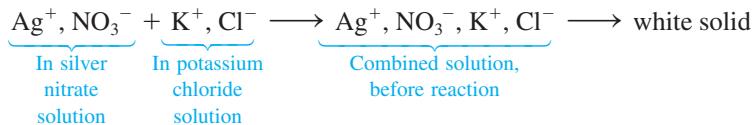


As long as water is present, the KNO_3 remains dissolved as separated ions. (See Fig. 4.15 to help visualize what is happening in this reaction. Note the solid $BaCrO_4$ on the bottom of the container, while the K^+ and NO_3^- ions remain dispersed in the solution.) If we removed the solid $BaCrO_4$ and then evaporated the water, white solid KNO_3 would be obtained; the K^+ and NO_3^- ions would assemble themselves into solid KNO_3 when the water is removed.

Now let's consider another example. When an aqueous solution of silver nitrate is added to an aqueous solution of potassium chloride, a white precipitate forms, as shown in Fig. 4.16. We can represent what we know so far as



Remembering that when ionic substances dissolve in water, the ions separate, we can write

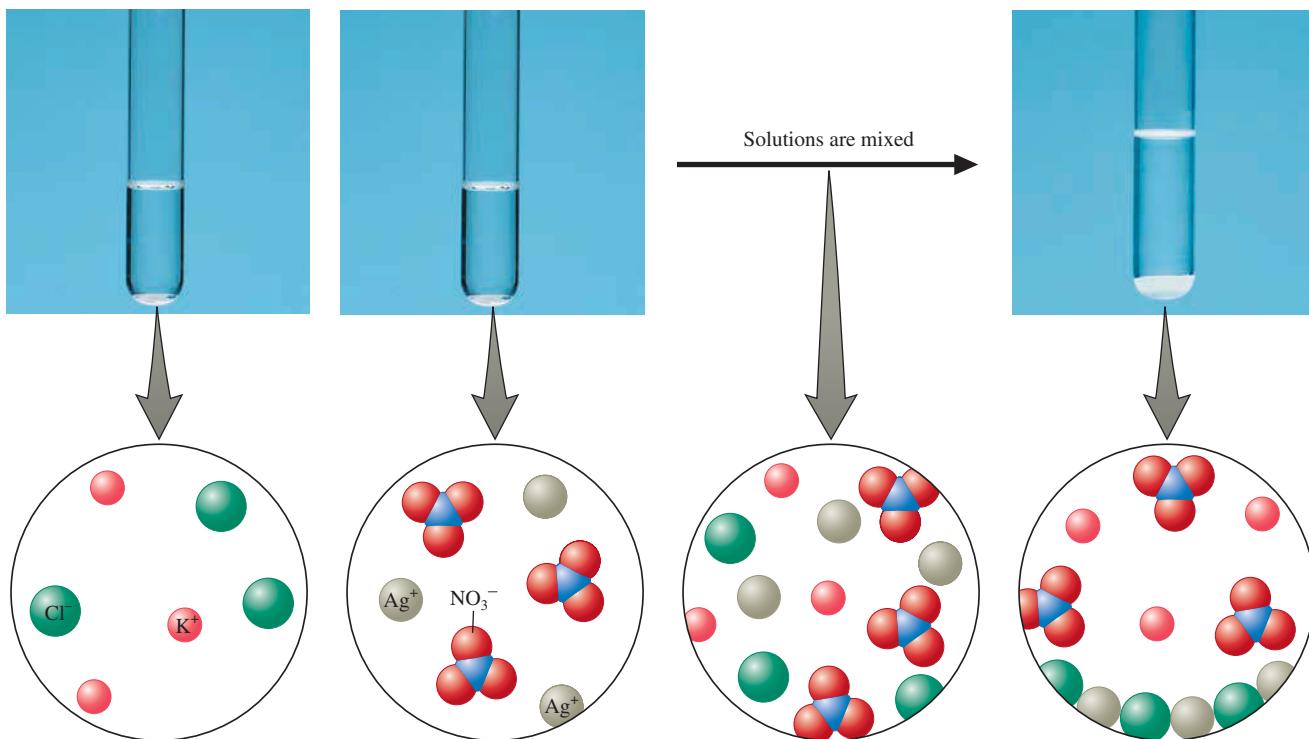


Since we know the white solid must contain both positive and negative ions, the possible compounds that can be assembled from this collection of ions are



FIGURE 4.16

Precipitation of silver chloride by mixing solutions of silver nitrate and potassium chloride. The K^+ and NO_3^- ions remain in solution.

**FIGURE 4.17**

Photos and accompanying molecular-level representations illustrating the reaction of $\text{KCl}(aq)$ with $\text{AgNO}_3(aq)$ to form $\text{AgCl}(s)$. Note that it is not possible to have a photo of the mixed solution before the reaction occurs, because it is an imaginary step that we use to help visualize the reaction. Actually, the reaction occurs immediately when the two solutions are mixed.



Visualization: Reactions of Silver I

Since AgNO_3 and KCl are the substances dissolved in the two reactant solutions, we know that they do not represent the white solid product. Therefore, the only real possibilities are



From the first example considered, we know that KNO_3 is quite soluble in water. Thus solid KNO_3 will not form when the reactant solids are mixed. The product must be $\text{AgCl}(s)$ (which can be proved by experiment to be true). The overall equation for the reaction now can be written

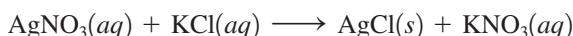


Figure 4.17 shows the result of mixing aqueous solutions of AgNO_3 and KCl , including a microscopic visualization of the reaction.

Notice that in these two examples we had to apply both concepts (solids must have a zero net charge) and facts (KNO_3 is very soluble in water, CrO_4^{2-} is yellow, and so on). Doing chemistry requires both understanding ideas and remembering key information. Predicting the identity of the solid product in a precipitation reaction requires knowledge of the solubilities of common ionic substances. As an aid in predicting the products of precipitation reactions, some simple solubility rules are given in Table 4.1. You should memorize these rules.

The phrase *slightly soluble* used in the solubility rules in Table 4.1 means that the tiny amount of solid that dissolves is not noticeable. The solid appears to be insoluble to the naked eye. Thus the terms *insoluble* and *slightly soluble* are often used interchangeably.

Note that the information in Table 4.1 allows us to predict that AgCl is the white solid formed when solutions of AgNO_3 and KCl are mixed. Rules 1 and 2 indicate that KNO_3 is soluble, and Rule 3 states that AgCl is insoluble.

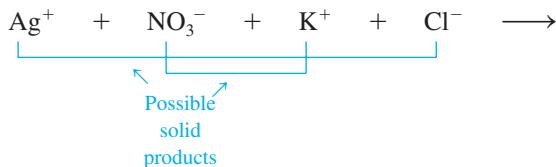


Visualization: Solubility Rules

TABLE 4.1 Simple Rules for the Solubility of Salts in Water

1. Most nitrate (NO_3^-) salts are soluble.
2. Most salts containing the alkali metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Rb^+) and the ammonium ion (NH_4^+) are soluble.
3. Most chloride, bromide, and iodide salts are soluble. Notable exceptions are salts containing the ions Ag^+ , Pb^{2+} , and Hg_2^{2+} .
4. Most sulfate salts are soluble. Notable exceptions are BaSO_4 , PbSO_4 , Hg_2SO_4 , and CaSO_4 .
5. Most hydroxide salts are only slightly soluble. The important soluble hydroxides are NaOH and KOH . The compounds $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and $\text{Ca}(\text{OH})_2$ are marginally soluble.
6. Most sulfide (S^{2-}), carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), and phosphate (PO_4^{3-}) salts are only slightly soluble.

When solutions containing ionic substances are mixed, it will be helpful in determining the products if you think in terms of *ion interchange*. For example, in the preceding discussion we considered the results of mixing $\text{AgNO}_3(aq)$ and $\text{KCl}(aq)$. In determining the products, we took the cation from one reactant and combined it with the anion of the other reactant:



The solubility rules in Table 4.1 allow us to predict whether either product forms as a solid.

The key to dealing with the chemistry of an aqueous solution is first to *focus on the actual components of the solution before any reaction occurs* and then to figure out how these components will react with each other. Sample Exercise 4.8 illustrates this process for three different reactions.

Sample Exercise 4.8

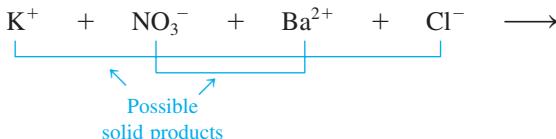
Predicting Reaction Products

Using the solubility rules in Table 4.1, predict what will happen when the following pairs of solutions are mixed.

- $\text{KNO}_3(aq)$ and $\text{BaCl}_2(aq)$
- $\text{Na}_2\text{SO}_4(aq)$ and $\text{Pb}(\text{NO}_3)_2(aq)$
- $\text{KOH}(aq)$ and $\text{Fe}(\text{NO}_3)_3(aq)$

Solution

- The formula $\text{KNO}_3(aq)$ represents an aqueous solution obtained by dissolving solid KNO_3 in water to form a solution containing the hydrated ions $\text{K}^+(aq)$ and $\text{NO}_3^-(aq)$. Likewise, $\text{BaCl}_2(aq)$ represents a solution formed by dissolving solid BaCl_2 in water to produce $\text{Ba}^{2+}(aq)$ and $\text{Cl}^-(aq)$. When these two solutions are mixed, the resulting solution contains the ions K^+ , NO_3^- , Ba^{2+} , and Cl^- . All ions are hydrated, but the *(aq)* is omitted for simplicity. To look for possible solid products, combine the cation from one reactant with the anion from the other:



Lead sulfate is a white solid.



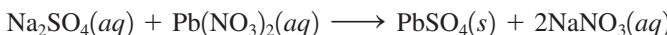
Solid Fe(OH)_3 forms when aqueous KOH and $\text{Fe(NO}_3)_3$ are mixed.

Note from Table 4.1 that the rules predict that both KCl and $\text{Ba}(\text{NO}_3)_2$ are soluble in water. Thus no precipitate forms when $\text{KNO}_3(aq)$ and $\text{BaCl}_2(aq)$ are mixed. All the ions remain dissolved in solution. No chemical reaction occurs.

- b. Using the same procedures as in part a, we find that the ions present in the combined solution before any reaction occurs are Na^+ , SO_4^{2-} , Pb^{2+} , and NO_3^- . The possible salts that could form precipitates are



The compound NaNO_3 is soluble, but PbSO_4 is insoluble (see Rule 4 in Table 4.1). When these solutions are mixed, PbSO_4 will precipitate from the solution. The balanced equation is



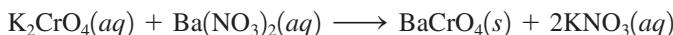
- c. The combined solution (before any reaction occurs) contains the ions K^+ , OH^- , Fe^{3+} , and NO_3^- . The salts that might precipitate are KNO_3 and Fe(OH)_3 . The solubility rules in Table 4.1 indicate that both K^+ and NO_3^- salts are soluble. However, Fe(OH)_3 is only slightly soluble (Rule 5) and hence will precipitate. The balanced equation is



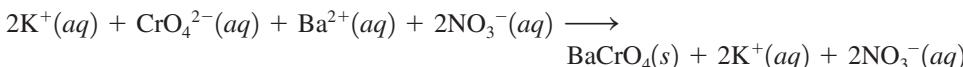
See Exercises 4.37 and 4.38.

4.6 Describing Reactions in Solution

In this section we will consider the types of equations used to represent reactions in solution. For example, when we mix aqueous potassium chromate with aqueous barium nitrate, a reaction occurs to form a precipitate (BaCrO_4) and dissolved potassium nitrate. So far we have written the overall or **formula equation** for this reaction:

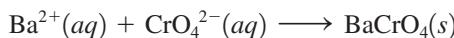


Although the formula equation shows the reactants and products of the reaction, it does not give a correct picture of what actually occurs in solution. As we have seen, aqueous solutions of potassium chromate, barium nitrate, and potassium nitrate contain individual ions, not collections of ions, as implied by the formula equation. Thus the **complete ionic equation**



better represents the actual forms of the reactants and products in solution. *In a complete ionic equation, all substances that are strong electrolytes are represented as ions.*

The complete ionic equation reveals that only some of the ions participate in the reaction. The K^+ and NO_3^- ions are present in solution both before and after the reaction. The ions that do not participate directly in the reaction are called **spectator ions**. The ions that participate in this reaction are the Ba^{2+} and CrO_4^{2-} ions, which combine to form solid BaCrO_4 :



This equation, called the **net ionic equation**, includes only those solution components directly involved in the reaction. Chemists usually write the net ionic equation for a reaction in solution because it gives the actual forms of the reactants and products and includes only the species that undergo a change.

A strong electrolyte is a substance that completely breaks apart into ions when dissolved in water.

Net ionic equations include only those components that undergo changes in the reaction.

Three Types of Equations Are Used to Describe Reactions in Solution

- The **formula equation** gives the overall reaction stoichiometry but not necessarily the actual forms of the reactants and products in solution.
- The **complete ionic equation** represents as ions all reactants and products that are strong electrolytes.
- The **net ionic equation** includes only those solution components undergoing a change. Spectator ions are not included.

Sample Exercise 4.9

Writing Equations for Reactions

For each of the following reactions, write the formula equation, the complete ionic equation, and the net ionic equation.

- Aqueous potassium chloride is added to aqueous silver nitrate to form a silver chloride precipitate plus aqueous potassium nitrate.
- Aqueous potassium hydroxide is mixed with aqueous iron(III) nitrate to form a precipitate of iron(III) hydroxide and aqueous potassium nitrate.

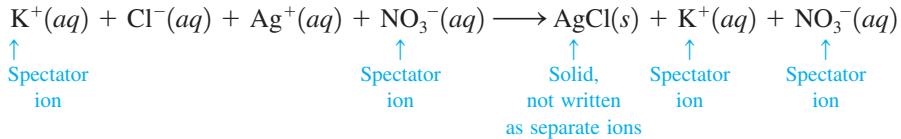
Solution

a. Formula Equation

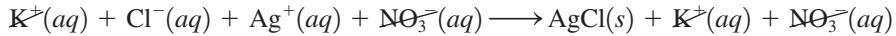


Complete Ionic Equation

(Remember: Any ionic compound dissolved in water will be present as the separated ions.)

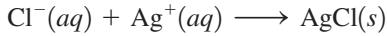


Cancelling the spectator ions



gives the following net ionic equation.

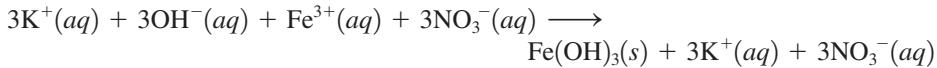
Net Ionic Equation



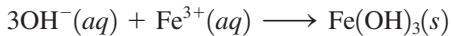
b. Formula Equation



Complete Ionic Equation



Net Ionic Equation



See Exercises 4.39 through 4.44.

4.7 Stoichiometry of Precipitation Reactions

In Chapter 3 we covered the principles of chemical stoichiometry: the procedures for calculating quantities of reactants and products involved in a chemical reaction. Recall that in performing these calculations we first convert all quantities to moles and then use the coefficients of the balanced equation to assemble the appropriate mole ratios. In cases where reactants are mixed we must determine which reactant is limiting, since the reactant that is consumed first will limit the amounts of products formed. *These same principles apply to reactions that take place in solutions.* However, two points about solution reactions need special emphasis. The first is that it is sometimes difficult to tell immediately what reaction will occur when two solutions are mixed. Usually we must do some thinking about the various possibilities and then decide what probably will happen. The first step in this process *always* should be to write down the species that are actually present in the solution, as we did in Section 4.5. The second special point about solution reactions is that to obtain the moles of reactants we must use the volume of the solution and its molarity. This procedure was covered in Section 4.3.

We will introduce stoichiometric calculations for reactions in solution in Sample Exercise 4.10.

Sample Exercise 4.10

Determining the Mass of Product Formed

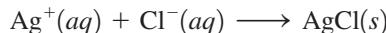
Calculate the mass of solid NaCl that must be added to 1.50 L of a 0.100 M AgNO₃ solution to precipitate all the Ag⁺ ions in the form of AgCl.

Solution

When added to the AgNO₃ solution (which contains Ag⁺ and NO₃⁻ ions), the solid NaCl dissolves to yield Na⁺ and Cl⁻ ions. Thus the mixed solution contains the ions



Note from Table 4.1 that NaNO₃ is soluble and AgCl is insoluble. Therefore, solid AgCl forms according to the following net ionic equation:



In this case we must add enough Cl⁻ ions to react with all the Ag⁺ ions present. Thus we must calculate the moles of Ag⁺ ions present in 1.50 L of a 0.100 M AgNO₃ solution (remember that a 0.100 M AgNO₃ solution contains 0.100 M Ag⁺ ions and 0.100 M NO₃⁻ ions):

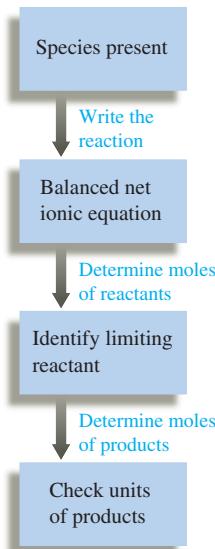
$$1.50 \text{ L} \times \frac{0.100 \text{ mol Ag}^+}{\text{L}} = 0.150 \text{ mol Ag}^+$$

Because Ag⁺ and Cl⁻ react in a 1:1 ratio, 0.150 mol Cl⁻ ions and thus 0.150 mol NaCl are required. We calculate the mass of NaCl required as follows:

$$0.150 \text{ mol NaCl} \times \frac{58.45 \text{ g NaCl}}{\text{mol NaCl}} = 8.77 \text{ g NaCl}$$

See Exercise 4.47.

Notice from Sample Exercise 4.10 that the procedures for doing stoichiometric calculations for solution reactions are very similar to those for other types of reactions. It is useful to think in terms of the following steps for reactions in solution.



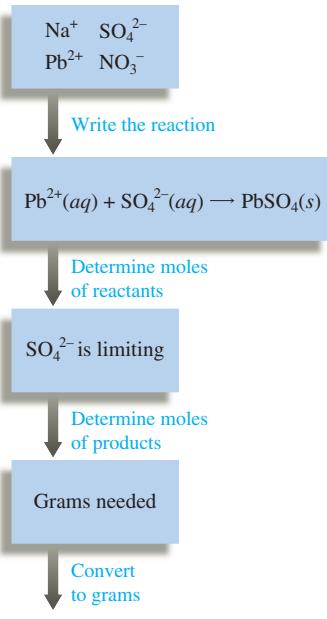
Solving Stoichiometry Problems for Reactions in Solution

- 1 Identify the species present in the combined solution, and determine what reaction occurs.
- 2 Write the balanced net ionic equation for the reaction.
- 3 Calculate the moles of reactants.
- 4 Determine which reactant is limiting.
- 5 Calculate the moles of product or products, as required.
- 6 Convert to grams or other units, as required.

Sample Exercise 4.11

Determining the Mass of Product Formed

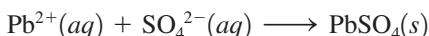
When aqueous solutions of Na_2SO_4 and $\text{Pb}(\text{NO}_3)_2$ are mixed, PbSO_4 precipitates. Calculate the mass of PbSO_4 formed when 1.25 L of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ and 2.00 L of 0.0250 M Na_2SO_4 are mixed.



Solution

→ 1 *Identify the species present in the combined solution, and determine what reaction occurs.* When the aqueous solutions of Na_2SO_4 (containing Na^+ and SO_4^{2-} ions) and $\text{Pb}(\text{NO}_3)_2$ (containing Pb^{2+} and NO_3^- ions) are mixed, the resulting solution contains the ions Na^+ , SO_4^{2-} , Pb^{2+} , and NO_3^- . Since NaNO_3 is soluble and PbSO_4 is insoluble (see Rule 4 in Table 4.1), solid PbSO_4 will form.

→ 2 *Write the balanced net ionic equation for the reaction.* The net ionic equation is



→ 3 *Calculate the moles of reactants.* Since 0.0500 M $\text{Pb}(\text{NO}_3)_2$ contains 0.0500 M Pb^{2+} ions, we can calculate the moles of Pb^{2+} ions in 1.25 L of this solution as follows:

$$1.25 \text{ L} \times \frac{0.0500 \text{ mol Pb}^{2+}}{\text{L}} = 0.0625 \text{ mol Pb}^{2+}$$

The 0.0250 M Na_2SO_4 solution contains 0.0250 M SO_4^{2-} ions, and the number of moles of SO_4^{2-} ions in 2.00 L of this solution is

$$2.00 \text{ L} \times \frac{0.0250 \text{ mol SO}_4^{2-}}{\text{L}} = 0.0500 \text{ mol SO}_4^{2-}$$

→ 4 *Determine which reactant is limiting.* Because Pb^{2+} and SO_4^{2-} react in a 1:1 ratio, the amount of SO_4^{2-} will be limiting (0.0500 mol SO_4^{2-} is less than 0.0625 mol Pb^{2+}).

→ 5 *Calculate the moles of product.* Since the Pb^{2+} ions are present in excess, only 0.0500 mol of solid PbSO_4 will be formed.

→ 6 *Convert to grams of product.* The mass of PbSO_4 formed can be calculated using the molar mass of PbSO_4 (303.3 g/mol):

$$0.0500 \text{ mol PbSO}_4 \times \frac{303.3 \text{ g PbSO}_4}{1 \text{ mol PbSO}_4} = 15.2 \text{ g PbSO}_4$$

See Exercises 4.49 and 4.50.

4.8 Acid–Base Reactions



Visualization: Proton Transfer

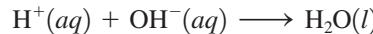
The Brønsted–Lowry concept of acids and bases will be discussed in detail in Chapter 14.

Earlier in this chapter we considered Arrhenius's concept of acids and bases: An acid is a substance that produces H^+ ions when dissolved in water, and a base is a substance that produces OH^- ions. Although these ideas are fundamentally correct, it is convenient to have a more general definition of a base, which includes substances that do not contain OH^- ions. Such a definition was provided by Johannes N. Brønsted (1879–1947) and Thomas M. Lowry (1874–1936), who defined acids and bases as follows:

An **acid** is a proton donor.

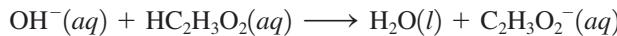
A **base** is a proton acceptor.

How do we know when to expect an acid–base reaction? One of the most difficult tasks for someone inexperienced in chemistry is to predict what reaction might occur when two solutions are mixed. With precipitation reactions, we found that the best way to deal with this problem is to focus on the species actually present in the mixed solution. This idea also applies to acid–base reactions. For example, when an aqueous solution of hydrogen chloride (HCl) is mixed with an aqueous solution of sodium hydroxide (NaOH), the combined solution contains the ions H^+ , Cl^- , Na^+ , and OH^- . The separated ions are present because HCl is a strong acid and NaOH is a strong base. How can we predict what reaction occurs, if any? First, will NaCl precipitate? From Table 4.1 we can see that NaCl is soluble in water and thus will not precipitate. Therefore, the Na^+ and Cl^- ions are spectator ions. On the other hand, because water is a nonelectrolyte, large quantities of H^+ and OH^- ions cannot coexist in solution. They react to form H_2O molecules:



This is the net ionic equation for the reaction that occurs when aqueous solutions of HCl and NaOH are mixed.

Next, consider mixing an aqueous solution of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) with an aqueous solution of potassium hydroxide (KOH). In our earlier discussion of conductivity we said that an aqueous solution of acetic acid is a weak electrolyte. This tells us that acetic acid does not dissociate into ions to any great extent. In fact, in 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ approximately 99% of the $\text{HC}_2\text{H}_3\text{O}_2$ molecules remain undissociated. However, when solid KOH is dissolved in water, it dissociates completely to produce K^+ and OH^- ions. Therefore, in the solution formed by mixing aqueous solutions of $\text{HC}_2\text{H}_3\text{O}_2$ and KOH, *before any reaction occurs*, the principal species are $\text{HC}_2\text{H}_3\text{O}_2$, K^+ , and OH^- . What reaction will occur? A possible precipitation reaction could occur between K^+ and OH^- . However, we know that KOH is soluble, so precipitation does not occur. Another possibility is a reaction involving the hydroxide ion (a proton acceptor) and some proton donor. Is there a source of protons in the solution? The answer is yes—the $\text{HC}_2\text{H}_3\text{O}_2$ molecules. The OH^- ion has such a strong affinity for protons that it can strip them from the $\text{HC}_2\text{H}_3\text{O}_2$ molecules. The net ionic equation for this reaction is

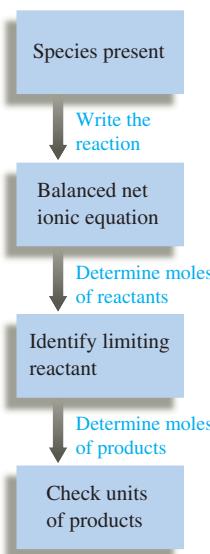


This reaction illustrates a very important general principle: *The hydroxide ion is such a strong base that for purposes of stoichiometric calculations it can be assumed to react completely with any weak acid that we will encounter.* Of course, OH^- ions also react completely with the H^+ ions in solutions of strong acids.

We will now deal with the stoichiometry of acid–base reactions in aqueous solutions. The procedure is fundamentally the same as that used previously for precipitation reactions.

Performing Calculations for Acid–Base Reactions

- 1 List the species present in the combined solution *before any reaction occurs*, and decide what reaction will occur.



- 2 Write the balanced net ionic equation for this reaction.
- 3 Calculate the moles of reactants. For reactions in solution, use the volumes of the original solutions and their molarities.
- 4 Determine the limiting reactant where appropriate.
- 5 Calculate the moles of the required reactant or product.
- 6 Convert to grams or volume (of solution), as required.

An acid–base reaction is often called a **neutralization reaction**. When just enough base is added to react exactly with the acid in a solution, we say the acid has been *neutralized*.

Sample Exercise 4.12

Neutralization Reactions I

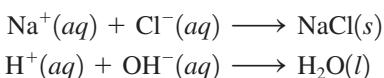
What volume of a 0.100 *M* HCl solution is needed to neutralize 25.0 mL of 0.350 *M* NaOH?

Solution

- 1 List the species present in the combined solution before any reaction occurs, and decide what reaction will occur. The species present in the mixed solutions before any reaction occurs are

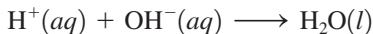


What reaction will occur? The two possibilities are



Since we know that NaCl is soluble, the first reaction does not take place (Na^+ and Cl^- are spectator ions). However, as we have seen before, the reaction of the H^+ and OH^- ions to form H_2O does occur.

- 2 Write the balanced net ionic equation. The balanced net ionic equation for this reaction is



- 3 Calculate the moles of reactants. The number of moles of OH^- ions in the 25.0-mL sample of 0.350 *M* NaOH is

$$25.0 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.350 \text{ mol OH}^-}{\text{L NaOH}} = 8.75 \times 10^{-3} \text{ mol OH}^-$$

- 4 Determine the limiting reactant. This problem requires the addition of just enough H^+ ions to react exactly with the OH^- ions present. Thus we need not be concerned with determining a limiting reactant.

- 5 Calculate the moles of reactant needed. Since H^+ and OH^- ions react in a 1:1 ratio, 8.75×10^{-3} mol H^+ ions is required to neutralize the OH^- ions present.

- 6 Convert to volume required. The volume V of 0.100 *M* HCl required to furnish 8.75×10^{-3} mol H^+ ions can be calculated as follows:

$$V \times \frac{0.100 \text{ mol H}^+}{\text{L}} = 8.75 \times 10^{-3} \text{ mol H}^+$$

Solving for V gives

$$V = \frac{8.75 \times 10^{-3} \text{ mol H}^+}{\frac{0.100 \text{ mol H}^+}{\text{L}}} = 8.75 \times 10^{-2} \text{ L}$$

Thus 8.75×10^{-2} L (87.5 mL) of 0.100 M HCl is required to neutralize 25.0 mL of 0.350 M NaOH.

See Exercises 4.59 and 4.60.

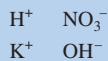
Sample Exercise 4.13

Neutralization Reactions II

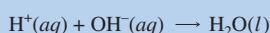
In a certain experiment, 28.0 mL of 0.250 M HNO₃ and 53.0 mL of 0.320 M KOH are mixed. Calculate the amount of water formed in the resulting reaction. What is the concentration of H⁺ or OH⁻ ions in excess after the reaction goes to completion?

Solution

The species available for reaction are



Write the reaction



Find moles H⁺, OH⁻

Limiting reactant is H⁺

Find moles OH⁻ that react

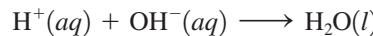
Concentration of OH⁻ needed

Find excess OH⁻ concentration

0.123 M OH⁻



Since KNO₃ is soluble, K⁺ and NO₃⁻ are spectator ions, so the net ionic equation is



We next compute the amounts of H⁺ and OH⁻ ions present:

$$28.0 \text{ mL HNO}_3 \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol H}^+}{1 \text{ L HNO}_3} = 7.00 \times 10^{-3} \text{ mol H}^+$$

$$53.0 \text{ mL KOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.320 \text{ mol OH}^-}{1 \text{ L KOH}} = 1.70 \times 10^{-2} \text{ mol OH}^-$$

Since H⁺ and OH⁻ react in a 1:1 ratio, the limiting reactant is H⁺. This means that 7.00×10^{-3} mol H⁺ ions will react with 7.00×10^{-3} mol OH⁻ ions to form 7.00×10^{-3} mol H₂O.

The amount of OH⁻ ions in excess is obtained from the following difference:

$$\text{Original amount} - \text{amount consumed} = \text{amount in excess}$$

$$1.70 \times 10^{-2} \text{ mol OH}^- - 7.00 \times 10^{-3} \text{ mol OH}^- = 1.00 \times 10^{-2} \text{ mol OH}^-$$

The volume of the combined solution is the sum of the individual volumes:

$$\text{Original volume of HNO}_3 + \text{original volume of KOH} = \text{total volume}$$

$$28.0 \text{ mL} + 53.0 \text{ mL} = 81.0 \text{ mL} = 8.10 \times 10^{-2} \text{ L}$$

Thus the molarity of OH⁻ ions in excess is

$$\frac{\text{mol OH}^-}{\text{L solution}} = \frac{1.00 \times 10^{-2} \text{ mol OH}^-}{8.10 \times 10^{-2} \text{ L}} = 0.123 \text{ M OH}^-$$

See Exercises 4.61 and 4.62.

Acid–Base Titrations

Volumetric analysis is a technique for determining the amount of a certain substance by doing a titration. A **titration** involves delivery (from a buret) of a measured volume of a solution of known concentration (the *titrant*) into a solution containing the substance being analyzed (the *analyte*). The titrant contains a substance that reacts in a known manner with the analyte. The point in the titration where enough titrant has been added to react exactly with the analyte is called the **equivalence point** or the **stoichiometric point**. This point is often marked by an **indicator**, a substance added at the beginning of the titration that changes color at (or very near) the equivalence point. The point where the indicator



Visualization: Neutralization of a Strong Acid by a Strong Base

Ideally, the endpoint and stoichiometric point should coincide.



Visualization: Titrations

actually changes color is called the **endpoint** of the titration. The goal is to choose an indicator such that the endpoint (where the indicator changes color) occurs exactly at the equivalence point (where just enough titrant has been added to react with all the analyte).

The following three requirements must be met for a titration to be successful:

1. The exact reaction between titrant and analyte must be known (and rapid).
2. The stoichiometric (equivalence) point must be marked accurately.
3. The volume of titrant required to reach the stoichiometric point must be known accurately.

When the analyte is a base or an acid, the required titrant is a strong acid or strong base, respectively. This procedure is called an *acid–base titration*. An indicator very commonly used for acid–base titrations is phenolphthalein, which is colorless in an acidic solution and pink in a basic solution. Thus, when an acid is titrated with a base, the phenolphthalein remains colorless until after the acid is consumed and the first drop of excess base is added. In this case, the endpoint (the solution changes from colorless to pink) occurs approximately one drop of base beyond the stoichiometric point. This type of titration is illustrated in the three photos in Fig. 4.18.

We will deal with the acid–base titrations only briefly here but will return to the topic of titrations and indicators in more detail in Chapter 15. The titration of an acid with a standard solution containing hydroxide ions is described in Sample Exercise 4.15. In Sample Exercise 4.14 we show how to determine accurately the concentration of a sodium hydroxide solution. This procedure is called *standardizing the solution*.

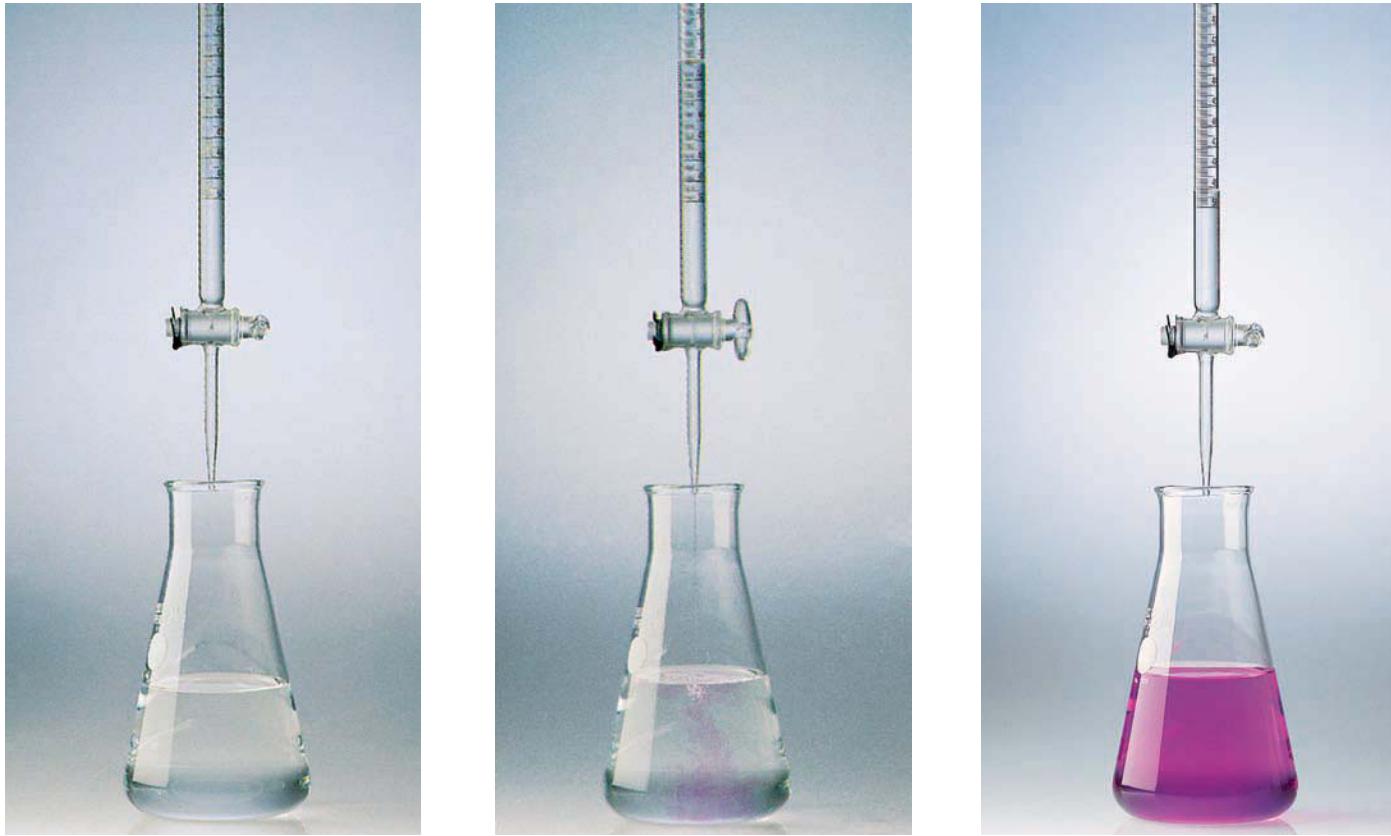
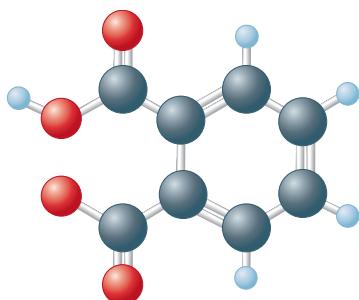


FIGURE 4.18

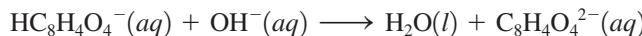
The titration of an acid with a base. (a) The titrant (the base) is in the buret, and the flask contains the acid solution along with a small amount of indicator. (b) As base is added drop by drop to the acid solution in the flask during the titration, the indicator changes color, but the color disappears on mixing. (c) The stoichiometric (equivalence) point is marked by a permanent indicator color change. The volume of base added is the difference between the final and initial buret readings.

Sample Exercise 4.14**Neutralization Titration**

A student carries out an experiment to standardize (determine the exact concentration of) a sodium hydroxide solution. To do this, the student weighs out a 1.3009-g sample of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, often abbreviated KHP). KHP (molar mass 204.22 g/mol) has one acidic hydrogen. The student dissolves the KHP in distilled water, adds phenolphthalein as an indicator, and titrates the resulting solution with the sodium hydroxide solution to the phenolphthalein endpoint. The difference between the final and initial buret readings indicates that 41.20 mL of the sodium hydroxide solution is required to react exactly with the 1.3009 g KHP. Calculate the concentration of the sodium hydroxide solution.

Solution

Aqueous sodium hydroxide contains the Na^+ and OH^- ions, and $\text{KHC}_8\text{H}_4\text{O}_4$ dissolves in water to give the K^+ and $\text{HC}_8\text{H}_4\text{O}_4^-$ ions. As the titration proceeds, the mixed solution contains the following ions: K^+ , $\text{HC}_8\text{H}_4\text{O}_4^-$, Na^+ , and OH^- . The OH^- will remove an H^+ from the $\text{HC}_8\text{H}_4\text{O}_4^-$ to give the following net ionic reaction:



Since the reaction exhibits 1:1 stoichiometry, we know that 41.20 mL of the sodium hydroxide solution must contain exactly the same number of moles of OH^- as there are moles of $\text{HC}_8\text{H}_4\text{O}_4^-$ in 1.3009 g $\text{KHC}_8\text{H}_4\text{O}_4$.

We calculate the moles of $\text{KHC}_8\text{H}_4\text{O}_4$ in the usual way:

$$1.3009 \text{ g } \text{KHC}_8\text{H}_4\text{O}_4 \times \frac{1 \text{ mol } \text{KHC}_8\text{H}_4\text{O}_4}{204.22 \text{ g } \text{KHC}_8\text{H}_4\text{O}_4} = 6.3701 \times 10^{-3} \text{ mol } \text{KHC}_8\text{H}_4\text{O}_4$$

This means that 6.3701×10^{-3} mol OH^- must be added to react with the 6.3701×10^{-3} mol $\text{HC}_8\text{H}_4\text{O}_4^-$. Thus 41.20 mL (4.120×10^{-2} L) of the sodium hydroxide solution must contain 6.3701×10^{-3} mol OH^- (and Na^+), and the concentration of the sodium hydroxide solution is

$$\begin{aligned} \text{Molarity of NaOH} &= \frac{\text{mol NaOH}}{\text{L solution}} = \frac{6.3701 \times 10^{-3} \text{ mol NaOH}}{4.120 \times 10^{-2} \text{ L}} \\ &= 0.1546 \text{ M} \end{aligned}$$

This standard sodium hydroxide solution can now be used in other experiments (see Sample Exercise 4.15).

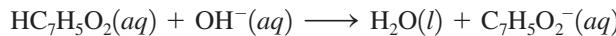
See Exercises 4.63 and 4.66.

Sample Exercise 4.15**Neutralization Analysis**

An environmental chemist analyzed the effluent (the released waste material) from an industrial process known to produce the compounds carbon tetrachloride (CCl_4) and benzoic acid ($\text{HC}_7\text{H}_5\text{O}_2$), a weak acid that has one acidic hydrogen atom per molecule. A sample of this effluent weighing 0.3518 g was shaken with water, and the resulting aqueous solution required 10.59 mL of 0.1546 M NaOH for neutralization. Calculate the mass percent of $\text{HC}_7\text{H}_5\text{O}_2$ in the original sample.

Solution

In this case, the sample was a mixture containing CCl_4 and $\text{HC}_7\text{H}_5\text{O}_2$, and it was titrated with OH^- ions. Clearly, CCl_4 is not an acid (it contains no hydrogen atoms), so we can assume it does not react with OH^- ions. However, $\text{HC}_7\text{H}_5\text{O}_2$ is an acid that donates one H^+ ion per molecule to react with an OH^- ion as follows:



Although $\text{HC}_7\text{H}_5\text{O}_2$ is a weak acid, the OH^- ion is such a strong base that we can assume that each OH^- ion added will react with a $\text{HC}_7\text{H}_5\text{O}_2$ molecule until all the benzoic acid is consumed.

We must first determine the number of moles of OH^- ions required to react with all the $\text{HC}_7\text{H}_5\text{O}_2$:

$$10.59 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1546 \text{ mol OH}^-}{1 \text{ L NaOH}} = 1.637 \times 10^{-3} \text{ mol OH}^-$$

This number is also the number of moles of $\text{HC}_7\text{H}_5\text{O}_2$ present. The number of grams of the acid is calculated using its molar mass (122.12 g/mol):

$$1.637 \times 10^{-3} \text{ mol } \text{HC}_7\text{H}_5\text{O}_2 \times \frac{122.12 \text{ g } \text{HC}_7\text{H}_5\text{O}_2}{1 \text{ mol } \text{HC}_7\text{H}_5\text{O}_2} = 0.1999 \text{ g } \text{HC}_7\text{H}_5\text{O}_2$$

The mass percent of $\text{HC}_7\text{H}_5\text{O}_2$ in the original sample is

$$\frac{0.1999 \text{ g}}{0.3518 \text{ g}} \times 100 = 56.82\%$$

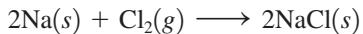
See Exercise 4.65.

The first step in the analysis of a complex solution is to write down the components and focus on the chemistry of each one. When a strong electrolyte is present, write it as separated ions.

In doing problems involving titrations, you must first decide what reaction is occurring. Sometimes this seems difficult because the titration solution contains several components. *The key to success is to first write down all the components in the solution and focus on the chemistry of each one.* We have been emphasizing this approach in dealing with the reactions between ions in solution. Make it a habit to write down the components of solutions before trying to decide what reaction(s) might take place as you attempt the end-of-chapter problems involving titrations.

4.9 Oxidation–Reduction Reactions

We have seen that many important substances are ionic. Sodium chloride, for example, can be formed by the reaction of elemental sodium and chlorine:



In this reaction, solid sodium, which contains neutral sodium atoms, reacts with chlorine gas, which contains diatomic Cl_2 molecules, to form the ionic solid NaCl , which contains Na^+ and Cl^- ions. This process is represented in Fig. 4.19. *Reactions like this one, in which one or more electrons are transferred, are called oxidation–reduction reactions or redox reactions.*

Many important chemical reactions involve oxidation and reduction. Photosynthesis, which stores energy from the sun in plants by converting carbon dioxide and water to sugar, is a very important oxidation–reduction reaction. In fact, most reactions used for energy production are redox reactions. In humans, the oxidation of sugars, fats, and proteins provides the energy necessary for life. Combustion reactions, which provide most of the energy to power our civilization, also involve oxidation and reduction. An example is the reaction of methane with oxygen:



Even though none of the reactants or products in this reaction is ionic, the reaction is still assumed to involve a transfer of electrons from carbon to oxygen. To explain this, we must introduce the concept of oxidation states.



Visualization: Zinc and Iodine



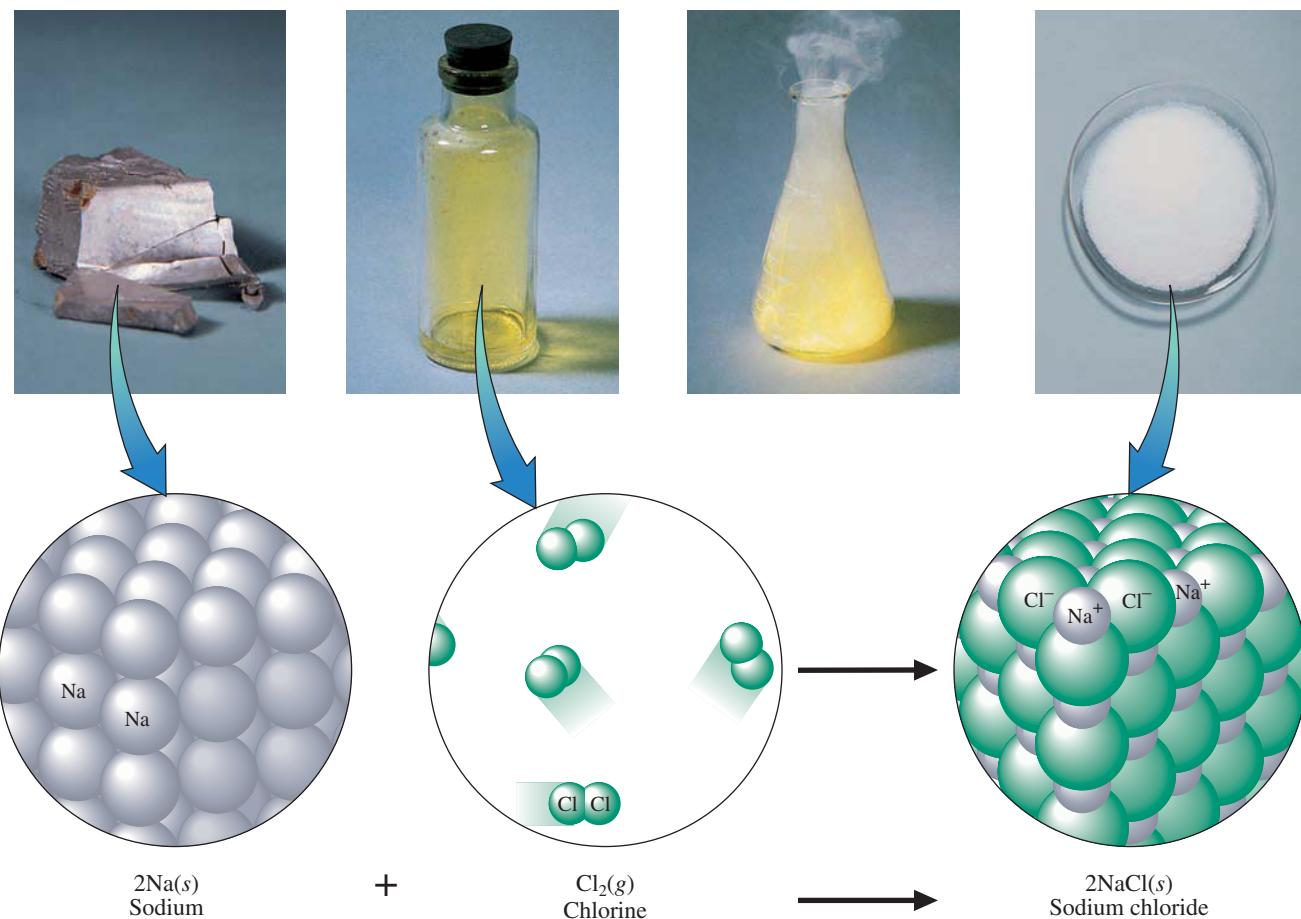
Visualization: Barking Dogs: Reaction of Phosphorus



Visualization: Dry Ice and Magnesium



Visualization: Sugar and Potassium Chlorate

**FIGURE 4.19**

The reaction of solid sodium and gaseous chlorine to form solid sodium chloride.

Oxidation States

The concept of **oxidation states** (also called *oxidation numbers*) provides a way to keep track of electrons in oxidation–reduction reactions, particularly redox reactions involving covalent substances. Recall that electrons are shared by atoms in covalent bonds. The oxidation states of atoms in covalent compounds are obtained by arbitrarily assigning the electrons (which are actually shared) to particular atoms. We do this as follows: For a covalent bond between two identical atoms, the electrons are split equally between the two. In cases where two different atoms are involved (and the electrons are thus shared unequally), the shared electrons are assigned completely to the atom that has the stronger attraction for electrons. For example, recall from the discussion of the water molecule in Section 4.1 that oxygen has a greater attraction for electrons than does hydrogen. Therefore, in assigning the oxidation state of oxygen and hydrogen in H_2O , we assume that the oxygen atom actually possesses all the electrons. Recall that a hydrogen atom has one electron. Thus, in water, oxygen has formally “taken” the electrons from two hydrogen atoms. This gives the oxygen an *excess* of two electrons (its oxidation state is -2) and leaves each hydrogen with no electrons (the oxidation state of each hydrogen is thus $+1$).

We define the *oxidation states* (or *oxidation numbers*) of the atoms in a covalent compound as the imaginary charges the atoms would have if the shared electrons were divided equally between identical atoms bonded to each other or, for different atoms, were all assigned to the atom in each bond that has the greater attraction for electrons. Of course,



CHEMICAL IMPACT

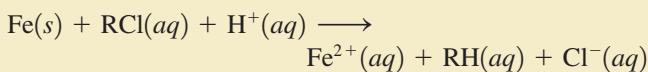
Iron Zeroes in on Pollution

Treating groundwater contaminated with pollutants is typically very complicated and very expensive. However, chemists have discovered a low-tech, economical method for treating the contaminated groundwater near a former semiconductor manufacturing plant in Sunnyvale, California. They have replaced the elaborate decontamination machinery used at the site for more than a decade with 220 tons of iron filings buried in a giant trough. Because there are no pumps to maintain and no electricity to purchase, this simple system will save approximately \$300,000 per year. The property, which was thought to be unusable for the 30-year lifetime of the old clean-up process because of the need for constant monitoring and access, can now be used immediately.

A schematic of the iron treatment method is shown in the accompanying figure. At Sunnyvale, the iron barrier is 40 feet long, 4 feet wide, and 20 feet deep. In the 4 days it takes for contaminated water to seep through the wall of iron,

the chlorinated organic contaminants are degraded into products that are then themselves decomposed to simpler substances. According to engineers on the site, the polluted water that seeps through the wall meets Environmental Protection Agency (EPA) standards when it emerges on the other side.

How does iron metal clean up contaminated groundwater? It's a result of the ability of iron metal (oxidation state = 0) to act as a reducing agent toward the chlorine-containing organic pollutant molecules. The reaction can be represented as follows:



where RCl represents a chlorinated organic molecule. The reaction appears to involve a direct reaction between the metal and an RCl molecule adsorbed on the metal surface.

for ionic compounds containing monatomic ions, the oxidation states of the ions are equal to the ion charges.

These considerations lead to a series of rules for assigning oxidation states that are summarized in Table 4.2. Application of these simple rules allows the assignment of oxidation states in most compounds. To apply these rules recognize that *the sum of the oxidation states must be zero for an electrically neutral compound*. For an ion, the sum of the oxidation states must equal the charge of the ion. The principles are illustrated by Sample Exercise 4.16.



Oxidation of copper metal by nitric acid. The copper atoms lose two electrons to form Cu^{2+} ions, which give a deep green color that becomes turquoise when diluted with water.

TABLE 4.2 Rules for Assigning Oxidation States

The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	$\text{Na}(s), \text{O}_2(g), \text{O}_3(g), \text{Hg}(l)$
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+, Cl^-
• Fluorine is -1 in its compounds	Fluorine: -1	HF, PF_3
• Oxygen is usually -2 in its compounds Exception: peroxides (containing O_2^{2-}) in which oxygen is -1	Oxygen: -2	$\text{H}_2\text{O}, \text{CO}_2$
• Hydrogen is $+1$ in its covalent compounds	Hydrogen: $+1$	$\text{H}_2\text{O}, \text{HCl}, \text{NH}_3$

In addition to decomposing chlorinated organic contaminants, iron appears to be useful against other pollutants as well. Iron can degrade dye wastes from textile mills and can reduce soluble Cr(VI) compounds to insoluble Cr(III) products, which are much less harmful. Iron's reducing abilities also appear useful in removing radioactive technetium, a common pollutant at nuclear processing facilities. Iron also appears to be effective for removing nitrates from the soil.

Other metals, such as zinc, tin, and palladium, have shown promise for use in groundwater clean-up, too. These metals generally react more quickly than iron but are more expensive and pose their own environmental hazards.

Inexpensive and environmentally benign, iron seems to be the metal of choice for most groundwater clean-up. It's cheap, it's effective, it's almost a miracle!

It is worthwhile to note at this point that the convention is to write actual charges on ions as $n+$ or $n-$, the number being written *before* the plus or minus sign. On the other hand, oxidation states (not actual charges) are written $+n$ or $-n$, the number being written *after* the plus or minus sign.

Sample Exercise 4.16

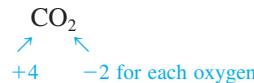
Assigning Oxidation States

Assign oxidation states to all atoms in the following.

- CO_2
- SF_6
- NO_3^-

Solution

- Since we have a specific rule for the oxidation state of oxygen, we will assign its value first. The oxidation state of oxygen is -2 . The oxidation state of the carbon atom can be determined by recognizing that since CO_2 has no charge, the sum of the oxidation states for oxygen and carbon must be zero. Since each oxygen is -2 and there are two oxygen atoms, the carbon atom must be assigned an oxidation state of $+4$:



We can check the assigned oxidation states by noting that when the number of atoms is taken into account, the sum is zero as required:

$$\begin{array}{rcl} 1(+4) + 2(-2) & = & 0 \\ \swarrow \quad \searrow \\ \text{No. of C} & & \text{No. of O} \\ \text{atoms} & & \text{atoms} \end{array}$$

- b. Since we have no rule for sulfur, we first assign the oxidation state of each fluorine as -1 . The sulfur must then be assigned an oxidation state of $+6$ to balance the total of -6 from the fluorine atoms:



Reality Check: $+6 + 6(-1) = 0$

- c. Oxygen has an oxidation state of -2 . Because the sum of the oxidation states of the three oxygens is -6 and the net charge on the NO_3^- ion is $1-$, the nitrogen must have an oxidation state of $+5$:



Reality Check: $+5 + 3(-2) = -1$

Note that in this case the sum must be -1 (the overall charge on the ion).

See Exercises 4.67 through 4.70.

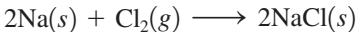


Magnetite is a magnetic ore containing Fe_3O_4 . Note that the compass needle points toward the ore.

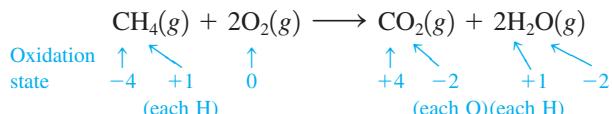
We need to make one more point about oxidation states, and this can be illustrated by the compound Fe_3O_4 , which is the main component in magnetite, an iron ore that accounts for the reddish color of many types of rocks and soils. To determine the oxidation states in Fe_3O_4 , we first assign each oxygen atom its usual oxidation state of -2 . The three iron atoms must yield a total of $+8$ to balance the total of -8 from the four oxygens. This means that each iron atom has an oxidation state of $+\frac{8}{3}$. A noninteger value for the oxidation state may seem strange because charge is expressed in whole numbers. However, although they are rare, noninteger oxidation states do occur because of the rather arbitrary way that electrons are divided up by the rules in Table 4.2. For Fe_3O_4 , for example, the rules assume that all the iron atoms are equal, when in fact this compound can best be viewed as containing four O^{2-} ions, two Fe^{3+} ions, and one Fe^{2+} ion per formula unit. (Note that the “average” charge on iron works out to be $\frac{8}{3}+$, which is equal to the oxidation state we determined above.) Noninteger oxidation states should not intimidate you. They are used in the same way as integer oxidation states—for keeping track of electrons.

The Characteristics of Oxidation–Reduction Reactions

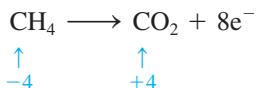
Oxidation–reduction reactions are characterized by a transfer of electrons. In some cases, the transfer occurs in a literal sense to form ions, such as in the reaction



However, sometimes the transfer is less obvious. For example, consider the combustion of methane (the oxidation state for each atom is given):



Note that the oxidation state for oxygen in O_2 is 0 because it is in elemental form. In this reaction there are no ionic compounds, but we can still describe the process in terms of a transfer of electrons. Note that carbon undergoes a change in oxidation state from -4 in CH_4 to $+4$ in CO_2 . Such a change can be accounted for by a loss of eight electrons (the symbol e^- stands for an electron);



CHEMICAL IMPACT

Pearly Whites

People have long been concerned about the “whiteness” of their teeth. In the Middle Ages the local barber-surgeon would whiten teeth using nitric acid—a procedure fraught with dangers, including the fact that nitric acid dissolves tooth enamel, which in turn leads to massive tooth decay. Today many safer procedures are available for keeping teeth sparkling white.

The outer layer of teeth, the enamel, consists of the mineral hydroxyapatite, which contains calcium phosphate. Underneath the enamel is dentin, an off-white mixture of calcium phosphate and collagen that protects the nerves and blood vessels at the center of the tooth.

The discoloration of teeth is usually due to colored molecules in our diet from sources such as blueberries, red wine, and coffee. The tar from cigarettes also stains teeth. Aging is another factor. As we get older, chemical changes occur that cause the dentin to become more yellow.

The stains produced when colored molecules are adsorbed to the surfaces of teeth can be removed by brushing. Toothpastes contain abrasives such as tiny particles of silica,

aluminum oxide, calcium carbonate, or calcium phosphate to help scrub off adsorbed stains.

Stains due to molecules lying below the surface are usually attacked with an oxidizing agent, hydrogen peroxide (H_2O_2). As H_2O_2 breaks down into water and oxygen, intermediates are produced that react with and decompose the molecules that produce teeth discoloration.

Off-the-shelf teeth whiteners typically contain carbamide peroxide (a 1:1 mixture of urea and hydrogen peroxide), glycerin, stannate and pyrophosphate salts (preservatives), and flavoring agents. These whiteners come in a form that can be brushed directly onto the teeth or are embedded in a plastic strip that can be stuck to the teeth. Because these products have a low strength for safety reasons, it may take several weeks of applying them for full whitening to occur.

Whitening treatments by dentists often involve the application of substances containing more than 30% hydrogen peroxide. These substances must be used with the appropriate protection of the tissues surrounding the teeth. Keeping your teeth white is another example of chemistry in action.

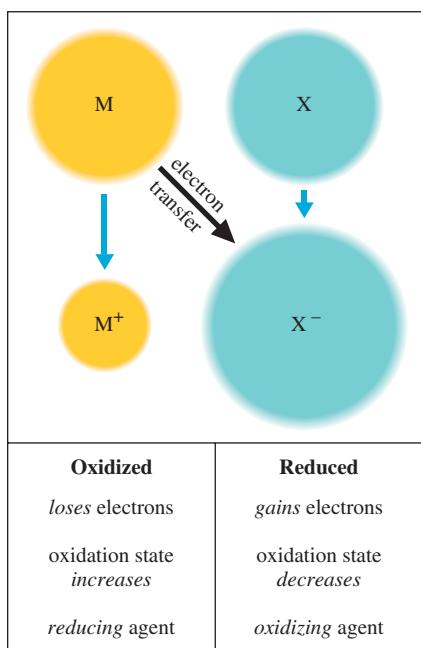
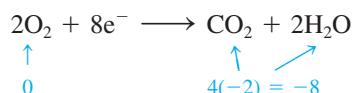


FIGURE 4.20

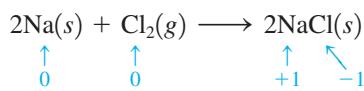
A summary of an oxidation-reduction process, in which M is oxidized and X is reduced.

On the other hand, each oxygen changes from an oxidation state of 0 in O_2 to -2 in H_2O and CO_2 , signifying a gain of two electrons per atom. Since four oxygen atoms are involved, this is a gain of eight electrons:



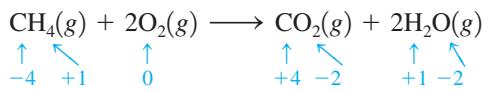
No change occurs in the oxidation state of hydrogen, and it is not formally involved in the electron-transfer process.

With this background, we can now define some important terms. **Oxidation** is an *increase* in oxidation state (a loss of electrons). **Reduction** is a *decrease* in oxidation state (a gain of electrons). Thus in the reaction



sodium is oxidized and chlorine is reduced. In addition, Cl_2 is called the **oxidizing agent (electron acceptor)**, and Na is called the **reducing agent (electron donor)**. These terms are summarized in Fig. 4.20.

Concerning the reaction





CHEMICAL IMPACT

Aging: Does It Involve Oxidation?

Although aging is supposed to bring wisdom, almost no one wants to get old. Along with wisdom, aging brings wrinkles, loss of physical strength, and greater susceptibility to disease.

Why do we age? No one knows for certain, but many scientists think that oxidation plays a major role. The oxygen molecule and other oxidizing agents in the body apparently can extract single electrons from the large molecules that make up cell membranes, thus making them very reactive. Subsequently, these activated molecules can link up, changing the properties of the cell membrane. At some point, enough of these reactions have occurred that the body's immune system comes to view the changed cell as an "enemy" and destroys it. This is particularly detrimental to the organism when the cells involved are irreplaceable. Nerve

cells, for example, fall into this category. They rarely regenerate in an adult.

The body has defenses against oxidation, such as vitamin E, a well-known antioxidant. Studies have shown that red blood cells age much faster than normal when they are deficient in vitamin E. Based on studies such as these, some have suggested large doses of vitamin E as a preventive measure against aging, but there is no solid evidence that this practice has any impact on aging.

Another protective antioxidant found in our bodies is superoxide dismutase (SOD), which protects us from the superoxide ion O_2^- , a powerful oxidizing agent that is particularly damaging to vital enzymes. The importance of SOD in opposing the aging process is indicated from the results of a study by Dr. Richard Cutler at the Gerontology Research

Oxidation is an increase in oxidation state. **Reduction** is a decrease in oxidation state.

A helpful mnemonic device is OIL RIG (**O**xidation **I**nvolves **L**oss; **R**eduction **I**nvolves **G**ain). Another common mnemonic is LEO says GER. (**L**oss of **E**lectrons, **O**xidation; **G**ain of **E**lectrons, **R**eduction).

An oxidizing agent is reduced and a reducing agent is oxidized in a redox reaction.

we can say the following:

Carbon is oxidized because there has been an increase in its oxidation state (carbon has formally lost electrons).

Oxygen is reduced because there has been a decrease in its oxidation state (oxygen has formally gained electrons).

CH_4 is the reducing agent.

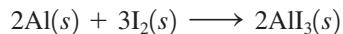
O_2 is the oxidizing agent.

Note that when the oxidizing or reducing agent is named, the *whole compound* is specified, not just the element that undergoes the change in oxidation state.

Sample Exercise 4.17

Oxidation–Reduction Reactions I

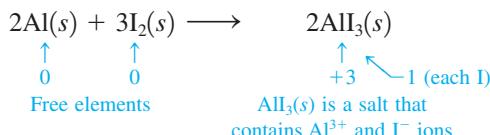
When powdered aluminum metal is mixed with pulverized iodine crystals and a drop of water is added to help the reaction get started, the resulting reaction produces a great deal of energy. The mixture bursts into flames, and a purple smoke of I_2 vapor is produced from the excess iodine. The equation for the reaction is



For this reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

Solution

The first step is to assign oxidation states:



Finely ground aluminum and iodine are mixed and react vigorously to form aluminum iodide after a drop of water is added. The purple cloud is excess iodine vaporized by the heat of the reaction.

Center of the National Institutes of Health in Baltimore that showed a strong correlation between the life spans of a dozen mammalian species and their levels of SOD. Human SOD is now being produced by the techniques of biotechnology in amounts that will enable scientists to carefully study its effects on aging and on various diseases such as rheumatoid arthritis and muscular dystrophy. Although SOD is available in health food stores in forms to be taken orally, this practice is useless because the SOD is digested (broken down into simpler substances) before it can reach the bloodstream.

Research does indicate that consuming certain foods may retard the aging process. For example, a recent study of 8000 male Harvard graduates found that chocolate and candy eaters live almost a year longer than those who abstain. Although the researchers from Harvard School of Public Health are not certain of the mechanism for this effect, they suggest that the antioxidants present in chocolate may provide the health benefits. For example, chocolate contains phenols,

antioxidants that are also present in wine, another substance that seems to promote good health if used in moderation.

Oxidation is only one possible cause for aging. Research continues on many fronts to try to discover why we get “older” as time passes.



Can eating chocolate slow down the aging process?

Since each aluminum atom changes its oxidation state from 0 to +3 (an increase in oxidation state), aluminum is *oxidized*. On the other hand, the oxidation state of each iodine atom decreases from 0 to -1, and iodine is *reduced*. Since Al furnishes electrons for the reduction of iodine, it is the *reducing agent*; I₂ is the *oxidizing agent*.

See Exercises 4.71 and 4.72.

Sample Exercise 4.18

Oxidation–Reduction Reactions II

Metallurgy, the process of producing a metal from its ore, always involves oxidation–reduction reactions. In the metallurgy of galena (PbS), the principal lead-containing ore, the first step is the conversion of lead sulfide to its oxide (a process called *roasting*):



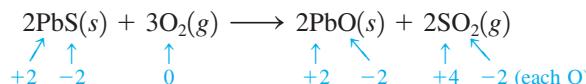
The oxide is then treated with carbon monoxide to produce the free metal:



For each reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

Solution

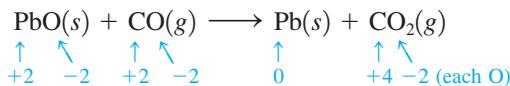
For the first reaction, we can assign the following oxidation states:



The oxidation state for the sulfur atom increases from -2 to +4. Thus sulfur is oxidized. The oxidation state for each oxygen atom decreases from 0 to -2. Oxygen is reduced. The

oxidizing agent (that accepts the electrons) is O₂, and the reducing agent (that donates electrons) is PbS.

For the second reaction we have



Lead is reduced (its oxidation state decreases from +2 to 0), and carbon is oxidized (its oxidation state increases from +2 to +4). PbO is the oxidizing agent, and CO is the reducing agent.

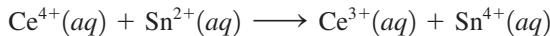
See Exercises 4.71 and 4.72.

4.10 Balancing Oxidation–Reduction Equations

Oxidation–reduction reactions in aqueous solutions are often complicated, which means that it can be difficult to balance their equations by simple inspection. In this section we will discuss a special technique for balancing the equations of redox reactions that occur in aqueous solutions. It is called the *half-reaction method*.

The Half-Reaction Method for Balancing Oxidation–Reduction Reactions in Aqueous Solutions

For oxidation–reduction reactions that occur in aqueous solution, it is useful to separate the reaction into two **half-reactions**: one involving oxidation and the other involving reduction. For example, consider the unbalanced equation for the oxidation–reduction reaction between cerium(IV) ion and tin(II) ion:



This reaction can be separated into a half-reaction involving the substance being *reduced*,



and one involving the substance being *oxidized*,



The general procedure is to balance the equations for the half-reactions separately and then to add them to obtain the overall balanced equation. The half-reaction method for balancing oxidation–reduction equations differs slightly depending on whether the reaction takes place in acidic or basic solution.

The Half-Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Acidic Solution

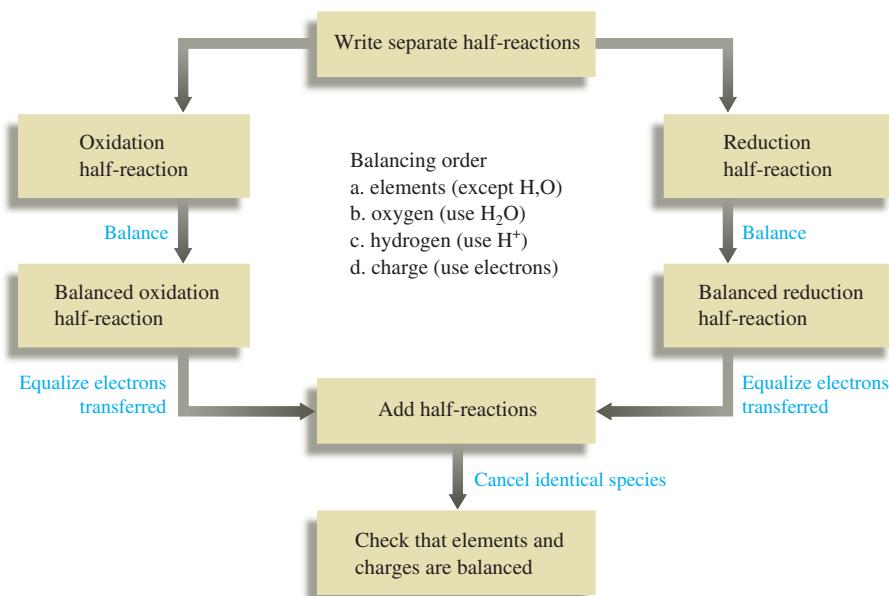
→ 1 Write separate equations for the oxidation and reduction half-reactions.

→ 2 For each half-reaction,

- a. Balance all the elements except hydrogen and oxygen.
- b. Balance oxygen using H₂O.

- c. Balance hydrogen using H^+ .
d. Balance the charge using electrons.
- 3 If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.
- 4 Add the half-reactions, and cancel identical species.
- 5 Check that the elements and charges are balanced.

These steps are summarized by the following flowchart:

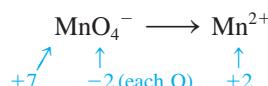


We will illustrate this method by balancing the equation for the reaction between permanganate and iron(II) ions in acidic solution:

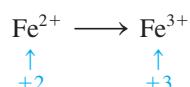


This reaction can be used to analyze iron ore for its iron content.

- 1 Identify and write equations for the half-reactions. The oxidation states for the half-reaction involving the permanganate ion show that manganese is reduced:



This is the *reduction half-reaction*. The other half-reaction involves the oxidation of iron(II) to iron(III) ion and is the *oxidation half-reaction*:



► 2 Balance each half-reaction. For the reduction reaction, we have



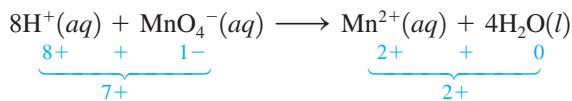
- a. The manganese is balanced.
- b. We balance oxygen by adding $4\text{H}_2\text{O}$ to the right side of the equation:



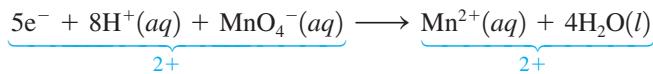
- c. Next, we balance hydrogen by adding 8H^+ to the left side:



- d. All the elements have been balanced, but we need to balance the charge using electrons. At this point we have the following overall charges for reactants and products in the reduction half-reaction:



We can equalize the charges by adding five electrons to the left side:

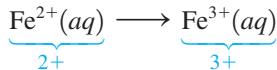


Both the *elements* and the *charges* are now balanced, so this represents the balanced reduction half-reaction. The fact that five electrons appear on the reactant side of the equation makes sense, since five electrons are required to reduce MnO_4^- (Mn has an oxidation state of +7) to Mn^{2+} (Mn has an oxidation state of +2).

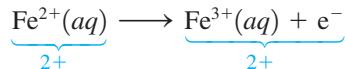
For the oxidation reaction



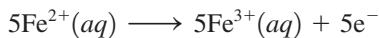
the elements are balanced, and we must simply balance the charge:



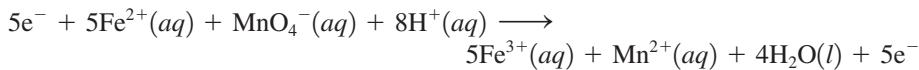
One electron is needed on the right side to give a net 2+ charge on both sides:



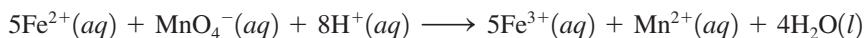
► 3 Equalize the electron transfer in the two half-reactions. Since the reduction half-reaction involves a transfer of five electrons and the oxidation half-reaction involves a transfer of only one electron, the oxidation half-reaction must be multiplied by 5:



► 4 Add the half-reactions. The half-reactions are added to give



Note that the electrons cancel (as they must) to give the final balanced equation:



The number of electrons gained in the reduction half-reaction must equal the number of electrons lost in the oxidation half-reaction.

→ 5 Check that elements and charges are balanced.

Elements balance: 5Fe, 1Mn, 4O, 8H → 5Fe, 1Mn, 4O, 8H

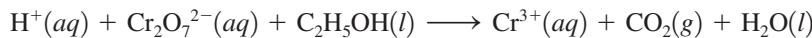
Charges balance: $5(2+) + (1-) + 8(1+) = 17+ \rightarrow 5(3+) + (2+) + 0 = 17+$

The equation is balanced.

Sample Exercise 4.19

Balancing Oxidation–Reduction Reactions (Acidic)

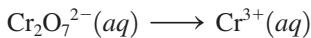
Potassium dichromate ($K_2Cr_2O_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $K_2Cr_2O_7$ reacts with ethyl alcohol (C_2H_5OH) as follows:



Balance this equation using the half-reaction method.

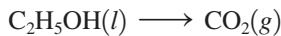
Solution

→ 1 The reduction half-reaction is



Chromium is reduced from an oxidation state of +6 in $Cr_2O_7^{2-}$ to one of +3 in Cr^{3+} .

The oxidation half-reaction is



Carbon is oxidized from an oxidation state of -2 in C_2H_5OH to +4 in CO_2 .

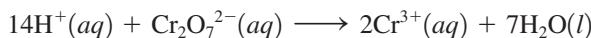
→ 2 Balancing all elements except hydrogen and oxygen in the first half-reaction, we have



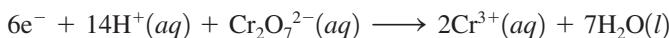
Balancing oxygen using H_2O , we have



Balancing hydrogen using H^+ , we have

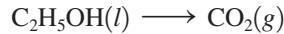


Balancing the charge using electrons, we have



When potassium dichromate reacts with ethanol, a blue-violet solution containing Cr^{3+} is formed.

Next, we turn to the oxidation half-reaction



Balancing carbon, we have



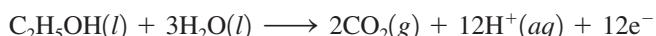
Balancing oxygen using H_2O , we have



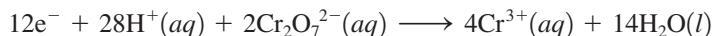
Balancing hydrogen using H^+ , we have



We then balance the charge by adding 12e^- to the right side:

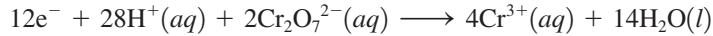


- 3 In the reduction half-reaction there are 6 electrons on the left-hand side, and there are 12 electrons on the right-hand side of the oxidation half-reaction. Thus we multiply the reduction half-reaction by 2 to give

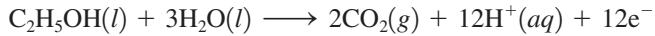


- 4 Adding the half-reactions and canceling identical species, we have

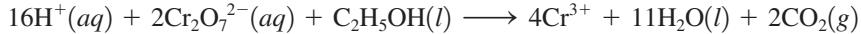
Reduction Half-Reaction:



Oxidation Half-Reaction:



Complete Reaction:



- 5 Check that elements and charges are balanced.

Elements balance: 22H, 4Cr, 15O, 2C → 22H, 4Cr, 15O, 2C

Charges balance: $+16 + 2(-2) + 0 = +12 \longrightarrow 4(+3) + 0 + 0 = +12$

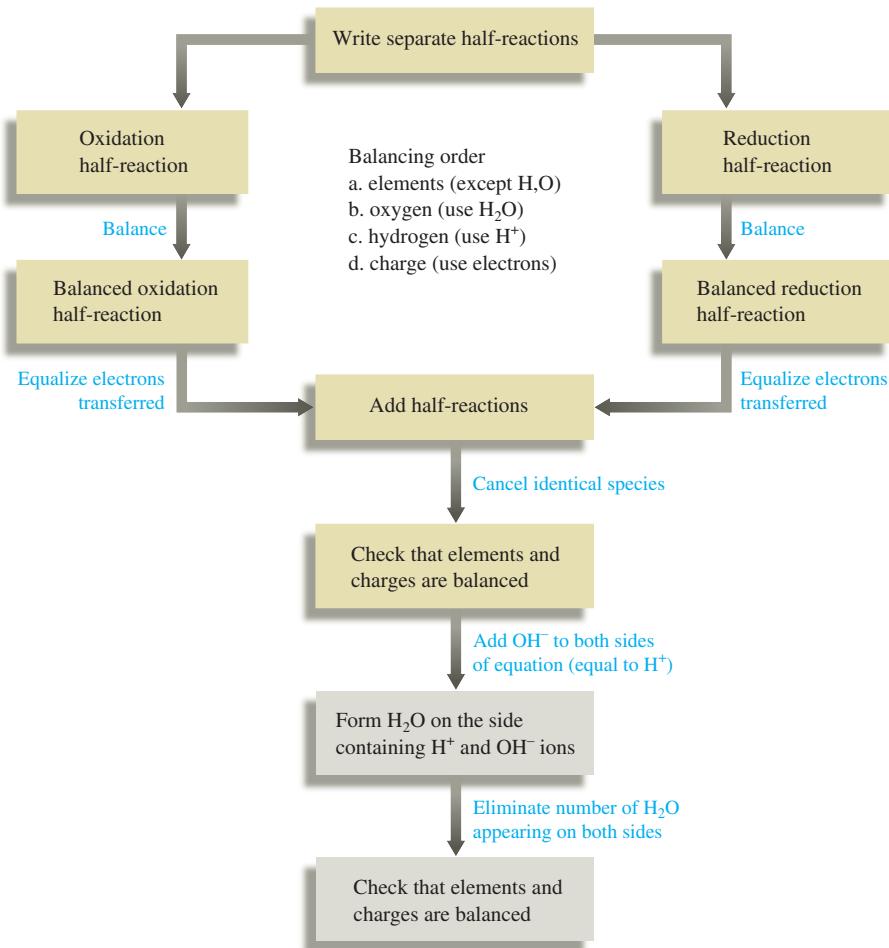
See Exercises 4.73 and 4.74.

Oxidation–reduction reactions can occur in basic solutions (the reactions involve OH^- ions) as well as in acidic solution (the reactions involve H^+ ions). The half-reaction method for balancing equations is slightly different for the two cases.

The Half-Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Basic Solution

- 1 Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation *as if H^+ ions were present.*
- 2 To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O .)
- 3 Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.
- 4 Check that elements and charges are balanced.

This method is summarized by the following flowchart:

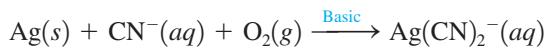


We will illustrate how this method is applied in Sample Exercise 4.20.

Sample Exercise 4.20

Balancing Oxidation–Reduction Reactions (Basic)

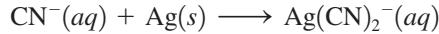
Silver is sometimes found in nature as large nuggets; more often it is found mixed with other metals and their ores. An aqueous solution containing cyanide ion is often used to extract the silver using the following reaction that occurs in basic solution:



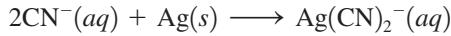
Balance this equation using the half-reaction method.

Solution

► 1 Balance the equation as if H^+ ions were present. Balance the oxidation half-reaction:



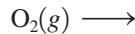
Balance carbon and nitrogen:



Balance the charge:



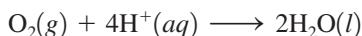
Balance the reduction half-reaction:



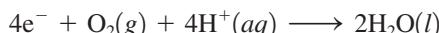
Balance oxygen:



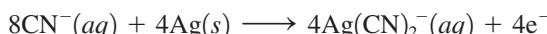
Balance hydrogen:



Balance the charge:

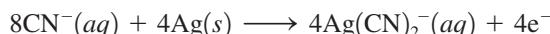


Multiply the balanced oxidation half-reaction by 4:



Add the half-reactions, and cancel identical species:

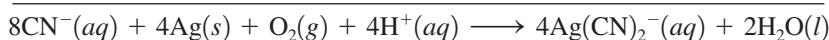
Oxidation Half-Reaction:



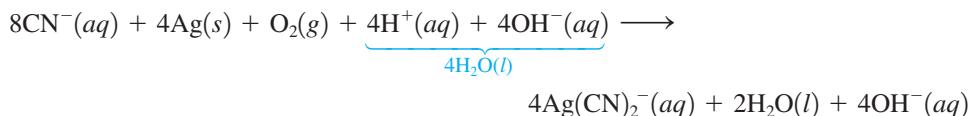
Reduction Half-Reaction:



Complete Reaction:



→ 2 Add OH^- ions to both sides of the balanced equation to eliminate the H^+ ions. We need to add 4OH^- to each side:



→ 3 Eliminate as many H_2O molecules as possible:



→ 4 Check that elements and charges are balanced.

Elements balance: 8C, 8N, 4Ag, 4O, 4H → 8C, 8N, 4Ag, 4O, 4H

Charges balance: $8(1-) + 0 + 0 + 0 = 8-$ → $4(1-) + 4(1-) = 8-$

See Exercises 4.75 and 4.76.

Key Terms

aqueous solution

Section 4.1

polar molecule
hydration
solubility

Section 4.2

solute
solvent
electrical conductivity
strong electrolyte
weak electrolyte
nonelectrolyte
acid
strong acid
strong base
weak acid
weak base

For Review

Chemical reactions in solution are very important in everyday life.

Water is a polar solvent that dissolves many ionic and polar substances.

Electrolytes

- Strong electrolyte: 100% dissociated to produce separate ions; strongly conducts an electric current
- Weak electrolyte: Only a small percentage of dissolved molecules produce ions; weakly conducts an electric current
- Nonelectrolyte: Dissolved substance produces no ions; does not conduct an electric current

Acids and bases

- Arrhenius model
 - Acid: produces H^+
 - Base: produces OH^-

Section 4.3

molarity
standard solution
dilution

Section 4.5

precipitation reaction
precipitate

Section 4.6

formula equation
complete ionic equation
spectator ions
net ionic equation

Section 4.8

acid
base
neutralization reaction
volumetric analysis
titration
stoichiometric (equivalence) point
indicator
endpoint

Section 4.9

oxidation–reduction (redox) reaction
oxidation state
oxidation
reduction
oxidizing agent (electron acceptor)
reducing agent (electron donor)

Section 4.10

half-reactions

- Brønsted–Lowry model
 - Acid: proton donor
 - Base: proton acceptor
- Strong acid: completely dissociates into separated H⁺ and anions
- Weak acid: dissociates to a slight extent

Molarity

- One way to describe solution composition

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{volume of solution } (L)}$$

- Moles solute = volume of solution (L) × molarity
- Standard solution: molarity is accurately known

Dilution

- Solvent is added to reduce the molarity
- Moles of solute after dilution = moles of solute before dilution

$$M_1V_1 = M_2V_2$$

Types of equations that describe solution reactions

- Formula equation: all reactants and products are written as complete formulas
- Complete ionic equation: all reactants and products that are strong electrolytes are written as separated ions
- Net ionic equation: only those compounds that undergo a change are written; spectator ions are not included

Solubility rules

- Based on experiment observation
- Help predict the outcomes of precipitation reactions

Important types of solution reactions

- Acid–base reactions: involve a transfer of H⁺ ions
- Precipitation reactions: formation of a solid occurs
- Oxidation–reduction reactions: involve electron transfer

Titrations

- Measures the volume of a standard solution (titrant) needed to react with a substance in solution
- Stoichiometric (equivalence) point: the point at which the required amount of titrant has been added to exactly react with the substance being analyzed
- Endpoint: the point at which a chemical indicator changes color

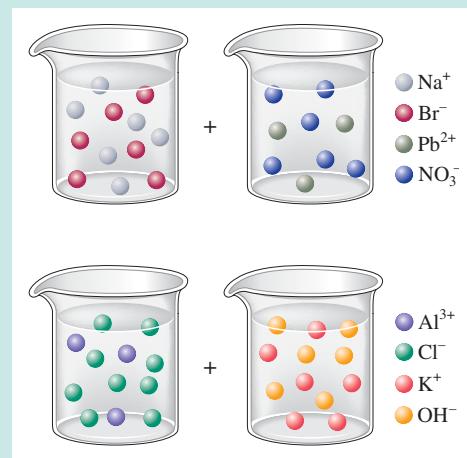
Oxidation–reduction reactions

- Oxidation states are assigned using a set of rules to keep track of electron flow
- Oxidation: increase in oxidation state (a loss of electrons)
- Reduction: decrease in oxidation state (a gain of electrons)
- Oxidizing agent: gains electrons (is reduced)
- Reducing agent: loses electrons (is oxidized)
- Equations for oxidation–reduction reactions are usually balanced by the half-reaction method

REVIEW QUESTIONS

- The (*aq*) designation listed after a solute indicates the process of hydration. Using KBr(*aq*) and C₂H₅OH(*aq*) as your examples, explain the process of hydration for soluble ionic compounds and for soluble covalent compounds.
- Characterize strong electrolytes versus weak electrolytes versus nonelectrolytes. Give examples of each. How do you experimentally determine whether a soluble substance is a strong electrolyte, weak electrolyte, or nonelectrolyte?

3. Distinguish between the terms *slightly soluble* and *weak electrolyte*.
4. Molarity is a conversion factor relating moles of solute in solution to the volume of the solution. How does one use molarity as a conversion factor to convert from moles of solute to volume of solution, and from volume of solution to moles of solute present?
5. What is a dilution? What stays constant in a dilution? Explain why the equation $M_1V_1 = M_2V_2$ works for dilution problems.
6. When the following beakers are mixed, draw a molecular-level representation of the product mixture (see Fig. 4.17).



7. Differentiate between the formula equation, the complete ionic equation, and the net ionic equation. For each reaction in Question 6, write all three balanced equations.
8. What is an acid–base reaction? Strong bases are soluble ionic compounds that contain the hydroxide ion. List the strong bases. When a strong base reacts with an acid, what is always produced? Explain the terms *titration*, *stoichiometric point*, *neutralization*, and *standardization*.
9. Define the terms *oxidation*, *reduction*, *oxidizing agent*, and *reducing agent*. Given a chemical reaction, how can you tell if it is a redox reaction?
10. What is a half-reaction? Why must the number of electrons lost in the oxidation equal the number of electrons gained in a reduction? Summarize briefly the steps in the half-reaction method for balancing redox reactions. What two items must be balanced in a redox reaction (or any reaction)?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- Assume you have a highly magnified view of a solution of HCl that allows you to “see” the HCl. Draw this magnified view. If you dropped in a piece of magnesium, the magnesium would disappear and hydrogen gas would be released. Represent this change using symbols for the elements, and write out the balanced equation.
- You have a solution of table salt in water. What happens to the salt concentration (increases, decreases, or stays the same) as the solution boils? Draw pictures to explain your answer.

- You have a sugar solution (solution A) with concentration x . You pour one-fourth of this solution into a beaker, and add an equivalent volume of water (solution B).
 - What is the ratio of sugar in solutions A and B?
 - Compare the volumes of solutions A and B.
 - What is the ratio of the concentrations of sugar in solutions A and B?
- You add an aqueous solution of lead nitrate to an aqueous solution of potassium iodide. Draw highly magnified views of each solution individually, and the mixed solution including any product that forms. Write the balanced equation for the reaction.
- Order the following molecules from lowest to highest oxidation state of the nitrogen atom: HNO₃, NH₄Cl, N₂O, NO₂, NaNO₂.
- Why is it that when something gains electrons, it is said to be *reduced*? What is being reduced?

7. Consider separate aqueous solutions of HCl and H₂SO₄ with the same molar concentrations. You wish to neutralize an aqueous solution of NaOH. For which acid solution would you need to add more volume (in milliliters) to neutralize the base?
- the HCl solution
 - the H₂SO₄ solution
 - You need to know the acid concentrations to answer this question.
 - You need to know the volume and concentration of the NaOH solution to answer this question.
 - c and d

Explain.

8. Draw molecular-level pictures to differentiate between concentrated and dilute solutions.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

- Differentiate between what happens when the following are dissolved in water.
 - polar solute versus nonpolar solute
 - KF versus C₆H₁₂O₆
 - RbCl versus AgCl
 - HNO₃ versus CO
- A student wants to prepare 1.00 L of a 1.00 M solution of NaOH (molar mass = 40.00 g/mol). If solid NaOH is available, how would the student prepare this solution? If 2.00 M NaOH is available, how would the student prepare the solution? To help insure three significant figures in the NaOH molarity, to how many significant figures should the volumes and mass be determined?
- List the formulas of three soluble bromide salts and three insoluble bromide salts. Do the same exercise for sulfate salts, hydroxide salts, and phosphate salts (list three soluble salts and three insoluble salts). List the formulas for six insoluble Pb²⁺ salts and one soluble Pb²⁺ salt.
- When 1.0 mol of solid lead nitrate is added to 2.0 mol of aqueous potassium iodide, a yellow precipitate forms. After the precipitate settles to the bottom, does the solution above the precipitate conduct electricity? Explain. Write the complete ionic equation to help you answer this question.
- What is an acid and what is a base? An acid–base reaction is sometimes called a proton-transfer reaction. Explain.
- A student had 1.00 L of a 1.00 M acid solution. Much to the surprise of the student, it took 2.00 L of 1.00 M NaOH solution to react completely with the acid. Explain why it took twice as much NaOH to react with all of the acid.

In a different experiment, a student had 10.0 mL of 0.020 M HCl. Again, much to the surprise of the student, it took only 5.00 mL of 0.020 M strong base to react completely with the HCl. Explain why it took only half as much strong base to react with all of the HCl.

- Differentiate between the following terms.
 - species reduced versus the reducing agent
 - species oxidized versus the oxidizing agent
 - oxidation state versus actual charge

16. When balancing reactions in Chapter 3, we did not mention that reactions must be charge balanced as well as mass balanced. What do *charge balanced* and *mass balanced* mean? How are redox reactions charge balanced?

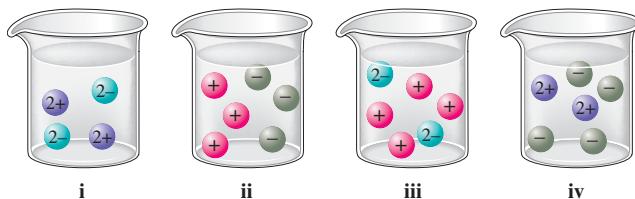
Exercises

In this section similar exercises are paired.

Aqueous Solutions: Strong and Weak Electrolytes

- Show how each of the following strong electrolytes “breaks up” into its component ions upon dissolving in water by drawing molecular-level pictures.
 - NaBr
 - MgCl₂
 - Al(NO₃)₃
 - (NH₄)₂SO₄
 - NaOH
 - FeSO₄
 - KMnO₄
 - HClO₄
 - NH₄C₂H₃O₂ (ammonium acetate)

18. Match each name below with the following microscopic pictures of that compound in aqueous solution.



- barium nitrate
- sodium chloride
- potassium carbonate
- magnesium sulfate

Which picture best represents HNO₃(aq)? Why aren't any of the pictures a good representation of HC₂H₃O₂(aq)?

- Calcium chloride is a strong electrolyte and is used to “salt” streets in the winter to melt ice and snow. Write a reaction to show how this substance breaks apart when it dissolves in water.
- Commercial cold packs and hot packs are available for treating athletic injuries. Both types contain a pouch of water and a dry chemical. When the pack is struck, the pouch of water breaks, dissolving the chemical, and the solution becomes either hot or cold. Many hot packs use magnesium sulfate, and many cold packs use ammonium nitrate. Write reactions to show how these strong electrolytes break apart when they dissolve in water.

Solution Concentration: Molarity

- Calculate the molarity of each of these solutions.
 - A 5.623-g sample of NaHCO₃ is dissolved in enough water to make 250.0 mL of solution.
 - A 184.6-mg sample of K₂Cr₂O₇ is dissolved in enough water to make 500.0 mL of solution.
 - A 0.1025-g sample of copper metal is dissolved in 35 mL of concentrated HNO₃ to form Cu²⁺ ions and then water is added to make a total volume of 200.0 mL. (Calculate the molarity of Cu²⁺.)
 - A solution of ethanol (C₂H₅OH) in water is prepared by dissolving 75.0 mL of ethanol (density = 0.79 g/cm³) in enough water to make 250.0 mL of solution. What is the molarity of the ethanol in this solution?

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- 23.** Calculate the concentration of all ions present in each of the following solutions of strong electrolytes.
- 0.100 mol of $\text{Ca}(\text{NO}_3)_2$ in 100.0 mL of solution
 - 2.5 mol of Na_2SO_4 in 1.25 L of solution
 - 5.00 g of NH_4Cl in 500.0 mL of solution
 - 1.00 g K_3PO_4 in 250.0 mL of solution
- 24.** Calculate the concentration of all ions present in each of the following solutions of strong electrolytes.
- 0.0200 mol of sodium phosphate in 10.0 mL of solution
 - 0.300 mol of barium nitrate in 600.0 mL of solution
 - 1.00 g of potassium chloride in 0.500 L of solution
 - 132 g of ammonium sulfate in 1.50 L of solution
- 25.** Which of the following solutions of strong electrolytes contains the largest number of moles of chloride ions: 100.0 mL of 0.30 M AlCl_3 , 50.0 mL of 0.60 M MgCl_2 , or 200.0 mL of 0.40 M NaCl ?
- 26.** Which of the following solutions of strong electrolytes contains the largest number of ions: 100.0 mL of 0.100 M NaOH , 50.0 mL of 0.200 M BaCl_2 , or 75.0 mL of 0.150 M Na_3PO_4 ?
- 27.** What mass of NaOH is contained in 250.0 mL of a 0.400 M sodium hydroxide solution?
- 28.** If 10. g of AgNO_3 is available, what volume of 0.25 M AgNO_3 solution can be prepared?
- 29.** Describe how you would prepare 2.00 L of each of the following solutions.
- 0.250 M NaOH from solid NaOH
 - 0.250 M NaOH from 1.00 M NaOH stock solution
 - 0.100 M K_2CrO_4 from solid K_2CrO_4
 - 0.100 M K_2CrO_4 from 1.75 M K_2CrO_4 stock solution
- 30.** How would you prepare 1.00 L of a 0.50 M solution of each of the following?
- H_2SO_4 from “concentrated” (18 M) sulfuric acid
 - HCl from “concentrated” (12 M) reagent
 - NiCl_2 from the salt $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
 - HNO_3 from “concentrated” (16 M) reagent
 - Sodium carbonate from the pure solid
- 31.** A solution is prepared by dissolving 10.8 g ammonium sulfate in enough water to make 100.0 mL of stock solution. A 10.00-mL sample of this stock solution is added to 50.00 mL of water. Calculate the concentration of ammonium ions and sulfate ions in the final solution.
- 32.** Calculate the sodium ion concentration when 70.0 mL of 3.0 M sodium carbonate is added to 30.0 mL of 1.0 M sodium bicarbonate.
- 33.** A standard solution is prepared for the analysis of fluoxymesterone ($\text{C}_{20}\text{H}_{29}\text{FO}_3$), an anabolic steroid. A stock solution is first prepared by dissolving 10.0 mg of fluoxymesterone in enough water to give a total volume of 500.0 mL. A 100.0- μL aliquot (portion) of this solution is diluted to a final volume of 100.0 mL. Calculate the concentration of the final solution in terms of molarity.
- 34.** A stock solution containing Mn^{2+} ions was prepared by dissolving 1.584 g pure manganese metal in nitric acid and diluting to a final volume of 1.000 L. The following solutions were then prepared by dilution:

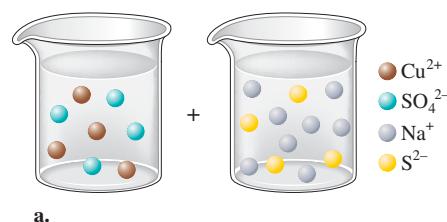
For solution A, 50.00 mL of stock solution was diluted to 1000.0 mL.

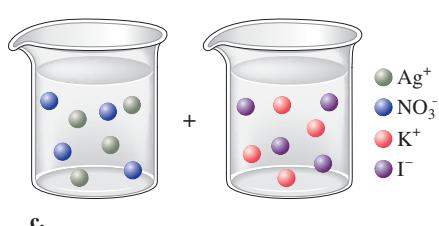
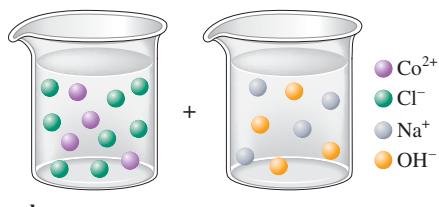
For solution B, 10.00 mL of solution A was diluted to 250.0 mL. For solution C, 10.00 mL of solution B was diluted to 500.0 mL.

Calculate the concentrations of the stock solution and solutions A, B, and C.

Precipitation Reactions

- 35.** On the basis of the general solubility rules given in Table 4.1, predict which of the following substances are likely to be soluble in water.
- aluminum nitrate
 - magnesium chloride
 - rubidium sulfate
 - nickel(II) hydroxide
 - lead(II) sulfide
 - magnesium hydroxide
 - iron(III) phosphate
- 36.** On the basis of the general solubility rules given in Table 4.1, predict which of the following substances are likely to be soluble in water.
- zinc chloride
 - lead(II) nitrate
 - lead(II) sulfate
 - sodium iodide
 - cobalt(III) sulfide
 - chromium(III) hydroxide
 - magnesium carbonate
 - ammonium carbonate
- 37.** When the following solutions are mixed together, what precipitate (if any) will form?
- $\text{FeSO}_4(aq) + \text{KCl}(aq)$
 - $\text{Al}(\text{NO}_3)_3(aq) + \text{Ba}(\text{OH})_2(aq)$
 - $\text{CaCl}_2(aq) + \text{Na}_2\text{SO}_4(aq)$
 - $\text{K}_2\text{S}(aq) + \text{Ni}(\text{NO}_3)_2(aq)$
- 38.** When the following solutions are mixed together, what precipitate (if any) will form?
- $\text{Hg}_2(\text{NO}_3)_2(aq) + \text{CuSO}_4(aq)$
 - $\text{Ni}(\text{NO}_3)_2(aq) + \text{CaCl}_2(aq)$
 - $\text{K}_2\text{CO}_3(aq) + \text{MgI}_2(aq)$
 - $\text{Na}_2\text{CrO}_4(aq) + \text{AlBr}_3(aq)$
- 39.** For the reactions in Exercise 37, write the balanced formula equation, complete ionic equation, and net ionic equation. If no precipitate forms, write “No reaction.”
- 40.** For the reactions in Exercise 38, write the balanced formula equation, complete ionic equation, and net ionic equation. If no precipitate forms, write “No reaction.”
- 41.** Write the balanced formula and net ionic equation for the reaction that occurs when the contents of the two beakers are added together. What colors represent the spectator ions in each reaction?





42. Give an example how each of the following insoluble ionic compounds could be produced using a precipitation reaction. Write the balanced formula equation for each reaction.

- a. $\text{Fe}(\text{OH})_3(s)$ c. $\text{PbSO}_4(s)$
b. $\text{Hg}_2\text{Cl}_2(s)$ d. $\text{BaCrO}_4(s)$

43. Write net ionic equations for the reaction, if any, that occurs when aqueous solutions of the following are mixed.

- a. ammonium sulfate and barium nitrate
b. lead(II) nitrate and sodium chloride
c. sodium phosphate and potassium nitrate
d. sodium bromide and rubidium chloride
e. copper(II) chloride and sodium hydroxide

44. Write net ionic equations for the reaction, if any, that occurs when aqueous solutions of the following are mixed.

- a. chromium(III) chloride and sodium hydroxide
b. silver nitrate and ammonium carbonate
c. copper(II) sulfate and mercury(I) nitrate
d. strontium nitrate and potassium iodide

45. Separate samples of a solution of an unknown soluble ionic compound are treated with KCl , Na_2SO_4 , and NaOH . A precipitate forms only when Na_2SO_4 is added. Which cations could be present in the unknown soluble ionic compound?

46. A sample may contain any or all of the following ions: Hg_2^{2+} , Ba^{2+} , and Mn^{2+} .

- a. No precipitate formed when an aqueous solution of NaCl was added to the sample solution.
b. No precipitate formed when an aqueous solution of Na_2SO_4 was added to the sample solution.
c. A precipitate formed when the sample solution was made basic with NaOH .

Which ion or ions are present in the sample solution?

47. What mass of Na_2CrO_4 is required to precipitate all of the silver ions from 75.0 mL of a 0.100 M solution of AgNO_3 ?

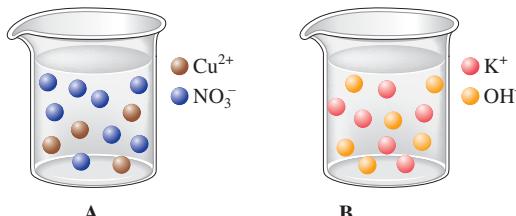
48. What volume of 0.100 M Na_3PO_4 is required to precipitate all the lead(II) ions from 150.0 mL of 0.250 M $\text{Pb}(\text{NO}_3)_2$?

49. What mass of solid aluminum hydroxide can be produced when 50.0 mL of 0.200 M $\text{Al}(\text{NO}_3)_3$ is added to 200.0 mL of 0.100 M KOH ?

50. What mass of barium sulfate can be produced when 100.0 mL of a 0.100 M solution of barium chloride is mixed with 100.0 mL of a 0.100 M solution of iron(III) sulfate?

51. How many grams of silver chloride can be prepared by the reaction of 100.0 mL of 0.20 M silver nitrate with 100.0 mL of 0.15 M calcium chloride? Calculate the concentrations of each ion remaining in solution after precipitation is complete.

52. The drawings below represent aqueous solutions. Solution A is 2.00 L of a 2.00 M aqueous solution of copper(II) nitrate. Solution B is 2.00 L of a 3.00 M aqueous solution of potassium hydroxide.



- a. Draw a picture of the solution made by mixing solutions A and B together after the precipitation reaction takes place. Make sure this picture shows the correct relative volume compared to solutions A and B, and the correct relative number of ions, along with the correct relative amount of solid formed.
b. Determine the concentrations (in M) of all ions left in solution (from part a) and the mass of solid formed.

53. A 1.42-g sample of a pure compound, with formula M_2SO_4 , was dissolved in water and treated with an excess of aqueous calcium chloride, resulting in the precipitation of all the sulfate ions as calcium sulfate. The precipitate was collected, dried, and found to weigh 1.36 g. Determine the atomic mass of M, and identify M.

54. You are given a 1.50-g mixture of sodium nitrate and sodium chloride. You dissolve this mixture into 100 mL of water and then add an excess of 0.500 M silver nitrate solution. You produce a white solid, which you then collect, dry, and measure. The white solid has a mass of 0.641 g.

- a. If you had an extremely magnified view of the solution (to the atomic-molecular level), list the species you would see (include charges, if any).
b. Write the balanced net ionic equation for the reaction that produces the solid. Include phases and charges.
c. Calculate the percent sodium chloride in the original unknown mixture.

Acid–Base Reactions

55. Write the balanced formula, complete ionic, and net ionic equations for each of the following acid–base reactions.

- a. $\text{HClO}_4(aq) + \text{Mg}(\text{OH})_2(s) \rightarrow$
b. $\text{HCN}(aq) + \text{NaOH}(aq) \rightarrow$
c. $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow$

56. Write the balanced formula, complete ionic, and net ionic equations for each of the following acid–base reactions.

- a. $\text{HNO}_3(aq) + \text{Al}(\text{OH})_3(s) \rightarrow$
b. $\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{KOH}(aq) \rightarrow$
c. $\text{Ca}(\text{OH})_2(aq) + \text{HCl}(aq) \rightarrow$

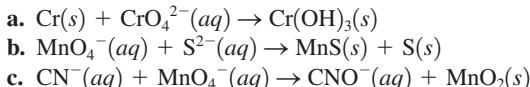
57. Write the balanced formula, complete ionic, and net ionic equations for the reactions that occur when the following are mixed.

- a. potassium hydroxide (aqueous) and nitric acid
b. barium hydroxide (aqueous) and hydrochloric acid
c. perchloric acid [$\text{HClO}_4(aq)$] and solid iron(III) hydroxide

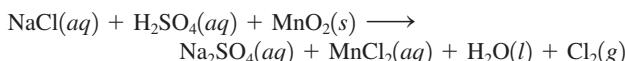
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- 58.** Write the balanced formula, complete ionic, and net ionic equations for the reactions that occur when the following are mixed.
- solid silver hydroxide and hydrobromic acid
 - aqueous strontium hydroxide and hydroiodic acid
 - solid chromium(III) hydroxide and nitric acid
- 59.** What volume of each of the following acids will react completely with 50.00 mL of 0.200 M NaOH?
- 0.100 M HCl
 - 0.150 M HNO₃
 - 0.200 M HC₂H₃O₂ (1 acidic hydrogen)
- 60.** What volume of each of the following bases will react completely with 25.00 mL of 0.200 M HCl?
- 0.100 M NaOH
 - 0.0500 M Ba(OH)₂
 - 0.250 M KOH
- 61.** Hydrochloric acid (75.0 mL of 0.250 M) is added to 225.0 mL of 0.0550 M Ba(OH)₂ solution. What is the concentration of the excess H⁺ or OH⁻ ions left in this solution?
- 62.** A student mixes four reagents together, thinking that the solutions will neutralize each other. The solutions mixed together are 50.0 mL of 0.100 M hydrochloric acid, 100.0 mL of 0.200 M of nitric acid, 500.0 mL of 0.0100 M calcium hydroxide, and 200.0 mL of 0.100 M rubidium hydroxide. Is the resulting solution neutral? If not, calculate the concentration of excess H⁺ or OH⁻ ions left in solution.
- 63.** A 25.00-mL sample of hydrochloric acid solution requires 24.16 mL of 0.106 M sodium hydroxide for complete neutralization. What is the concentration of the original hydrochloric acid solution?
- 64.** What volume of 0.0200 M calcium hydroxide is required to neutralize 35.00 mL of 0.0500 M nitric acid?
- 65.** A student titrates an unknown amount of potassium hydrogen phthalate (KHC₈H₄O₄, often abbreviated KHP) with 20.46 mL of a 0.1000 M NaOH solution. KHP (molar mass = 204.22 g/mol) has one acidic hydrogen. What mass of KHP was titrated (reacted completely) by the sodium hydroxide solution?
- 66.** The concentration of a certain sodium hydroxide solution was determined by using the solution to titrate a sample of potassium hydrogen phthalate (abbreviated as KHP). KHP is an acid with one acidic hydrogen and a molar mass of 204.22 g/mol. In the titration, 34.67 mL of the sodium hydroxide solution was required to react with 0.1082 g KHP. Calculate the molarity of the sodium hydroxide.
- Oxidation–Reduction Reactions**
- 67.** Assign oxidation states for all atoms in each of the following compounds.
- KMnO₄
 - NiO₂
 - Na₄Fe(OH)₆
 - (NH₄)₂HPO₄
 - P₄O₆
 - Fe₃O₄
 - XeOF₄
 - SF₄
 - CO
 - C₆H₁₂O₆
- 68.** Assign oxidation states for all atoms in each of the following compounds.
- UO₂²⁺
 - As₂O₃
 - NaBiO₃
 - As₄
 - HAsO₂
 - Mg₂P₂O₇
 - Na₂S₂O₃
 - Hg₂Cl₂
 - Ca(NO₃)₂
- 69.** Assign the oxidation state for nitrogen in each of the following.
- Li₃N
 - NH₃
 - N₂H₄
 - NO
 - N₂O
 - NO₂
 - NO₂⁻
 - NO₃⁻
 - N₂
- 70.** Assign oxidation numbers to all the atoms in each of the following.
- SrCr₂O₇
 - CuCl₂
 - O₂
 - H₂O₂
 - MgCO₃
 - Ag
 - PbSO₃
 - PbO₂
 - Na₂C₂O₄
 - CO₂
 - (NH₄)₂Ce(SO₄)₃
 - Cr₂O₃
- 71.** Specify which of the following are oxidation–reduction reactions, and identify the oxidizing agent, the reducing agent, the substance being oxidized, and the substance being reduced.
- Cu(s) + 2Ag⁺(aq) → 2Ag(s) + Cu²⁺(aq)
 - HCl(g) + NH₃(g) → NH₄Cl(s)
 - SiCl₄(l) + 2H₂O(l) → 4HCl(aq) + SiO₂(s)
 - SiCl₄(l) + 2Mg(s) → 2MgCl₂(s) + Si(s)
 - Al(OH)₄⁻(aq) → AlO₂⁻(aq) + 2H₂O(l)
- 72.** Specify which of the following equations represent oxidation–reduction reactions, and indicate the oxidizing agent, the reducing agent, the species being oxidized, and the species being reduced.
- CH₄(g) + H₂O(g) → CO(g) + 3H₂(g)
 - 2AgNO₃(aq) + Cu(s) → Cu(NO₃)₂(aq) + 2Ag(s)
 - Zn(s) + 2HCl(aq) → ZnCl₂(aq) + H₂(g)
 - 2H⁺(aq) + 2CrO₄²⁻(aq) → Cr₂O₇²⁻(aq) + H₂O(l)
- 73.** Balance the following oxidation–reduction reactions that occur in acidic solution.
- Zn(s) + HCl(aq) → Zn²⁺(aq) + H₂(g) + Cl⁻(aq)
 - I⁻(aq) + ClO⁻(aq) → I₃⁻(aq) + Cl⁻(aq)
 - As₂O₃(s) + NO₃⁻(aq) → H₃AsO₄(aq) + NO(g)
 - Br⁻(aq) + MnO₄⁻(aq) → Br₂(l) + Mn²⁺(aq)
 - CH₃OH(aq) + Cr₂O₇²⁻(aq) → CH₂O(aq) + Cr³⁺(aq)
- 74.** Balance the following oxidation–reduction reactions that occur in acidic solution using the half-reaction method.
- Cu(s) + NO₃⁻(aq) → Cu²⁺(aq) + NO(g)
 - Cr₂O₇²⁻(aq) + Cl⁻(aq) → Cr³⁺(aq) + Cl₂(g)
 - Pb(s) + PbO₂(s) + H₂SO₄(aq) → PbSO₄(s)
 - Mn²⁺(aq) + NaBiO₃(s) → Bi³⁺(aq) + MnO₄⁻(aq)
 - H₃AsO₄(aq) + Zn(s) → AsH₃(g) + Zn²⁺(aq)
- 75.** Balance the following oxidation–reduction reactions that occur in basic solution.
- Al(s) + MnO₄⁻(aq) → MnO₂(s) + Al(OH)₄⁻(aq)
 - Cl₂(g) → Cl⁻(aq) + OCl⁻(aq)
 - NO₂⁻(aq) + Al(s) → NH₃(g) + AlO₂⁻(aq)

- 76.** Balance the following oxidation–reduction reactions that occur in basic solution.



- 77.** Chlorine gas was first prepared in 1774 by C. W. Scheele by oxidizing sodium chloride with manganese(IV) oxide. The reaction is



Balance this equation.

- 78.** Gold metal will not dissolve in either concentrated nitric acid or concentrated hydrochloric acid. It will dissolve, however, in aqua regia, a mixture of the two concentrated acids. The products of the reaction are the AuCl_4^- ion and gaseous NO. Write a balanced equation for the dissolution of gold in aqua regia.

Additional Exercises

- 79.** Which of the following statements is (are) true? For the false statements, correct them.

- A concentrated solution in water will always contain a strong or weak electrolyte.
- A strong electrolyte will break up into ions when dissolved in water.
- An acid is a strong electrolyte.
- All ionic compounds are strong electrolytes in water.

- 80.** A 230.-mL sample of a 0.275 M CaCl_2 solution is left on a hot plate overnight; the following morning, the solution is 1.10 M. What volume of water evaporated from the 0.275 M CaCl_2 solution?

- 81.** Using the general solubility rules given in Table 4.1, name three reagents that would form precipitates with each of the following ions in aqueous solution. Write the net ionic equation for each of your suggestions.

- | | |
|------------------|---------------------------------------|
| a. chloride ion | d. sulfate ion |
| b. calcium ion | e. mercury(I) ion, Hg_2^{2+} |
| c. iron(III) ion | f. silver ion |

- 82.** Consider a 1.50-g mixture of magnesium nitrate and magnesium chloride. After dissolving this mixture in water, 0.500 M silver nitrate is added dropwise until precipitate formation is complete. The mass of the white precipitate formed is 0.641 g.

- Calculate the mass percent of magnesium chloride in the mixture.
- Determine the minimum volume of silver nitrate that must have been added to ensure complete formation of the precipitate.

- 83.** A 1.00-g sample of an alkaline earth metal chloride is treated with excess silver nitrate. All of the chloride is recovered as 1.38 g of silver chloride. Identify the metal.

- 84.** A mixture contains only NaCl and $\text{Al}_2(\text{SO}_4)_3$. A 1.45-g sample of the mixture is dissolved in water and an excess of NaOH is added, producing a precipitate of $\text{Al}(\text{OH})_3$. The precipitate is filtered, dried, and weighed. The mass of the precipitate is 0.107 g. What is the mass percent of $\text{Al}_2(\text{SO}_4)_3$ in the sample?

- 85.** Saccharin ($\text{C}_7\text{H}_5\text{NO}_3\text{S}$) is sometimes dispensed in tablet form. Ten tablets with a total mass of 0.5894 g were dissolved in water. They were oxidized to convert all the sulfur to sulfate ion,

which was precipitated by adding an excess of barium chloride solution. The mass of BaSO_4 obtained was 0.5032 g. What is the average mass of saccharin per tablet? What is the average mass percent of saccharin in the tablets?

- 86.** A mixture contains only NaCl and $\text{Fe}(\text{NO}_3)_3$. A 0.456-g sample of the mixture is dissolved in water, and an excess of NaOH is added, producing a precipitate of $\text{Fe}(\text{OH})_3$. The precipitate is filtered, dried, and weighed. Its mass is 0.107 g. Calculate the following.

- the mass of iron in the sample
- the mass of $\text{Fe}(\text{NO}_3)_3$ in the sample
- the mass percent of $\text{Fe}(\text{NO}_3)_3$ in the sample

- 87.** A student added 50.0 mL of an NaOH solution to 100.0 mL of 0.400 M HCl. The solution was then treated with an excess of aqueous chromium(III) nitrate, resulting in formation of 2.06 g of precipitate. Determine the concentration of the NaOH solution.

- 88.** What acid and what strong base would react in aqueous solution to produce the following salts in the formula equation? Write the balanced formula equation for each reaction.

- potassium perchlorate
- cesium nitrate
- calcium iodide

- 89.** A 10.00-mL sample of vinegar, an aqueous solution of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), is titrated with 0.5062 M NaOH, and 16.58 mL is required to reach the equivalence point.

- What is the molarity of the acetic acid?
- If the density of the vinegar is 1.006 g/cm³, what is the mass percent of acetic acid in the vinegar?

- 90.** When hydrochloric acid reacts with magnesium metal, hydrogen gas and aqueous magnesium chloride are produced. What volume of 5.0 M HCl is required to react completely with 3.00 g of magnesium?

- 91.** A 2.20-g sample of an unknown acid (empirical formula = $\text{C}_3\text{H}_4\text{O}_3$) is dissolved in 1.0 L of water. A titration required 25.0 mL of 0.500 M NaOH to react completely with all the acid present. Assuming the unknown acid has one acidic proton per molecule, what is the molecular formula of the unknown acid?

- 92.** Carminic acid, a naturally occurring red pigment extracted from the cochineal insect, contains only carbon, hydrogen, and oxygen. It was commonly used as a dye in the first half of the nineteenth century. It is 53.66% C and 4.09% H by mass. A titration required 18.02 mL of 0.0406 M NaOH to neutralize 0.3602 g carminic acid. Assuming that there is only one acidic hydrogen per molecule, what is the molecular formula of carminic acid?

- 93.** A 30.0-mL sample of an unknown strong base is neutralized after the addition of 12.0 mL of a 0.150 M HNO_3 solution. If the unknown base concentration is 0.0300 M, give some possible identities for the unknown base.

- 94.** Many oxidation–reduction reactions can be balanced by inspection. Try to balance the following reactions by inspection. In each reaction, identify the substance reduced and the substance oxidized.

- $\text{Al}(s) + \text{HCl}(aq) \rightarrow \text{AlCl}_3(aq) + \text{H}_2(g)$
- $\text{CH}_4(g) + \text{S}(s) \rightarrow \text{CS}_2(l) + \text{H}_2\text{S}(g)$
- $\text{C}_3\text{H}_8(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$
- $\text{Cu}(s) + \text{Ag}^+(aq) \rightarrow \text{Ag}(s) + \text{Cu}^{2+}(aq)$

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- 95.** One of the classical methods for the determination of the manganese content in steel is to convert all the manganese to the deeply colored permanganate ion and then to measure the absorption of light. The steel is dissolved in nitric acid, producing the manganese(II) ion and nitrogen dioxide gas. This solution is then reacted with an acidic solution containing periodate ion; the products are the permanganate and iodate ions. Write balanced chemical equations for both these steps.

Challenge Problems

- 96.** The units of parts per million (ppm) and parts per billion (ppb) are commonly used by environmental chemists. In general, 1 ppm means 1 part of solute for every 10^6 parts of solution. Mathematically, by mass:

$$\text{ppm} = \frac{\mu\text{g solute}}{\text{g solution}} = \frac{\text{mg solute}}{\text{kg solution}}$$

In the case of very dilute aqueous solutions, a concentration of 1.0 ppm is equal to 1.0 μg of solute per 1.0 mL, which equals 1.0 g solution. Parts per billion is defined in a similar fashion. Calculate the molarity of each of the following aqueous solutions.

a. 5.0 ppb Hg in H_2O

b. 1.0 ppb CHCl_3 in H_2O

c. 10.0 ppm As in H_2O

d. 0.10 ppm DDT ($\text{C}_{14}\text{H}_9\text{Cl}_5$) in H_2O

- 97.** In most of its ionic compounds, cobalt is either Co(II) or Co(III). One such compound, containing chloride ion and waters of hydration, was analyzed, and the following results were obtained. A 0.256-g sample of the compound was dissolved in water, and excess silver nitrate was added. The silver chloride was filtered, dried, and weighed, and it had a mass of 0.308 g. A second sample of 0.416 g of the compound was dissolved in water, and an excess of sodium hydroxide was added. The hydroxide salt was filtered and heated in a flame, forming cobalt(III) oxide. The mass of cobalt(III) oxide formed was 0.145 g.
- a. What is the percent composition, by mass, of the compound?
- b. Assuming the compound contains one cobalt atom per formula unit, what is the molecular formula?
- c. Write balanced equations for the three reactions described.

- 98.** Polychlorinated biphenyls (PCBs) have been used extensively as dielectric materials in electrical transformers. Because PCBs have been shown to be potentially harmful, analysis for their presence in the environment has become very important. PCBs are manufactured according to the following generic reaction:



This reaction results in a mixture of PCB products. The mixture is analyzed by decomposing the PCBs and then precipitating the resulting Cl^- as AgCl .

- a. Develop a general equation that relates the average value of n to the mass of a given mixture of PCBs and the mass of AgCl produced.
- b. A 0.1947-g sample of a commercial PCB yielded 0.4791 g of AgCl . What is the average value of n for this sample?

- 99.** You have two 500.0 mL aqueous solutions. Solution A is a solution of silver nitrate, and solution B is a solution of potassium chromate. The masses of the solutes in each of the solutions are

the same. When the solutions are added together, a blood-red precipitate forms. After the reaction has gone to completion, you dry the solid and find that it has a mass of 331.8 g.

- a. Calculate the concentration of the potassium ions in the original potassium chromate solution.
- b. Calculate the concentration of the chromate ions in the final solution.

- 100.** A sample is a mixture of KCl and KBr. When 0.1024 g of the sample is dissolved in water and reacted with excess silver nitrate, 0.1889 g solid is obtained. What is the composition by mass percent of the original mixture?

- 101.** You are given a solid that is a mixture of Na_2SO_4 and K_2SO_4 . A 0.205-g sample of the mixture is dissolved in water. An excess of an aqueous solution of BaCl_2 is added. The BaSO_4 that is formed is filtered, dried, and weighed. Its mass is 0.298 g. What mass of SO_4^{2-} ion is in the sample? What is the mass percent of SO_4^{2-} ion in the sample? What are the percent compositions by mass of Na_2SO_4 and K_2SO_4 in the sample?

- 102.** Zinc and magnesium metal each react with hydrochloric acid according to the following equations:

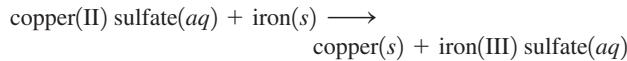
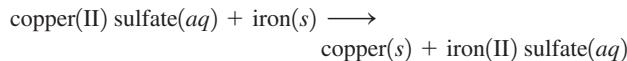


A 10.00-g mixture of zinc and magnesium is reacted with the stoichiometric amount of hydrochloric acid. The reaction mixture is then reacted with 156 mL of 3.00 M silver nitrate to produce the maximum possible amount of silver chloride.

- a. Determine the percent magnesium by mass in the original mixture.
- b. If 78.0 mL of HCl was added, what was the concentration of the HCl?

- 103.** You made 100.0 mL of a lead(II) nitrate solution for lab but forgot to cap it. The next lab session you noticed that there was only 80.0 mL left (the rest had evaporated). In addition, you forgot the initial concentration of the solution. You decide to take 2.00 mL of the solution and add an excess of a concentrated sodium chloride solution. You obtain a solid with a mass of 3.407 g. What was the concentration of the original lead(II) nitrate solution?

- 104.** Consider reacting copper(II) sulfate with iron. Two possible reactions can occur, as represented by the following equations.



You place 87.7 mL of a 0.500 M solution of copper(II) sulfate in a beaker. You then add 2.00 g of iron filings to the copper(II) sulfate solution. After one of the above reactions occurs, you isolate 2.27 g of copper. Which equation above describes the reaction that occurred? Support your answer.

- 105.** Consider an experiment in which two burets, Y and Z, are simultaneously draining into a beaker that initially contained 275.0 mL of 0.300 M HCl. Buret Y contains 0.150 M NaOH and buret Z contains 0.250 M KOH. The stoichiometric point in the titration is reached 60.65 minutes after Y and Z were started simultaneously. The total volume in the beaker at the stoichiometric point is 655 mL. Calculate the flow rates of burets Y and Z. Assume the flow rates remain constant during the experiment.

- 106.** Complete and balance each acid–base reaction.

- $\text{H}_3\text{PO}_4(aq) + \text{NaOH}(aq) \rightarrow$
Contains three acidic hydrogens
- $\text{H}_2\text{SO}_4(aq) + \text{Al(OH)}_3(s) \rightarrow$
Contains two acidic hydrogens
- $\text{H}_2\text{Se}(aq) + \text{Ba(OH)}_2(aq) \rightarrow$
Contains two acidic hydrogens
- $\text{H}_2\text{C}_2\text{O}_4(aq) + \text{NaOH}(aq) \rightarrow$
Contains two acidic hydrogens

- 107.** What volume of 0.0521 M Ba(OH)_2 is required to neutralize exactly 14.20 mL of 0.141 M H_3PO_4 ? Phosphoric acid contains three acidic hydrogens.

- 108.** A 10.00-mL sample of sulfuric acid from an automobile battery requires 35.08 mL of 2.12 M sodium hydroxide solution for complete neutralization. What is the molarity of the sulfuric acid? Sulfuric acid contains two acidic hydrogens.

- 109.** Some of the substances commonly used in stomach antacids are MgO , Mg(OH)_2 , and Al(OH)_3 .
- Write a balanced equation for the neutralization of hydrochloric acid by each of these substances.
 - Which of these substances will neutralize the greatest amount of 0.10 M HCl per gram?

- 110.** A 6.50-g sample of a diprotic acid requires 137.5 mL of a 0.750 M NaOH solution for complete reaction. Determine the molar mass of the acid.

- 111.** Citric acid, which can be obtained from lemon juice, has the molecular formula $\text{C}_6\text{H}_8\text{O}_7$. A 0.250-g sample of citric acid dissolved in 25.0 mL of water requires 37.2 mL of 0.105 M NaOH for complete neutralization. What number of acidic hydrogens per molecule does citric acid have?

- 112.** Balance the following equations by the half-reaction method.

- $\text{Fe}(s) + \text{HCl}(aq) \rightarrow \text{HFeCl}_4(aq) + \text{H}_2(g)$
- $\text{IO}_3^-(aq) + \text{I}^-(aq) \xrightarrow{\text{Acid}} \text{I}_3^-(aq)$
- $\text{Cr(NCS)}_6^{4-}(aq) + \text{Ce}^{4+}(aq) \xrightarrow{\text{Acid}}$
 $\text{Cr}^{3+}(aq) + \text{Ce}^{3+}(aq) + \text{NO}_3^-(aq) + \text{CO}_2(g) + \text{SO}_4^{2-}(aq)$
- $\text{CrI}_3(s) + \text{Cl}_2(g) \xrightarrow{\text{Base}} \text{CrO}_4^{2-}(aq) + \text{IO}_4^-(aq) + \text{Cl}^-(aq)$
- $\text{Fe(CN)}_6^{4-}(aq) + \text{Ce}^{4+}(aq) \xrightarrow{\text{Base}}$
 $\text{Ce(OH)}_3(s) + \text{Fe(OH)}_3(s) + \text{CO}_3^{2-}(aq) + \text{NO}_3^-(aq)$
- $\text{Fe(OH)}_2(s) + \text{H}_2\text{O}_2(aq) \xrightarrow{\text{Base}} \text{Fe(OH)}_3(s)$

- 113.** It took $25.06 \pm 0.05\text{ mL}$ of a sodium hydroxide solution to titrate a 0.4016-g sample of KHP (see Exercise 65). Calculate the concentration and uncertainty in the concentration of the sodium hydroxide solution. (See Appendix 1.5.) Neglect any uncertainty in the mass.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

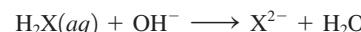
- 114.** Tris(pentafluorophenyl)borane, commonly known by its acronym BARF, is frequently used to initiate polymerization of ethylene or propylene in the presence of a catalytic transition metal compound. It is composed solely of C, F, and B; it is 42.23% C by mass and 55.66% F by mass.

- What is the empirical formula of BARF?
- A 2.251-g sample of BARF dissolved in 347.0 mL of solution produces a 0.01267 M solution. What is the molecular formula of BARF?

- 115.** In a 1-L beaker, 203 mL of 0.307 M ammonium chromate was mixed with 137 mL of 0.269 M chromium(III) nitrite to produce ammonium nitrite and chromium(III) chromate. Write the balanced chemical reaction occurring here. If the percent yield of the reaction was 88.0%, how much chromium(III) chromate was isolated?

- 116.** The vanadium in a sample of ore is converted to VO^{2+} . The VO^{2+} ion is subsequently titrated with MnO_4^- in acidic solution to form V(OH)_4^+ and manganese(II) ion. To titrate the solution, 26.45 mL of 0.02250 M MnO_4^- was required. If the mass percent of vanadium in the ore was 58.1%, what was the mass of the ore sample? Which of the four transition metal ions in this titration has the highest oxidation state?

- 117.** The unknown acid H_2X can be neutralized completely by OH^- according to the following (unbalanced) equation:



The ion formed as a product, X^{2-} , was shown to have 36 total electrons. What is element X? Propose a name for H_2X ? To completely neutralize a sample of H_2X , 35.6 mL of 0.175 M OH^- solution was required. What was the mass of the H_2X sample used?

Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

- 118.** Three students were asked to find the identity of the metal in a particular sulfate salt. They dissolved a 0.1472-g sample of the salt in water and treated it with excess barium chloride, resulting in the precipitation of barium sulfate. After the precipitate had been filtered and dried, it weighed 0.2327 g .

Each student analyzed the data independently and came to different conclusions. Pat decided that the metal was titanium. Chris thought it was sodium. Randy reported that it was gallium. What formula did each student assign to the sulfate salt?

Look for information on the sulfates of gallium, sodium, and titanium in this text and reference books such as the *CRC Handbook of Chemistry and Physics*. What further tests would you suggest to determine which student is most likely correct?

- 119.** You have two 500.0-mL aqueous solutions. Solution A is a solution of a metal nitrate that is 8.246% nitrogen by mass. The ionic compound in solution B consists of potassium, chromium, and oxygen; chromium has an oxidation state of +6 and there are 2 potassiums and 1 chromium in the formula. The masses of the solutes in each of the solutions are the same. When the solutions are added together, a blood-red precipitate forms. After the reaction has gone to completion, you dry the solid and find that it has a mass of 331.8 g .

- Identify the ionic compounds in solution A and solution B.
- Identify the blood-red precipitate.
- Calculate the concentration (molarity) of all ions in the original solutions.
- Calculate the concentration (molarity) of all ions in the final solution.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

5 Gases

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 - Units of Pressure
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 - Pressure and Volume (Boyle's Law)
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 - Effusion
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- 5.8 Real Gases**
- 5.9 Characteristics of Several Real Gases**
- 5.10 Chemistry in the Atmosphere**



The steaming fumaroles located in Bjarnarflag, Iceland release a variety of gases.

Matter exists in three distinct physical states: gas, liquid, and solid. Although relatively few substances exist in the gaseous state under typical conditions, gases are very important. For example, we live immersed in a gaseous solution. The earth's atmosphere is a mixture of gases that consists mainly of elemental nitrogen (N_2) and oxygen (O_2). The atmosphere both supports life and acts as a waste receptacle for the exhaust gases that accompany many industrial processes. The chemical reactions of these waste gases in the atmosphere lead to various types of pollution, including smog and acid rain. The gases in the atmosphere also shield us from harmful radiation from the sun and keep the earth warm by reflecting heat radiation back toward the earth. In fact, there is now great concern that an increase in atmospheric carbon dioxide, a product of the combustion of fossil fuels, is causing a dangerous warming of the earth.

In this chapter we will look carefully at the properties of gases. First we will see how measurements of gas properties lead to various types of laws—statements that show how the properties are related to each other. Then we will construct a model to explain why gases behave as they do. This model will show how the behavior of the individual particles of a gas leads to the observed properties of the gas itself (a collection of many, many particles).

The study of gases provides an excellent example of the scientific method in action. It illustrates how observations lead to natural laws, which in turn can be accounted for by models.

5.1 Pressure

A gas uniformly fills any container, is easily compressed, and mixes completely with any other gas. One of the most obvious properties of a gas is that it exerts pressure on its surroundings. For example, when you blow up a balloon, the air inside pushes against the elastic sides of the balloon and keeps it firm.

As mentioned earlier, the gases most familiar to us form the earth's atmosphere. The pressure exerted by this gaseous mixture that we call air can be dramatically demonstrated by the experiment shown in Fig. 5.1. A small volume of water is placed in a metal can,

As a gas, water occupies 1200 times as much space as it does as a liquid at 25°C and atmospheric pressure.

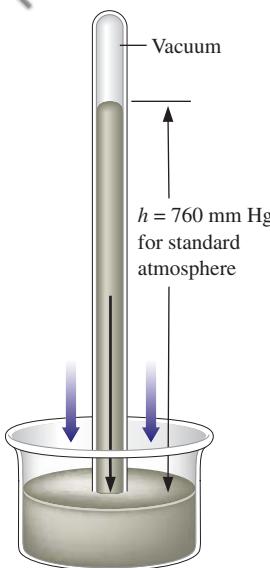


Visualization: Collapsing Can

FIGURE 5.1

The pressure exerted by the gases in the atmosphere can be demonstrated by boiling water in a large metal can (a) and then turning off the heat and sealing the can. As the can cools, the water vapor condenses, lowering the gas pressure inside the can. This causes the can to crumple (b).



**FIGURE 5.2**

A torricellian barometer. The tube, completely filled with mercury, is inverted in a dish of mercury. Mercury flows out of the tube until the pressure of the column of mercury (shown by the black arrow) "standing on the surface" of the mercury in the dish is equal to the pressure of the air (shown by the purple arrows) on the rest of the surface of the mercury in the dish.

Soon after Torricelli died, a German physicist named Otto von Guericke invented an air pump. In a famous demonstration for the King of Prussia in 1663, Guericke placed two hemispheres together, pumped the air out of the resulting sphere through a valve, and showed that teams of horses could not pull the hemispheres apart. Then, after secretly opening the air valve, Guericke easily separated the hemispheres by hand. The King of Prussia was so impressed that he awarded Guericke a lifetime pension!

and the water is boiled, which fills the can with steam. The can is then sealed and allowed to cool. Why does the can collapse as it cools? It is the atmospheric pressure that crumples the can. When the can is cooled after being sealed so that no air can flow in, the water vapor (steam) condenses to a very small volume of liquid water. As a gas, the water filled the can, but when it is condensed to a liquid, the liquid does not come close to filling the can. The H_2O molecules formerly present as a gas are now collected in a very small volume of liquid, and there are very few molecules of gas left to exert pressure outward and counteract the air pressure. As a result, the pressure exerted by the gas molecules in the atmosphere smashes the can.

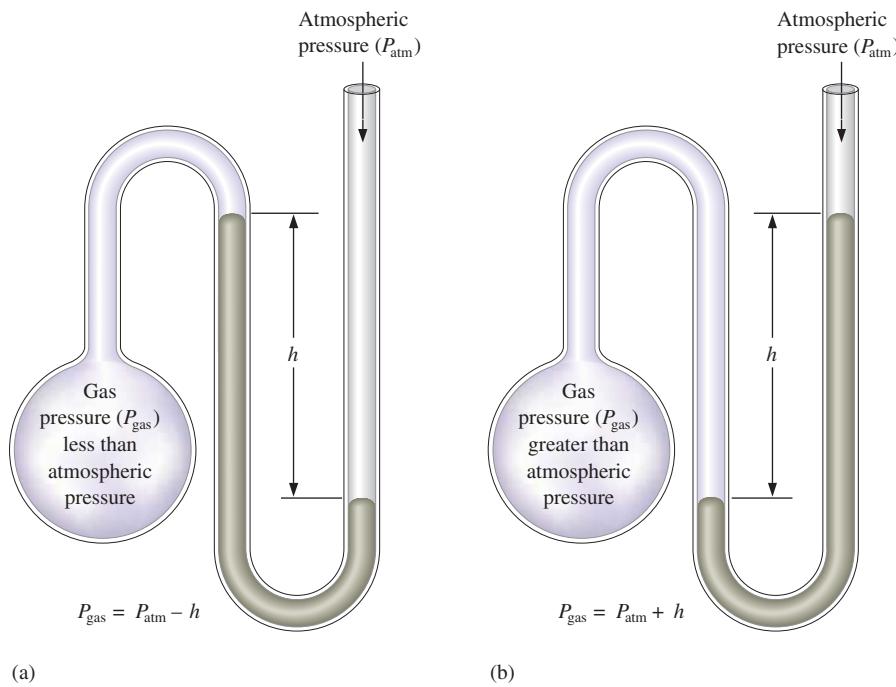
A device to measure atmospheric pressure, the **barometer**, was invented in 1643 by an Italian scientist named Evangelista Torricelli (1608–1647), who had been a student of Galileo. Torricelli's barometer is constructed by filling a glass tube with liquid mercury and inverting it in a dish of mercury, as shown in Fig. 5.2. Notice that a large quantity of mercury stays in the tube. In fact, at sea level the height of this column of mercury averages 760 mm. Why does this mercury stay in the tube, seemingly in defiance of gravity? Figure 5.2 illustrates how the pressure exerted by the atmospheric gases on the surface of mercury in the dish keeps the mercury in the tube.

Atmospheric pressure results from the mass of the air being pulled toward the center of the earth by gravity—in other words, it results from the weight of the air. Changing weather conditions cause the atmospheric pressure to vary, so the height of the column of Hg supported by the atmosphere at sea level varies; it is not always 760 mm. The meteorologist who says a "low" is approaching means that the atmospheric pressure is going to decrease. This condition often occurs in conjunction with a storm.

Atmospheric pressure also varies with altitude. For example, when Torricelli's experiment is done in Breckenridge, Colorado (elevation 9600 feet), the atmosphere supports a column of mercury only about 520 mm high because the air is "thinner." That is, there is less air pushing down on the earth's surface at Breckenridge than at sea level.

Units of Pressure

Because instruments used for measuring pressure, such as the **manometer** (Fig. 5.3), often contain mercury, the most commonly used units for pressure are based on the height

**FIGURE 5.3**

A simple manometer, a device for measuring the pressure of a gas in a container. The pressure of the gas is given by h (the difference in mercury levels) in units of torr (equivalent to mm Hg). (a) Gas pressure = atmospheric pressure $- h$. (b) Gas pressure = atmospheric pressure $+ h$.



Checking tire pressure.

of the mercury column (in millimeters) that the gas pressure can support. The unit **mm Hg** (millimeter of mercury) is often called the **torr** in honor of Torricelli. The terms *torr* and *mm Hg* are used interchangeably by chemists. A related unit for pressure is the **standard atmosphere** (abbreviated atm):

$$1 \text{ standard atmosphere} = 1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

However, since pressure is defined as force per unit area,

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

the fundamental units of pressure involve units of force divided by units of area. In the SI system, the unit of force is the newton (N) and the unit of area is meters squared (m^2). (For a review of the SI system, see Chapter 1.) Thus the unit of pressure in the SI system is newtons per meter squared (N/m^2) and is called the **pascal** (Pa). In terms of pascals, the standard atmosphere is

$$1 \text{ standard atmosphere} = 101,325 \text{ Pa}$$

Thus 1 atmosphere is about 10^5 pascals. Since the pascal is so small, and since it is not commonly used in the United States, we will use it sparingly in this book. However, converting from torrs or atmospheres to pascals is straightforward, as shown in Sample Exercise 5.1.

Sample Exercise 5.1

Pressure Conversions

The pressure of a gas is measured as 49 torr. Represent this pressure in both atmospheres and pascals.

Solution

$$\begin{aligned} 1 \text{ atm} &= 760 \text{ mm Hg} \\ &= 760 \text{ torr} \\ &= 101,325 \text{ Pa} \\ &= 29.92 \text{ in Hg} \\ &= 14.7 \text{ lb/in}^2 \end{aligned}$$

$$49 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 6.4 \times 10^{-2} \text{ atm}$$

$$6.4 \times 10^{-2} \text{ atm} \times \frac{101,325 \text{ Pa}}{1 \text{ atm}} = 6.5 \times 10^3 \text{ Pa}$$

See Exercises 5.27 and 5.28.

5.2 The Gas Laws of Boyle, Charles, and Avogadro

In this section we will consider several mathematical laws that relate the properties of gases. These laws derive from experiments involving careful measurements of the relevant gas properties. From these experimental results, the mathematical relationships among the properties can be discovered. These relationships are often represented pictorially by means of graphs (plots).

We will take a historical approach to these laws to give you some perspective on the scientific method in action.



Visualization: Boyle's Law: A Graphical View

Boyle's Law

The first quantitative experiments on gases were performed by an Irish chemist, Robert Boyle (1627–1691). Using a J-shaped tube closed at one end (Fig. 5.4), which he reportedly set up in the multistory entryway of his house, Boyle studied the relationship between the pressure of the trapped gas and its volume. Representative values from Boyle's experiments are given in Table 5.1. These data show that the product of the pressure and

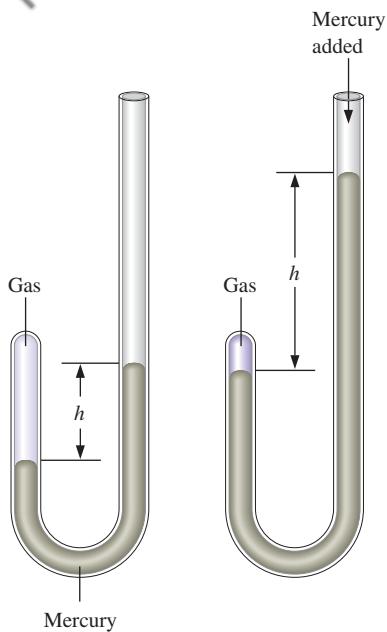


FIGURE 5.4
A J-tube similar to the one used by Boyle.

Boyle's law: $V \propto 1/P$ at constant temperature.

Graphing is reviewed in Appendix 1.3.

TABLE 5.1 Actual Data from Boyle's Experiment

Volume (in in^3)	Pressure (in Hg)	Pressure \times Volume (in Hg \times in^3)
117.5	12.0	14.1×10^2
87.2	16.0	14.0×10^2
70.7	20.0	14.1×10^2
58.8	24.0	14.1×10^2
44.2	32.0	14.1×10^2
35.3	40.0	14.1×10^2
29.1	48.0	14.0×10^2

volume for the trapped air sample is constant within the accuracies of Boyle's measurements (note the third column in Table 5.1). This behavior can be represented by the equation

$$PV = k$$

which is called **Boyle's law** and where k is a constant for a given sample of air at a specific temperature.

It is convenient to represent the data in Table 5.1 by using two different plots. The first type of plot, P versus V , forms a curve called a *hyperbola* shown in Fig. 5.5(a). Looking at this plot, note that as the volume drops by about half (from 58.8 to 29.1), the pressure doubles (from 24.0 to 48.0). In other words, there is an *inverse relationship* between pressure and volume. The second type of plot can be obtained by rearranging Boyle's law to give

$$V = \frac{k}{P} = k\frac{1}{P}$$

which is the equation for a straight line of the type

$$y = mx + b$$

where m represents the slope and b the intercept of the straight line. In this case, $y = V$, $x = 1/P$, $m = k$, and $b = 0$. Thus a plot of V versus $1/P$ using Boyle's data gives a straight line with an intercept of zero, as shown in Fig. 5.5(b).

In the three centuries since Boyle carried out his studies, the sophistication of measuring techniques has increased tremendously. The results of highly accurate measurements show that Boyle's law holds precisely only at very low pressures. Measurements at higher pressures reveal that PV is not constant but varies as the pressure is varied. Results for several gases at pressures below 1 atm are shown in Fig. 5.6. Note the very small changes that occur in the product PV as the pressure is changed at these low pressures. Such changes become

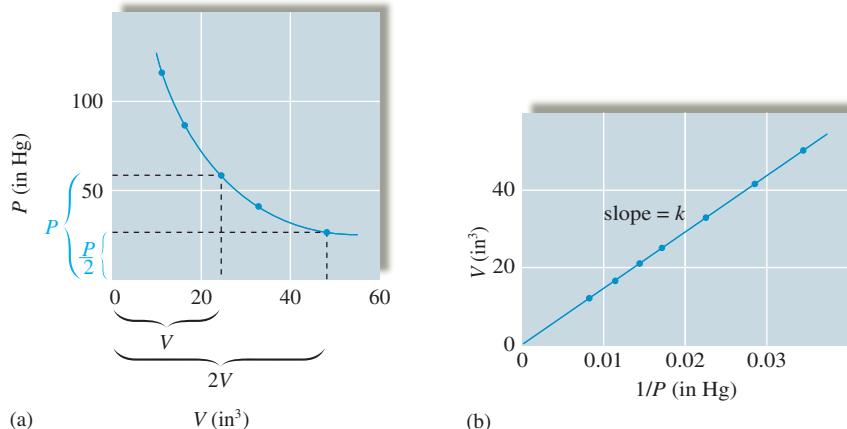
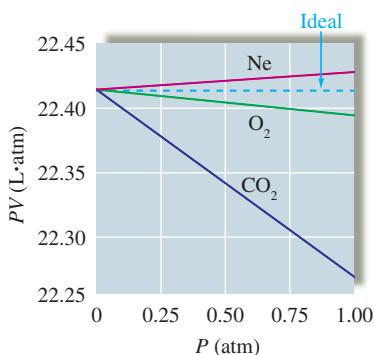


FIGURE 5.5
Plotting Boyle's data from Table 5.1. (a) A plot of P versus V shows that the volume doubles as the pressure is halved. (b) A plot of V versus $1/P$ gives a straight line. The slope of this line equals the value of the constant k .

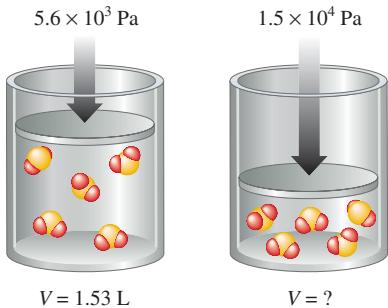
**FIGURE 5.6**

A plot of PV versus P for several gases at pressures below 1 atm. An ideal gas is expected to have a constant value of PV , as shown by the dotted line. Carbon dioxide shows the largest change in PV , and this change is actually quite small: PV changes from about $22.39 \text{ L} \cdot \text{atm}$ at 0.25 atm to $22.26 \text{ L} \cdot \text{atm}$ at 1.00 atm . Thus Boyle's law is a good approximation at these relatively low pressures.

more significant at much higher pressures, where the complex nature of the dependence of PV on pressure becomes more obvious. We will discuss these deviations and the reasons for them in detail in Section 5.8. A gas that strictly obeys Boyle's law is called an **ideal gas**. We will describe the characteristics of an ideal gas more completely in Section 5.3.

One common use of Boyle's law is to predict the new volume of a gas when the pressure is changed (at constant temperature), or vice versa. Because deviations from Boyle's law are so slight at pressures close to 1 atm, in our calculations we will assume that gases obey Boyle's law (unless stated otherwise).

Sample Exercise 5.2



As pressure increases, the volume of SO_2 decreases.

Boyle's law also can be written as

$$P_1 V_1 = P_2 V_2$$

Always check that your answer makes physical (common!) sense.

Boyle's Law I

Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53-L sample of gaseous SO_2 at a pressure of $5.6 \times 10^3 \text{ Pa}$. If the pressure is changed to $1.5 \times 10^4 \text{ Pa}$ at a constant temperature, what will be the new volume of the gas?

Solution

We can solve this problem using Boyle's law,

$$PV = k$$

which also can be written as

$$P_1 V_1 = k = P_2 V_2 \quad \text{or} \quad P_1 V_1 = P_2 V_2$$

where the subscripts 1 and 2 represent two states (conditions) of the gas (both at the same temperature). In this case,

$$\begin{aligned} P_1 &= 5.6 \times 10^3 \text{ Pa} & P_2 &= 1.5 \times 10^4 \text{ Pa} \\ V_1 &= 1.53 \text{ L} & V_2 &= ? \end{aligned}$$

We can solve the preceding equation for V_2 :

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{5.6 \times 10^3 \text{ Pa} \times 1.53 \text{ L}}{1.5 \times 10^4 \text{ Pa}} = 0.57 \text{ L}$$

The new volume will be 0.57 L.

See Exercise 5.33.

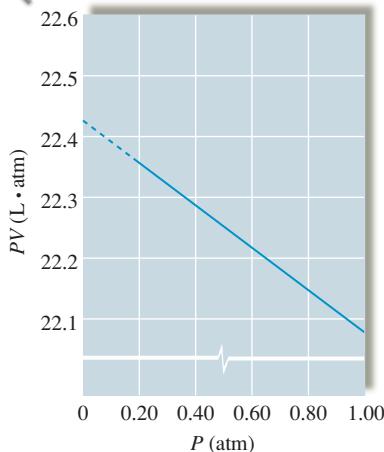
The fact that the volume decreases in Sample Exercise 5.2 makes sense because the pressure was increased. To help eliminate errors, make it a habit to check whether an answer to a problem makes physical sense.

We mentioned before that Boyle's law is only approximately true for real gases. To determine the significance of the deviations, studies of the effect of changing pressure on the volume of a gas are often done, as shown in Sample Exercise 5.3.

Sample Exercise 5.3

Boyle's Law II

In a study to see how closely gaseous ammonia obeys Boyle's law, several volume measurements were made at various pressures, using 1.0 mol NH_3 gas at a temperature of 0°C . Using the results listed on the following page, calculate the Boyle's law constant for NH_3 at the various pressures.

**FIGURE 5.7**

A plot of PV versus P for 1 mol of ammonia. The dashed line shows the extrapolation of the data to zero pressure to give the “ideal” value of PV of $22.41 \text{ L} \cdot \text{atm}$.

Experiment	Pressure (atm)	Volume (L)
1	0.1300	172.1
2	0.2500	89.28
3	0.3000	74.35
4	0.5000	44.49
5	0.7500	29.55
6	1.000	22.08

Solution

To determine how closely NH_3 gas follows Boyle’s law under these conditions, we calculate the value of k (in $\text{L} \cdot \text{atm}$) for each set of values:

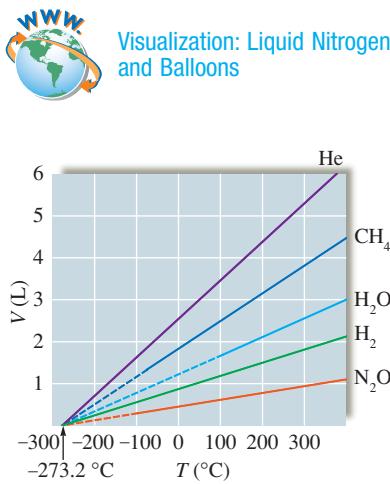
Experiment	1	2	3	4	5	6
$k = PV$	22.37	22.32	22.31	22.25	22.16	22.08

Although the deviations from true Boyle’s law behavior are quite small at these low pressures, note that the value of k changes regularly in one direction as the pressure is increased. Thus, to calculate the “ideal” value of k for NH_3 , we can plot PV versus P , as shown in Fig. 5.7, and extrapolate (extend the line beyond the experimental points) back to zero pressure, where, for reasons we will discuss later, a gas behaves most ideally. The value of k obtained by this extrapolation is $22.41 \text{ L} \cdot \text{atm}$. Notice that this is the same value obtained from similar plots for the gases CO_2 , O_2 , and Ne at 0°C , as shown in Fig. 5.6.

See Exercise 5.97.

Charles’s Law

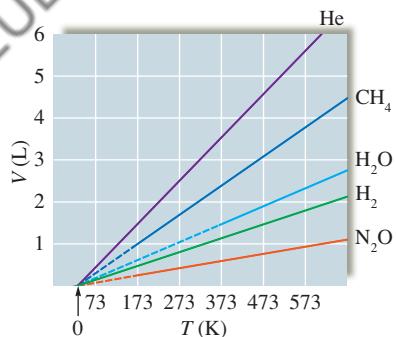
In the century following Boyle’s findings, scientists continued to study the properties of gases. One of these scientists was a French physicist, Jacques Charles (1746–1823), who was the first person to fill a balloon with hydrogen gas and who made the first solo balloon flight. Charles found in 1787 that the volume of a gas at constant pressure increases *linearly* with the temperature of the gas. That is, a plot of the volume of a gas (at constant pressure) versus its temperature ($^\circ\text{C}$) gives a straight line. This behavior is shown for samples of several gases in Fig. 5.8. The slopes of the lines in this graph are different

**FIGURE 5.8**

Plots of V versus T ($^\circ\text{C}$) for several gases. The solid lines represent experimental measurements on gases. The dashed lines represent extrapolation of the data into regions where these gases would become liquids or solids. Note that the samples of the various gases contain different numbers of moles.



A snowmaking machine, in which water is blown through nozzles by compressed air. The mixture is cooled by expansion to form ice crystals of snow.

**FIGURE 5.9**

Plots of V versus T as in Fig. 5.8, except here the Kelvin scale is used for temperature.



Visualization: Charles's Law: A Graphical View

Charles's law: $V \propto T$ (expressed in K) of constant pressure.

Sample Exercise 5.4

because the samples contain different numbers of moles of gas. A very interesting feature of these plots is that the volumes of all the gases extrapolate to zero at the same temperature, -273.2°C . On the Kelvin temperature scale this point is defined as 0 K, which leads to the following relationship between the Kelvin and Celsius scales:

$$K = ^\circ\text{C} + 273$$

When the volumes of the gases shown in Fig. 5.8 are plotted versus temperature on the Kelvin scale, the plots in Fig. 5.9 result. In this case, the volume of each gas is *directly proportional to temperature* and extrapolates to zero when the temperature is 0 K. This behavior is represented by the equation known as **Charles's law**,

$$V = bT$$

where T is in kelvins and b is a proportionality constant.

Before we illustrate the uses of Charles's law, let us consider the importance of 0 K. At temperatures below this point, the extrapolated volumes would become negative. The fact that a gas cannot have a negative volume suggests that 0 K has a special significance. In fact, 0 K is called **absolute zero**, and there is much evidence to suggest that this temperature cannot be attained. Temperatures of approximately 0.000001 K have been produced in laboratories, but 0 K has never been reached.

Charles's Law

A sample of gas at 15°C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38°C and 1 atm?

Solution

Charles's law, which describes the dependence of the volume of a gas on temperature at constant pressure, can be used to solve this problem. Charles's law in the form $V = bT$ can be rearranged to

$$\frac{V}{T} = b$$

An equivalent statement is

$$\frac{V_1}{T_1} = b = \frac{V_2}{T_2}$$

where the subscripts 1 and 2 represent two states for a given sample of gas at constant pressure. In this case, we are given the following (note that the temperature values *must* be changed to the Kelvin scale):

$$\begin{aligned} T_1 &= 15^\circ\text{C} + 273 = 288 \text{ K} & T_2 &= 38^\circ\text{C} + 273 = 311 \text{ K} \\ V_1 &= 2.58 \text{ L} & V_2 &= ? \end{aligned}$$

Solving for V_2 gives

$$V_2 = \left(\frac{T_2}{T_1} \right) V_1 = \left(\frac{311 \text{ K}}{288 \text{ K}} \right) 2.58 \text{ L} = 2.79 \text{ L}$$

Reality Check: The new volume is greater than the initial volume, which makes physical sense because the gas will expand as it is heated.

See Exercise 5.35.

Avogadro's Law

In Chapter 2 we noted that in 1811 the Italian chemist Avogadro postulated that equal volumes of gases at the same temperature and pressure contain the same number of

“particles.” This observation is called **Avogadro’s law**, which is illustrated by Fig. 5.10. Stated mathematically, Avogadro’s law is

$$V = an$$

where V is the volume of the gas, n is the number of moles of gas particles, and a is a proportionality constant. This equation states that *for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles of gas*. This relationship is obeyed closely by gases at low pressures.

Sample Exercise 5.5

Avogadro’s Law

Avogadro’s law also can be written as

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Solution

The balanced equation for the reaction is



To calculate the moles of O_3 produced, we must use the appropriate mole ratio:

$$0.50 \text{ mol O}_2 \times \frac{2 \text{ mol O}_3}{3 \text{ mol O}_2} = 0.33 \text{ mol O}_3$$

Avogadro’s law states that $V = an$, which can be rearranged to give

$$\frac{V}{n} = a$$

Since a is a constant, an alternative representation is

$$\frac{V_1}{n_1} = a = \frac{V_2}{n_2}$$

where V_1 is the volume of n_1 moles of O_2 gas and V_2 is the volume of n_2 moles of O_3 gas. In this case we have

$$\begin{aligned} n_1 &= 0.50 \text{ mol} & n_2 &= 0.33 \text{ mol} \\ V_1 &= 12.2 \text{ L} & V_2 &= ? \end{aligned}$$

Solving for V_2 gives

$$V_2 = \left(\frac{n_2}{n_1} \right) V_1 = \left(\frac{0.33 \text{ mol}}{0.50 \text{ mol}} \right) 12.2 \text{ L} = 8.1 \text{ L}$$

Reality Check: Note that the volume decreases, as it should, since fewer moles of gas molecules will be present after O_2 is converted to O_3 .

See Exercises 5.35 and 5.36.

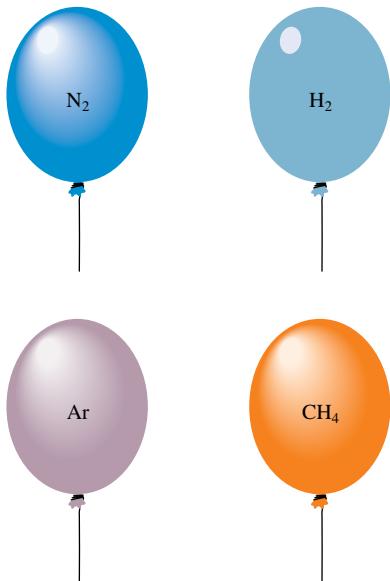


FIGURE 5.10

These balloons each hold 1.0 L of gas at 25°C and 1 atm. Each balloon contains 0.041 mol of gas, or 2.5×10^{22} molecules.

5.3 The Ideal Gas Law

We have considered three laws that describe the behavior of gases as revealed by experimental observations:

$$\text{Boyle's law: } V = \frac{k}{P} \quad (\text{at constant } T \text{ and } n)$$

$$\text{Charles's law: } V = bT \quad (\text{at constant } P \text{ and } n)$$

$$\text{Avogadro's law: } V = an \quad (\text{at constant } T \text{ and } P)$$

These relationships, which show how the volume of a gas depends on pressure, temperature, and number of moles of gas present, can be combined as follows:

$$V = R \left(\frac{Tn}{P} \right)$$

where R is the combined proportionality constant called the **universal gas constant**. When the pressure is expressed in atmospheres and the volume in liters, R has the value $0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$. The preceding equation can be rearranged to the more familiar form of the **ideal gas law**:

$$PV = nRT$$

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

Visualization: The Ideal Gas Law, $PV = nRT$



The ideal gas law applies best at pressures smaller than 1 atm.

The ideal gas law is an *equation of state* for a gas, where the state of the gas is its condition at a given time. A particular *state* of a gas is described by its pressure, volume, temperature, and number of moles. Knowledge of any three of these properties is enough to completely define the state of a gas, since the fourth property can then be determined from the equation for the ideal gas law.

It is important to recognize that the ideal gas law is an empirical equation—it is based on experimental measurements of the properties of gases. A gas that obeys this equation is said to behave *ideally*. The ideal gas equation is best regarded as a limiting law—it expresses behavior that real gases *approach* at low pressures and high temperatures. Therefore, an ideal gas is a hypothetical substance. However, most gases obey the ideal gas equation closely enough at pressures below 1 atm that only minimal errors result from assuming ideal behavior. Unless you are given information to the contrary, you should assume ideal gas behavior when solving problems involving gases in this text.

The ideal gas law can be used to solve a variety of problems. Sample Exercise 5.6 demonstrates one type, where you are asked to find one property characterizing the state of a gas, given the other three.

Sample Exercise 5.6

Ideal Gas Law I

A sample of hydrogen gas (H_2) has a volume of 8.56 L at a temperature of 0°C and a pressure of 1.5 atm. Calculate the moles of H_2 molecules present in this gas sample.

Solution

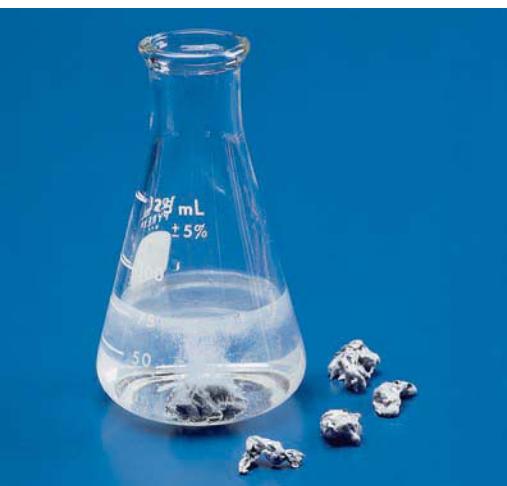
Solving the ideal gas law for n gives

$$n = \frac{PV}{RT}$$

In this case $P = 1.5 \text{ atm}$, $V = 8.56 \text{ L}$, $T = 0^\circ\text{C} + 273 = 273 \text{ K}$, and $R = 0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$. Thus

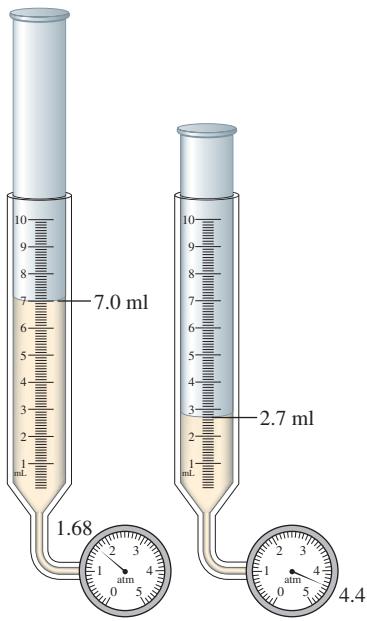
$$n = \frac{(1.5 \text{ atm})(8.56 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(273 \text{ K})} = 0.57 \text{ mol}$$

See Exercises 5.37 through 5.42.



The reaction of zinc with hydrochloric acid to produce bubbles of hydrogen gas.

The ideal gas law is also used to calculate the changes that will occur when the conditions of the gas are changed.

Sample Exercise 5.7**Ideal Gas Law II**

As pressure increases, the volume decreases.

Suppose we have a sample of ammonia gas with a volume of 7.0 mL at a pressure of 1.68 atm. The gas is compressed to a volume of 2.7 mL at a constant temperature. Use the ideal gas law to calculate the final pressure.

Solution

The basic assumption we make when using the ideal gas law to describe a change in state for a gas is that the equation applies equally well to both the initial and the final states. In dealing with a change in state, we always *place the variables that change on one side of the equals sign and the constants on the other*. In this case the pressure and volume change, and the temperature and the number of moles remain constant (as does R , by definition). Thus we write the ideal gas law as

$$PV = nRT$$

↑ ↑
Change Remain constant

Since n and T remain the same in this case, we can write $P_1V_1 = nRT$ and $P_2V_2 = nRT$. Combining these gives

$$P_1V_1 = nRT = P_2V_2 \quad \text{or} \quad P_1V_1 = P_2V_2$$

We are given $P_1 = 1.68$ atm, $V_1 = 7.0$ mL, and $V_2 = 2.7$ mL. Solving for P_2 thus gives

$$P_2 = \left(\frac{V_1}{V_2} \right) P_1 = \left(\frac{7.0 \text{ mL}}{2.7 \text{ mL}} \right) 1.68 \text{ atm} = 4.4 \text{ atm}$$

Reality Check: Does this answer make sense? The volume decreased (at constant temperature), so the pressure should increase, as the result of the calculation indicates. Note that the calculated final pressure is 4.4 atm. Most gases do not behave ideally above 1 atm. Therefore, we might find that if we *measured* the pressure of this gas sample, the observed pressure would differ slightly from 4.4 atm.

See Exercises 5.43 and 5.44.

Sample Exercise 5.8**Ideal Gas Law III**

A sample of methane gas that has a volume of 3.8 L at 5°C is heated to 86°C at constant pressure. Calculate its new volume.

Solution

To solve this problem, we take the ideal gas law and segregate the changing variables and the constants by placing them on opposite sides of the equation. In this case, volume and temperature change, and the number of moles and pressure (and, of course, R) remain constant. Thus $PV = nRT$ becomes

$$\frac{V}{T} = \frac{nR}{P}$$

which leads to

$$\frac{V_1}{T_1} = \frac{nR}{P} \quad \text{and} \quad \frac{V_2}{T_2} = \frac{nR}{P}$$

Combining these gives

$$\frac{V_1}{T_1} = \frac{nR}{P} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

We are given

$$\begin{aligned} T_1 &= 5^\circ\text{C} + 273 = 278 \text{ K} & T_2 &= 86^\circ\text{C} + 273 = 359 \text{ K} \\ V_1 &= 3.8 \text{ L} & V_2 &= ? \end{aligned}$$

Thus

$$V_2 = \frac{T_2 V_1}{T_1} = \frac{(359 \text{ K})(3.8 \text{ L})}{278 \text{ K}} = 4.9 \text{ L}$$

Reality Check: Is the answer sensible? In this case the temperature increased (at constant pressure), so the volume should increase. Thus the answer makes sense.

See Exercises 5.45 and 5.46.

The problem in Sample Exercise 5.8 could be described as a “Charles’s law problem,” whereas the problem in Sample Exercise 5.7 might be called a “Boyle’s law problem.” In both cases, however, we started with the ideal gas law. The real advantage of using the ideal gas law is that it applies to virtually any problem dealing with gases and is easy to remember.

Sample Exercise 5.9

Ideal Gas Law IV

A sample of diborane gas (B_2H_6), a substance that bursts into flame when exposed to air, has a pressure of 345 torr at a temperature of -15°C and a volume of 3.48 L. If conditions are changed so that the temperature is 36°C and the pressure is 468 torr, what will be the volume of the sample?

Solution

Since, for this sample, pressure, temperature, and volume all change while the number of moles remains constant, we use the ideal gas law in the form

$$\frac{PV}{T} = nR$$

which leads to

$$\frac{P_1 V_1}{T_1} = nR = \frac{P_2 V_2}{T_2} \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Then

$$V_2 = \frac{T_2 P_1 V_1}{T_1 P_2}$$

We have

$$\begin{aligned} P_1 &= 345 \text{ torr} & P_2 &= 468 \text{ torr} \\ T_1 &= -15^\circ\text{C} + 273 = 258 \text{ K} & T_2 &= 36^\circ\text{C} + 273 = 309 \text{ K} \\ V_1 &= 3.48 \text{ L} & V_2 &= ? \end{aligned}$$

Thus

$$V_2 = \frac{(309 \text{ K})(345 \text{ torr})(3.48 \text{ L})}{(258 \text{ K})(468 \text{ torr})} = 3.07 \text{ L}$$

See Exercises 5.47 and 5.48.



Visualization: Changes in Gas Volume, Pressure, and Concentration

Always convert the temperature to the Kelvin scale when applying the ideal gas law.

Since the equation used in Sample Exercise 5.9 involves a *ratio* of pressures, it was unnecessary to convert pressures to units of atmospheres. The units of torrs cancel. (You

will obtain the same answer by inserting $P_1 = \frac{345}{760}$ and $P_2 = \frac{468}{760}$ into the equation.) However, temperature *must always* be converted to the Kelvin scale; since this conversion involves *addition* of 273, the conversion factor does not cancel. Be careful.

One of the many other types of problems dealing with gases that can be solved using the ideal gas law is illustrated in Sample Exercise 5.10.

Sample Exercise 5.10

Ideal Gas Law V

A sample containing 0.35 mol argon gas at a temperature of 13°C and a pressure of 568 torr is heated to 56°C and a pressure of 897 torr. Calculate the change in volume that occurs.

Solution

We use the ideal gas law to find the volume for each set of conditions:

State 1	State 2
$n_1 = 0.35 \text{ mol}$	$n_2 = 0.35 \text{ mol}$
$P_1 = 568 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.747 \text{ atm}$	$P_2 = 897 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.18 \text{ atm}$
$T_1 = 13^\circ\text{C} + 273 = 286 \text{ K}$	$T_2 = 56^\circ\text{C} + 273 = 329 \text{ K}$

Solving the ideal gas law for volume gives

$$V_1 = \frac{n_1RT_1}{P_1} = \frac{(0.35 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(286 \text{ K})}{(0.747 \text{ atm})} = 11 \text{ L}$$

and

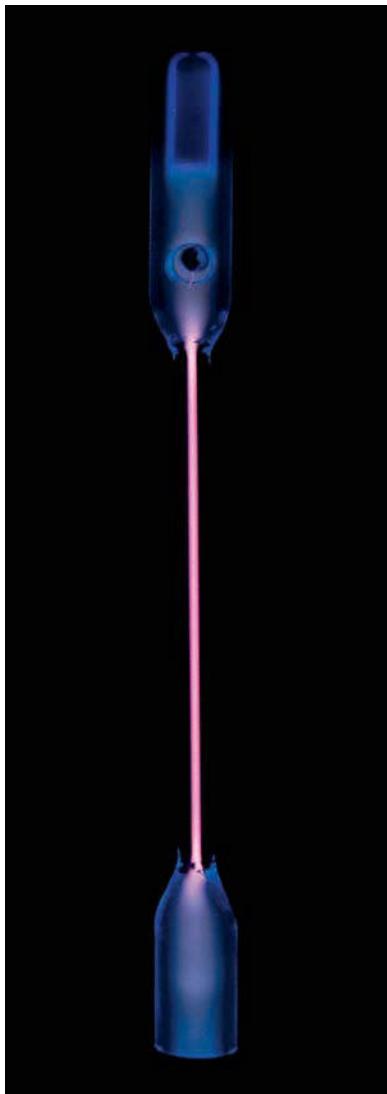
$$V_2 = \frac{n_2RT_2}{P_2} = \frac{(0.35 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(329 \text{ K})}{(1.18 \text{ atm})} = 8.0 \text{ L}$$

Thus, in going from state 1 to state 2, the volume changes from 11 L to 8.0 L. The change in volume, ΔV (Δ is the Greek capital letter delta), is then

$$\Delta V = V_2 - V_1 = 8.0 \text{ L} - 11 \text{ L} = -3 \text{ L}$$

The *change* in volume is negative because the volume decreases. Note that for this problem (unlike Sample Exercise 5.9) the pressures must be converted from torrs to atmospheres, as required by the atmosphere part of the units for R , since each volume was found separately and the conversion factor does not cancel.

See Exercise 5.49.



Argon glowing in a discharge tube.

When 273.15 K is used in this calculation, the molar volume obtained in Sample Exercise 5.3 is the same value as 22.41 L.

5.4 Gas Stoichiometry

Suppose we have 1 mole of an ideal gas at 0°C (273.2 K) and 1 atm. From the ideal gas law, the volume of the gas is given by

$$V = \frac{nRT}{P} = \frac{(1.000 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(273.2 \text{ K})}{1.000 \text{ atm}} = 22.42 \text{ L}$$

TABLE 5.2 Molar Volumes for Various Gases at 0°C and 1 atm

Gas	Molar Volume (L)
Oxygen (O ₂)	22.397
Nitrogen (N ₂)	22.402
Hydrogen (H ₂)	22.433
Helium (He)	22.434
Argon (Ar)	22.397
Carbon dioxide (CO ₂)	22.260
Ammonia (NH ₃)	22.079



FIGURE 5.11

22.4 L of a gas would just fit into this box.

This volume of 22.42 liters is the **molar volume** of an ideal gas (at 0°C and 1 atm). The measured molar volumes of several gases are listed in Table 5.2. Note that the molar volumes of some of the gases are very close to the ideal value, while others deviate significantly. Later in this chapter we will discuss some of the reasons for the deviations.

The conditions 0°C and 1 atm, called **standard temperature and pressure** (abbreviated **STP**), are common reference conditions for the properties of gases. For example, the molar volume of an ideal gas is 22.42 liters at STP (see Fig. 5.11).

STP: 0°C and 1 atm

Sample Exercise 5.11

Gas Stoichiometry I

A sample of nitrogen gas has a volume of 1.75 L at STP. How many moles of N₂ are present?

Solution

We could solve this problem by using the ideal gas equation, but we can take a shortcut by using the molar volume of an ideal gas at STP. Since 1 mole of an ideal gas at STP has a volume of 22.42 L, 1.75 L of N₂ at STP will contain less than 1 mole. We can find how many moles using the ratio of 1.75 L to 22.42 L:

$$1.75 \text{ L N}_2 \times \frac{1 \text{ mol N}_2}{22.42 \text{ L N}_2} = 7.81 \times 10^{-2} \text{ mol N}_2$$

See Exercises 5.51 and 5.52.

Many chemical reactions involve gases. By assuming ideal behavior for these gases, we can carry out stoichiometric calculations if the pressure, volume, and temperature of the gases are known.

Sample Exercise 5.12

Gas Stoichiometry II

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate (CaCO₃). Calculate the volume of CO₂ at STP produced from the decomposition of 152 g CaCO₃ by the reaction



Solution

We employ the same strategy we used in the stoichiometry problems earlier in this book. That is, we compute the number of moles of CaCO_3 consumed and the number of moles of CO_2 produced. The moles of CO_2 can then be converted to volume using the molar volume of an ideal gas.

Using the molar mass of CaCO_3 (100.09 g/mol), we can calculate the number of moles of CaCO_3 :

$$152 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} = 1.52 \text{ mol CaCO}_3$$

Since each mole of CaCO_3 produces a mole of CO_2 , 1.52 mol CO_2 will be formed. We can compute the volume of CO_2 at STP by using the molar volume:

$$1.52 \text{ mol CO}_2 \times \frac{22.42 \text{ L CO}_2}{1 \text{ mol CO}_2} = 34.1 \text{ L CO}_2$$

Thus the decomposition of 152 g CaCO_3 produces 34.1 L CO_2 at STP.

See Exercises 5.53 through 5.56.

Remember that the molar volume of an ideal gas is 22.42 L when measured at STP.

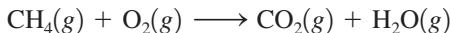
Note that in Sample Exercise 5.12 the final step involved calculation of the volume of gas from the number of moles. Since the conditions were specified as STP, we were able to use the molar volume of a gas at STP. If the conditions of a problem are different from STP, the ideal gas law must be used to compute the volume.

Sample Exercise 5.13**Gas Stoichiometry III**

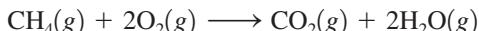
A sample of methane gas having a volume of 2.80 L at 25°C and 1.65 atm was mixed with a sample of oxygen gas having a volume of 35.0 L at 31°C and 1.25 atm. The mixture was then ignited to form carbon dioxide and water. Calculate the volume of CO_2 formed at a pressure of 2.50 atm and a temperature of 125°C.

Solution

From the description of the reaction, the unbalanced equation is



which can be balanced to give



Next, we must find the limiting reactant, which requires calculating the numbers of moles of each reactant. We convert the given volumes of methane and oxygen to moles using the ideal gas law as follows:

$$n_{\text{CH}_4} = \frac{PV}{RT} = \frac{(1.65 \text{ atm})(2.80 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 0.189 \text{ mol}$$

$$n_{\text{O}_2} = \frac{PV}{RT} = \frac{(1.25 \text{ atm})(35.0 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(304 \text{ K})} = 1.75 \text{ mol}$$

In the balanced equation for the combustion reaction, 1 mol CH_4 requires 2 mol O_2 . Thus the moles of O_2 required by 0.189 mol CH_4 can be calculated as follows:

$$0.189 \text{ mol CH}_4 \times \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} = 0.378 \text{ mol O}_2$$

Since 1.75 mol O₂ is available, O₂ is in excess. The limiting reactant is CH₄. The number of moles of CH₄ available must be used to calculate the number of moles of CO₂ produced:

$$0.189 \text{ mol CH}_4 \times \frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} = 0.189 \text{ mol CO}_2$$

Since the conditions stated are not STP, we must use the ideal gas law to calculate the volume:

$$V = \frac{nRT}{P}$$

In this case $n = 0.189 \text{ mol}$, $T = 125^\circ\text{C} + 273 = 398 \text{ K}$, $P = 2.50 \text{ atm}$, and $R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$. Thus

$$V = \frac{(0.189 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(398 \text{ K})}{2.50 \text{ atm}} = 2.47 \text{ L}$$

This represents the volume of CO₂ produced under these conditions.

See Exercises 5.57 and 5.58.

Molar Mass of a Gas

One very important use of the ideal gas law is in the calculation of the molar mass (molecular weight) of a gas from its measured density. To see the relationship between gas density and molar mass, consider that the number of moles of gas n can be expressed as

$$n = \frac{\text{grams of gas}}{\text{molar mass}} = \frac{\text{mass}}{\text{molar mass}} = \frac{m}{\text{molar mass}}$$

Substitution into the ideal gas equation gives

$$P = \frac{nRT}{V} = \frac{(m/\text{molar mass})RT}{V} = \frac{m(RT)}{V(\text{molar mass})}$$

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

However, m/V is the gas density d in units of grams per liter. Thus

$$P = \frac{dRT}{\text{molar mass}}$$

or

$$\text{Molar mass} = \frac{dRT}{P} \quad (5.1)$$

Thus, if the density of a gas at a given temperature and pressure is known, its molar mass can be calculated.

Sample Exercise 5.14

Gas Density/Molar Mass

The density of a gas was measured at 1.50 atm and 27°C and found to be 1.95 g/L. Calculate the molar mass of the gas.

Solution

Using Equation (5.1), we calculate the molar mass as follows:

$$\text{Molar mass} = \frac{dRT}{P} = \frac{\left(1.95 \frac{\text{g}}{\text{L}}\right)\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(300. \text{ K})}{1.50 \text{ atm}} = 32.0 \text{ g/mol}$$

Reality Check: These are the units expected for molar mass.

See Exercises 5.61 through 5.64.

You could memorize the equation involving gas density and molar mass, but it is better simply to remember the total gas equation, the definition of density, and the relationship between number of moles and molar mass. You can then derive the appropriate equation when you need it. This approach ensures that you understand the concepts and means one less equation to memorize.

5.5 Dalton's Law of Partial Pressures

Among the experiments that led John Dalton to propose the atomic theory were his studies of mixtures of gases. In 1803 Dalton summarized his observations as follows: *For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.* This statement, known as **Dalton's law of partial pressures**, can be expressed as follows:

$$P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \dots$$

where the subscripts refer to the individual gases (gas 1, gas 2, and so on). The symbols P_1 , P_2 , P_3 , and so on represent each **partial pressure**, the pressure that a particular gas would exert if it were alone in the container.

Assuming that each gas behaves ideally, the partial pressure of each gas can be calculated from the ideal gas law:

$$P_1 = \frac{n_1RT}{V}, \quad P_2 = \frac{n_2RT}{V}, \quad P_3 = \frac{n_3RT}{V}, \quad \dots$$

The total pressure of the mixture P_{TOTAL} can be represented as

$$\begin{aligned} P_{\text{TOTAL}} &= P_1 + P_2 + P_3 + \dots = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \dots \\ &= (n_1 + n_2 + n_3 + \dots) \left(\frac{RT}{V} \right) \\ &= n_{\text{TOTAL}} \left(\frac{RT}{V} \right) \end{aligned}$$

where n_{TOTAL} is the sum of the numbers of moles of the various gases. Thus, for a mixture of ideal gases, it is the *total number of moles of particles* that is important, not the identity or composition of the involved gas particles. This idea is illustrated in Fig. 5.12.

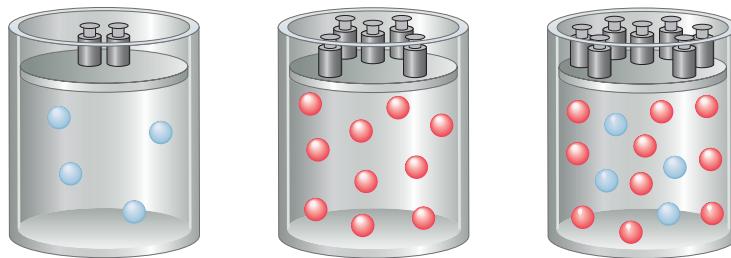


FIGURE 5.12

The partial pressure of each gas in a mixture of gases in a container depends on the number of moles of that gas. The total pressure is the sum of the partial pressures and depends on the total moles of gas particles present, no matter what they are.

This important observation indicates some fundamental characteristics of an ideal gas. The fact that the pressure exerted by an ideal gas is not affected by the identity (composition) of the gas particles reveals two things about ideal gases: (1) the volume of the individual gas particle must not be important, and (2) the forces among the particles must not be important. If these factors were important, the pressure exerted by the gas would depend on the nature of the individual particles. These observations will strongly influence the model that we will eventually construct to explain ideal gas behavior.

Sample Exercise 5.15

Dalton's Law I

Mixtures of helium and oxygen can be used in scuba diving tanks to help prevent “the bends.” For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O₂ at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

Solution

The first step is to calculate the number of moles of each gas using the ideal gas law in the form:

$$n = \frac{PV}{RT}$$

$$n_{\text{He}} = \frac{(1.0 \text{ atm})(46 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 1.9 \text{ mol}$$

$$n_{\text{O}_2} = \frac{(1.0 \text{ atm})(12 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.49 \text{ mol}$$

The tank containing the mixture has a volume of 5.0 L, and the temperature is 25°C. We can use these data and the ideal gas law to calculate the partial pressure of each gas:

$$P = \frac{nRT}{V}$$

$$P_{\text{He}} = \frac{(1.9 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{5.0 \text{ L}} = 9.3 \text{ atm}$$

$$P_{\text{O}_2} = \frac{(0.49 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{5.0 \text{ L}} = 2.4 \text{ atm}$$

The total pressure is the sum of the partial pressures:

$$P_{\text{TOTAL}} = P_{\text{He}} + P_{\text{O}_2} = 9.3 \text{ atm} + 2.4 \text{ atm} = 11.7 \text{ atm}$$

See Exercises 5.65 and 5.66.

At this point we need to define the **mole fraction**: *the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture*. The Greek lowercase letter chi (χ) is used to symbolize the mole fraction. For example, for a given component in a mixture, the mole fraction χ_1 is

$$\chi_1 = \frac{n_1}{n_{\text{TOTAL}}} = \frac{n_1}{n_1 + n_2 + n_3 + \dots}$$



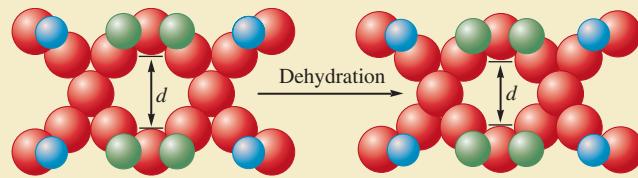
CHEMICAL IMPACT

Separating Gases

Assume you work for an oil company that owns a huge natural gas reservoir containing a mixture of methane and nitrogen gases. In fact, the gas mixture contains so much nitrogen that it is unusable as a fuel. Your job is to separate the nitrogen (N_2) from the methane (CH_4). How might you accomplish this task? You clearly need some sort of “molecular filter” that will stop the slightly larger methane molecules (size ≈ 430 pm) and allow the nitrogen molecules (size ≈ 410 pm) to pass through. To accomplish the separation of molecules so similar in size will require a very precise “filter.”

The good news is that such a filter exists. Recent work by Steven Kuznick and Valerie Bell at Engelhard Corporation in New Jersey and Michael Tsapatsis at the University of Massachusetts has produced a “molecular sieve” in which the pore (passage) sizes can be adjusted precisely enough to separate N_2 molecules from CH_4 molecules. The material involved is a special hydrated titanosilicate (contains H_2O , Ti, Si, O, and Sr) compound patented by Engelhard known

as ETS-4 (Engelhard TitanoSilicate-4). When sodium ions are substituted for the strontium ions in ETS-4 and the new material is carefully dehydrated, a uniform and controllable pore-size reduction occurs (see figure). The researchers have shown that the material can be used to separate N_2 (≈ 410 pm) from O_2 (≈ 390 pm). They have also shown that it is possible to reduce the nitrogen content of natural gas from 18% to less than 5% with a 90% recovery of methane.



Molecular sieve framework of titanium (blue), silicon (green), and oxygen (red) atoms contracts on heating—at room temperature (left), $d = 4.27 \text{ \AA}$; at 250°C (right), $d = 3.94 \text{ \AA}$.

From the ideal gas equation we know that the number of moles of a gas is directly proportional to the pressure of the gas, since

$$n = P \left(\frac{V}{RT} \right)$$

That is, for each component in the mixture,

$$n_1 = P_1 \left(\frac{V}{RT} \right), \quad n_2 = P_2 \left(\frac{V}{RT} \right), \quad \dots$$

Therefore, we can represent the mole fraction in terms of pressures:

$$\begin{aligned} \chi_1 &= \frac{n_1}{n_{\text{TOTAL}}} = \frac{\overbrace{P_1(V/RT)}^{n_1}}{\underbrace{P_1(V/RT)}_{n_1} + \underbrace{P_2(V/RT)}_{n_2} + \underbrace{P_3(V/RT)}_{n_3} + \dots} \\ &= \frac{(V/RT)P_1}{(V/RT)(P_1 + P_2 + P_3 + \dots)} \\ &= \frac{P_1}{P_1 + P_2 + P_3 + \dots} = \frac{P_1}{P_{\text{TOTAL}}} \end{aligned}$$

In fact, the mole fraction of each component in a mixture of ideal gases is directly related to its partial pressure:

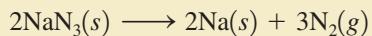
$$\chi_2 = \frac{n_2}{n_{\text{TOTAL}}} = \frac{P_2}{P_{\text{TOTAL}}}$$



CHEMICAL IMPACT

The Chemistry of Air Bags

Most experts agree that air bags represent a very important advance in automobile safety. These bags, which are stored in the auto's steering wheel or dash, are designed to inflate rapidly (within about 40 ms) in the event of a crash, cushioning the front-seat occupants against impact. The bags then deflate immediately to allow vision and movement after the crash. Air bags are activated when a severe deceleration (an impact) causes a steel ball to compress a spring and electrically ignite a detonator cap, which, in turn, causes sodium azide (NaN_3) to decompose explosively, forming sodium and nitrogen gas:



This system works very well and requires a relatively small amount of sodium azide (100 g yields 56 L $\text{N}_2(g)$ at 25°C and 1.0 atm).

When a vehicle containing air bags reaches the end of its useful life, the sodium azide present in the activators must be given proper disposal. Sodium azide, besides being explosive, has a toxicity roughly equal to that of sodium

cyanide. It also forms hydrazoic acid (HN_3), a toxic and explosive liquid, when treated with acid.

The air bag represents an application of chemistry that has already saved thousands of lives.



Inflated air bags.

Sample Exercise 5.16

Dalton's Law II

The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present.

Solution

The mole fraction of O_2 can be calculated from the equation

$$\chi_{\text{O}_2} = \frac{P_{\text{O}_2}}{P_{\text{TOTAL}}} = \frac{156 \text{ torr}}{743 \text{ torr}} = 0.210$$

Note that the mole fraction has no units.

See Exercise 5.69.

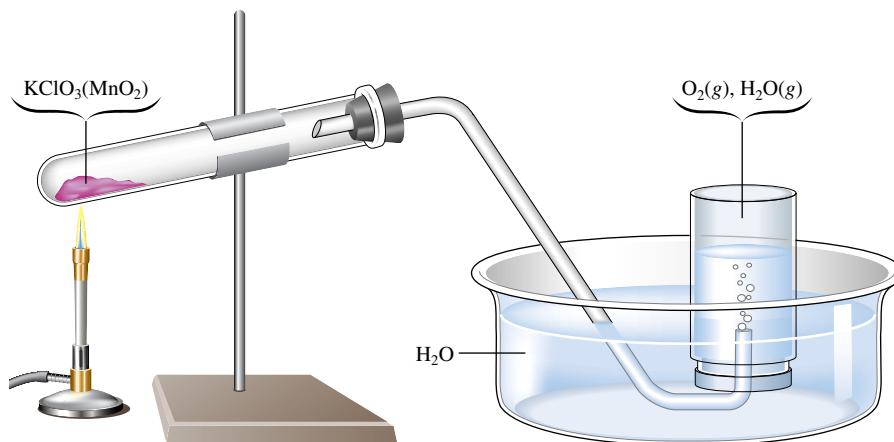
The expression for the mole fraction,

$$\chi_1 = \frac{P_1}{P_{\text{TOTAL}}}$$

can be rearranged to give

$$P_1 = \chi_1 \times P_{\text{TOTAL}}$$

That is, *the partial pressure of a particular component of a gaseous mixture is the mole fraction of that component times the total pressure.*

**FIGURE 5.13**

The production of oxygen by thermal decomposition of KClO_3 . The MnO_2 is mixed with the KClO_3 to make the reaction faster.

Sample Exercise 5.17**Dalton's Law III**

The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N_2 in air when the atmospheric pressure is 760. torr.

Solution

The partial pressure of N_2 can be calculated as follows:

$$P_{\text{N}_2} = \chi_{\text{N}_2} \times P_{\text{TOTAL}} = 0.7808 \times 760. \text{ torr} = 593 \text{ torr}$$

See Exercise 5.70.

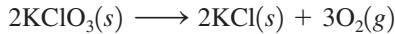
Collecting a Gas over Water

Vapor pressure will be discussed in detail in Chapter 10. A table of water vapor pressure values is given in Section 10.8.

A mixture of gases results whenever a gas is collected by displacement of water. For example, Fig. 5.13 shows the collection of oxygen gas produced by the decomposition of solid potassium chlorate. In this situation, the gas in the bottle is a mixture of water vapor and the oxygen being collected. Water vapor is present because molecules of water escape from the surface of the liquid and collect in the space above the liquid. Molecules of water also return to the liquid. When the rate of escape equals the rate of return, the number of water molecules in the vapor state remains constant, and thus the pressure of water vapor remains constant. This pressure, which depends on temperature, is called the *vapor pressure of water*.

Sample Exercise 5.18**Gas Collection over Water**

A sample of solid potassium chlorate (KClO_3) was heated in a test tube (see Fig. 5.13) and decomposed by the following reaction:



The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22°C is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of KClO_3 in the sample that was decomposed.

Solution

First we find the partial pressure of O_2 from Dalton's law of partial pressures:

$$P_{\text{TOTAL}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}} = P_{\text{O}_2} + 21 \text{ torr} = 754 \text{ torr}$$

Thus

$$P_{O_2} = 754 \text{ torr} - 21 \text{ torr} = 733 \text{ torr}$$

Now we use the ideal gas law to find the number of moles of O₂:

$$n_{O_2} = \frac{P_{O_2}V}{RT}$$

In this case,

$$P_{O_2} = 733 \text{ torr} = \frac{733 \text{ torr}}{760 \text{ torr/atm}} = 0.964 \text{ atm}$$

$$V = 0.650 \text{ L}$$

$$T = 22^\circ\text{C} + 273 = 295 \text{ K}$$

$$R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$$

Thus

$$n_{O_2} = \frac{(0.964 \text{ atm})(0.650 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(295 \text{ K})} = 2.59 \times 10^{-2} \text{ mol}$$

Next we will calculate the moles of KClO₃ needed to produce this quantity of O₂. From the balanced equation for the decomposition of KClO₃, we have a mole ratio of 2 mol KClO₃/3 mol O₂. The moles of KClO₃ can be calculated as follows:

$$2.59 \times 10^{-2} \text{ mol O}_2 \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} = 1.73 \times 10^{-2} \text{ mol KClO}_3$$

Using the molar mass of KClO₃ (122.6 g/mol), we calculate the grams of KClO₃:

$$1.73 \times 10^{-2} \text{ mol KClO}_3 \times \frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} = 2.12 \text{ g KClO}_3$$

Thus the original sample contained 2.12 g KClO₃.

See Exercises 5.71 through 5.73.

5.6 The Kinetic Molecular Theory of Gases

We have so far considered the behavior of gases from an experimental point of view. Based on observations from different types of experiments, we know that at pressures of less than 1 atm most gases closely approach the behavior described by the ideal gas law. Now we want to construct a model to explain this behavior.

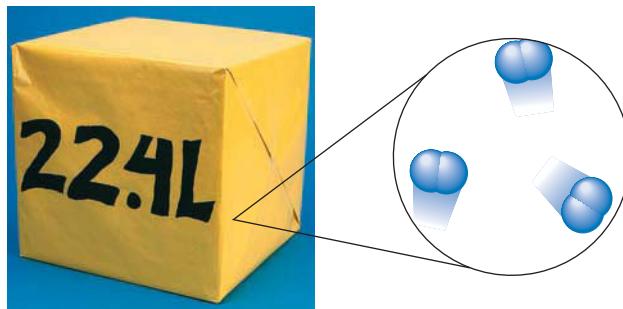
Before we do this, let's briefly review the scientific method. Recall that a law is a way of generalizing behavior that has been observed in many experiments. Laws are very useful, since they allow us to predict the behavior of similar systems. For example, if a chemist prepares a new gaseous compound, a measurement of the gas density at known pressure and temperature can provide a reliable value for the compound's molar mass.

However, although laws summarize observed behavior, they do not tell us *why* nature behaves in the observed fashion. This is the central question for scientists. To try to answer this question, we construct theories (build models). The models in chemistry consist of speculations about what the individual atoms or molecules (microscopic particles) might be doing to cause the observed behavior of the macroscopic systems (collections of very large numbers of atoms and molecules).

A model is considered successful if it explains the observed behavior in question and predicts correctly the results of future experiments. It is important to understand that a model can never be proved absolutely true. In fact, *any model is an approximation* by its



(a)



(b)

FIGURE 5.14

(a) One mole of $\text{N}_2(l)$ has a volume of approximately 35 mL and a density of 0.81 g/mL. (b) One mole of $\text{N}_2(g)$ has a volume of 22.4 L (STP) and a density of 1.2×10^{-3} g/mL. Thus the ratio of the volumes of gaseous N_2 and liquid N_2 is $22.4/0.035 = 640$ and the spacing of the molecules is 9 times farther apart in $\text{N}_2(g)$.

very nature and is bound to fail at some point. Models range from the simple to the extraordinarily complex. We use simple models to predict approximate behavior and more complicated models to account very precisely for observed quantitative behavior. In this text we will stress simple models that provide an approximate picture of what might be happening and that fit the most important experimental results.

An example of this type of model is the **kinetic molecular theory (KMT)**, a simple model that attempts to explain the properties of an ideal gas. This model is based on speculations about the behavior of the individual gas particles (atoms or molecules). The postulates of the kinetic molecular theory as they relate to the particles of an ideal gas can be stated as follows:

1. The particles are so small compared with the distances between them that *the volume of the individual particles can be assumed to be negligible (zero)*. See Fig. 5.14.
2. *The particles are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.*
3. *The particles are assumed to exert no forces on each other; they are assumed neither to attract nor to repel each other.*
4. *The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.*

Of course, the molecules in a real gas have finite volumes and do exert forces on each other. Thus *real gases* do not conform to these assumptions. However, we will see that these postulates do indeed explain *ideal gas* behavior.

The true test of a model is how well its predictions fit the experimental observations. The postulates of the kinetic molecular model picture an ideal gas as consisting of particles having no volume and no attractions for each other, and the model assumes that the gas produces pressure on its container by collisions with the walls.

Let's consider how this model accounts for the properties of gases as summarized by the ideal gas law: $PV = nRT$.

Pressure and Volume (Boyle's Law)

We have seen that for a given sample of gas at a given temperature (n and T are constant) that if the volume of a gas is decreased, the pressure increases:

$$P = (nRT) \frac{1}{V}$$

↑
Constant



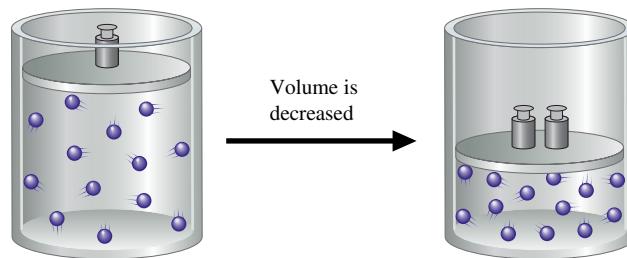
Visualization: Visualizing Molecular Motion: Single Molecule



Visualization: Visualizing Molecular Motion: Many Molecules



Visualization: Boyle's Law: A Molecular-Level View

**FIGURE 5.15**

The effects of decreasing the volume of a sample of gas at constant temperature.

This makes sense based on the kinetic molecular theory, since a decrease in volume means that the gas particles will hit the wall more often, thus increasing pressure, as illustrated in Fig. 5.15.

Pressure and Temperature

From the ideal gas law we can predict that for a given sample of an ideal gas at a constant volume, the pressure will be directly proportional to the temperature:

$$P = \left(\frac{nR}{V} \right) T$$

↑
Constant

The KMT accounts for this behavior because when the temperature of a gas increases, the speeds of its particles increase, the particles hitting the wall with greater force and greater frequency. Since the volume remains the same, this would result in increased gas pressure, as illustrated in Fig. 5.16.

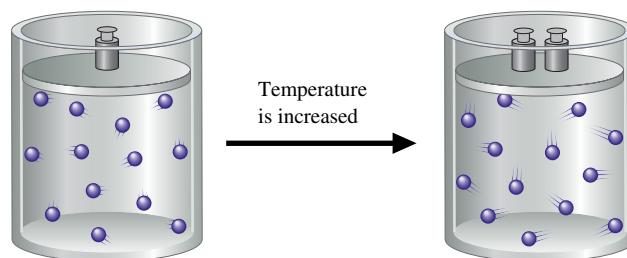
Volume and Temperature (Charles's Law)

The ideal gas law indicates that for a given sample of gas at a constant pressure, the volume of the gas is directly proportional to the temperature in kelvins:

$$V = \left(\frac{nR}{P} \right) T$$

↑
Constant

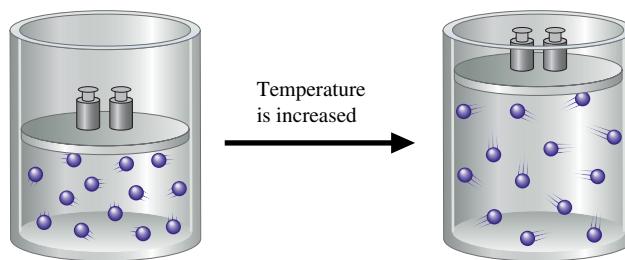
This can be visualized from the KMT, as shown in Fig. 5.17. When the gas is heated to a higher temperature, the speeds of its molecules increase and thus they hit the walls more often and with more force. The only way to keep the pressure constant in this situation is to increase the volume of the container. This compensates for the increased particle speeds.



Visualization: Charles's Law: A Molecular-Level View

FIGURE 5.16

The effects of increasing the temperature of a sample of gas at constant volume.

**FIGURE 5.17**

The effects of increasing the temperature of a sample of gas at constant pressure.

Volume and Number of Moles (Avogadro's Law)

The ideal gas law predicts that the volume of a gas at a constant temperature and pressure depends directly on the number of gas particles present:

$$V = \left(\frac{RT}{P} \right) n$$

↑
Constant

This makes sense in terms of the KMT, because an increase in the number of gas particles at the same temperature would cause the pressure to increase if the volume were held constant (see Fig. 5.18). The only way to return the pressure to its original value is to increase the volume.

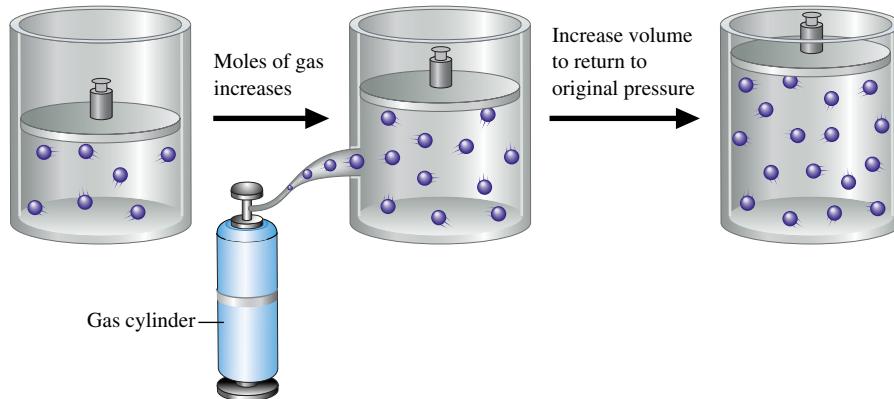
It is important to recognize that the volume of a gas (at constant P and T) depends only on the *number* of gas particles present. The individual volumes of the particles are not a factor because the particle volumes are so small compared with the distances between the particles (for a gas behaving ideally).

Mixture of Gases (Dalton's Law)

The observation that the total pressure exerted by a mixture of gases is the sum of the pressures of the individual gases is expected because the KMT assumes that all gas particles are independent of each other and that the volumes of the individual particles are unimportant. Thus the identities of the gas particles do not matter.

Deriving the Ideal Gas Law

We have shown qualitatively that the assumptions of the KMT successfully account for the observed behavior of an ideal gas. We can go further. By applying the principles of physics to the assumptions of the KMT, we can in effect derive the ideal gas law.

**FIGURE 5.18**

The effects of increasing the number of moles of gas particles at constant temperature and pressure.

As shown in detail in Appendix 2, we can apply the definitions of velocity, momentum, force, and pressure to the collection of particles in an ideal gas and *derive* the following expression for pressure:

$$P = \frac{2}{3} \left[\frac{nN_A(\frac{1}{2}mu^2)}{V} \right]$$

where P is the pressure of the gas, n is the number of moles of gas, N_A is Avogadro's number, m is the mass of each particle, $\bar{u^2}$ is the average of the square of the velocities of the particles, and V is the volume of the container.

The quantity $\frac{1}{2}mu^2$ represents the average kinetic energy of a gas particle. If the average kinetic energy of an individual particle is multiplied by N_A , the number of particles in a mole, we get the average kinetic energy for a mole of gas particles:

$$(KE)_{\text{avg}} = N_A(\frac{1}{2}mu^2)$$

Using this definition, we can rewrite the expression for pressure as

$$P = \frac{2}{3} \left[\frac{n(KE)_{\text{avg}}}{V} \right] \quad \text{or} \quad \frac{PV}{n} = \frac{2}{3}(KE)_{\text{avg}}$$

The fourth postulate of the kinetic molecular theory is that the average kinetic energy of the particles in the gas sample is directly proportional to the temperature in Kelvins. Thus, since $(KE)_{\text{avg}} \propto T$, we can write

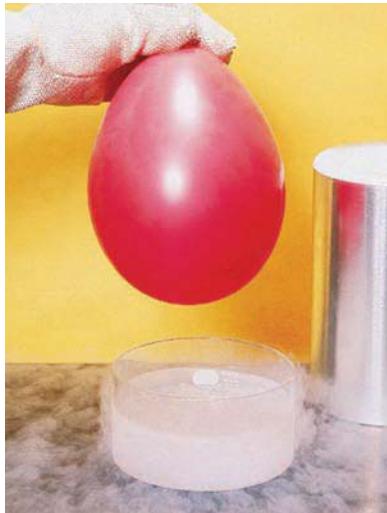
$$\frac{PV}{n} = \frac{2}{3}(KE)_{\text{avg}} \propto T \quad \text{or} \quad \frac{PV}{n} \propto T$$

Note that this expression has been *derived* from the assumptions of the kinetic molecular theory. How does it compare to the ideal gas law—the equation obtained from experiment? Compare the ideal gas law,

$$\frac{PV}{n} = RT \quad \text{From experiment}$$

with the result from the kinetic molecular theory,

$$\frac{PV}{n} \propto T \quad \text{From theory}$$



(a) A balloon filled with air at room temperature. (b) The balloon is dipped into liquid nitrogen at 77 K. (c) The balloon collapses as the molecules inside slow down due to the decreased temperature. Slower molecules produce a lower pressure.



Visualization: Liquid Nitrogen and Balloons

Kinetic energy (KE) given by the equation $KE = \frac{1}{2}mu^2$ is the energy due to the motion of a particle. We will discuss this further in Section 6.1.

These expressions have exactly the same form if R , the universal gas constant, is considered the proportionality constant in the second case.

The agreement between the ideal gas law and the predictions of the kinetic molecular theory gives us confidence in the validity of the model. The characteristics we have assumed for ideal gas particles must agree, at least under certain conditions, with their actual behavior.

The Meaning of Temperature

We have seen from the kinetic molecular theory that the Kelvin temperature indicates the average kinetic energy of the gas particles. The exact relationship between temperature and average kinetic energy can be obtained by combining the equations:

$$\frac{PV}{n} = RT = \frac{2}{3}(\text{KE})_{\text{avg}}$$

which yields the expression

$$(\text{KE})_{\text{avg}} = \frac{3}{2}RT$$

This is a very important relationship. It summarizes the meaning of the Kelvin temperature of a gas: The Kelvin temperature is an index of the random motions of the particles of a gas, with higher temperature meaning greater motion. (As we will see in Chapter 10, temperature is an index of the random motions in solids and liquids as well as in gases.)

Root Mean Square Velocity

In the equation from the kinetic molecular theory, the average velocity of the gas particles is a special kind of average. The symbol $\bar{u^2}$ means the average of the *squares* of the particle velocities. The square root of $\bar{u^2}$ is called the **root mean square velocity** and is symbolized by u_{rms} :

$$u_{\text{rms}} = \sqrt{\bar{u^2}}$$

We can obtain an expression for u_{rms} from the equations

$$(\text{KE})_{\text{avg}} = N_A(\frac{1}{2}m\bar{u^2}) \quad \text{and} \quad (\text{KE})_{\text{avg}} = \frac{3}{2}RT$$

Combination of these equations gives

$$N_A(\frac{1}{2}m\bar{u^2}) = \frac{3}{2}RT \quad \text{or} \quad \bar{u^2} = \frac{3RT}{N_A m}$$

Taking the square root of both sides of the last equation produces

$$\sqrt{\bar{u^2}} = u_{\text{rms}} = \sqrt{\frac{3RT}{N_A m}}$$

In this expression m represents the mass in kilograms of a single gas particle. When N_A , the number of particles in a mole, is multiplied by m , the product is the mass of a *mole* of gas particles in *kilograms*. We will call this quantity M . Substituting M for $N_A m$ in the equation for u_{rms} , we obtain

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Before we can use this equation, we need to consider the units for R . So far we have used $0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$ as the value of R . But to obtain the desired units (meters

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

Sample Exercise 5.19

Visualization: Kinetic-Molecular Theory/Heat Transfer

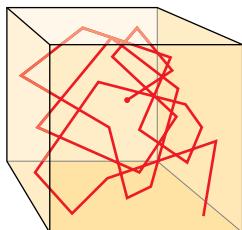


FIGURE 5.19

Path of one particle in a gas. Any given particle will continuously change its course as a result of collisions with other particles, as well as with the walls of the container.

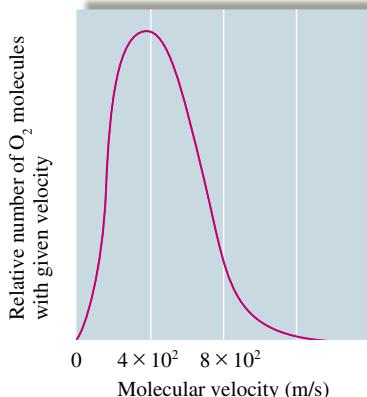


FIGURE 5.20

A plot of the relative number of O₂ molecules that have a given velocity at STP.

per second) for u_{rms} , R must be expressed in different units. As we will see in more detail in Chapter 6, the energy unit most often used in the SI system is the joule (J). A **joule** is defined as a kilogram meter squared per second squared (kg · m²/s²). When R is converted to include the unit of joules, it has the value 8.3145 J/K · mol. When R in these units is used in the expression $\sqrt{3RT/M}$, u_{rms} is obtained in the units of meters per second as desired.

Root Mean Square Velocity

Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C.

Solution

The formula for root mean square velocity is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

In this case $T = 25^\circ\text{C} + 273 = 298\text{ K}$, $R = 8.3145\text{ J/K} \cdot \text{mol}$, and M is the mass of a mole of helium in kilograms:

$$M = 4.00 \frac{\text{g}}{\text{mol}} \times \frac{1\text{ kg}}{1000\text{ g}} = 4.00 \times 10^{-3}\text{ kg/mol}$$

Thus

$$u_{\text{rms}} = \sqrt{\frac{3\left(8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}\right)(298\text{ K})}{4.00 \times 10^{-3} \frac{\text{kg}}{\text{mol}}}} = \sqrt{1.86 \times 10^6 \frac{\text{J}}{\text{kg}}}$$

Since the units of J are kg · m²/s², this expression becomes

$$\sqrt{1.86 \times 10^6 \frac{\text{kg} \cdot \text{m}^2}{\text{kg} \cdot \text{s}^2}} = 1.36 \times 10^3\text{ m/s}$$

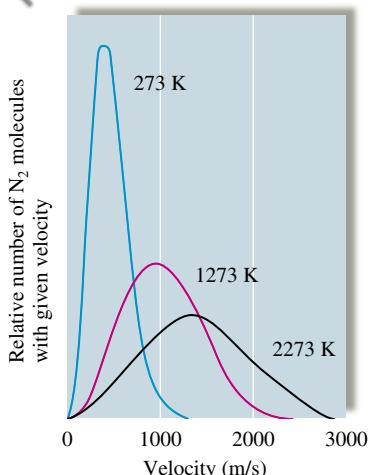
Note that the resulting units (m/s) are appropriate for velocity.

See Exercises 5.79 and 5.80.

So far we have said nothing about the range of velocities actually found in a gas sample. In a real gas there are large numbers of collisions between particles. For example, as we will see in the next section, when an odorous gas such as ammonia is released in a room, it takes some time for the odor to permeate the air. This delay results from collisions between the NH₃ molecules and the O₂ and N₂ molecules in the air, which greatly slow the mixing process.

If the path of a particular gas particle could be monitored, it would look very erratic, something like that shown in Fig. 5.19. The average distance a particle travels between collisions in a particular gas sample is called the *mean free path*. It is typically a very small distance ($1 \times 10^{-7}\text{ m}$ for O₂ at STP). One effect of the many collisions among gas particles is to produce a large range of velocities as the particles collide and exchange kinetic energy. Although u_{rms} for oxygen gas at STP is approximately 500 meters per second, the majority of O₂ molecules do not have this velocity. The actual distribution of molecular velocities for oxygen gas at STP is shown in Fig. 5.20. This figure shows the relative number of gas molecules having each particular velocity.

We are also interested in the effect of *temperature* on the velocity distribution in a gas. Figure 5.21 shows the velocity distribution for nitrogen gas at three temperatures. Note that as the temperature is increased, the curve peak moves toward higher values and the range

**FIGURE 5.21**

A plot of the relative number of N_2 molecules that have a given velocity at three temperatures. Note that as the temperature increases, both the average velocity and the spread of velocities increase.



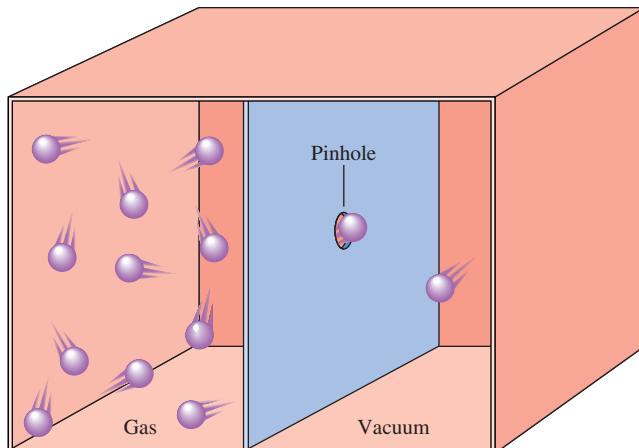
Visualization: Effusion of a Gas

In Graham's law the units for molar mass can be g/mol or kg/mol, since the units cancel in the ratio $\sqrt{M_2}/\sqrt{M_1}$.

Sample Exercise 5.20

Effusion Rates

Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6), a gas used in the enrichment process to produce fuel for nuclear reactors (see Fig. 5.23).

**FIGURE 5.22**

The effusion of a gas into an evacuated chamber. The rate of effusion (the rate at which the gas is transferred across the barrier through the pin hole) is inversely proportional to the square root of the mass of the gas molecules.

of velocities becomes much larger. The peak of the curve reflects the most probable velocity (the velocity found most often as we sample the movement of the various particles in the gas). Because the kinetic energy increases with temperature, it makes sense that the peak of the curve should move to higher values as the temperature of the gas is increased.

5.7 Effusion and Diffusion

We have seen that the postulates of the kinetic molecular theory, when combined with the appropriate physical principles, produce an equation that successfully fits the experimentally observed behavior of gases as they approach ideal behavior. Two phenomena involving gases provide further tests of this model.

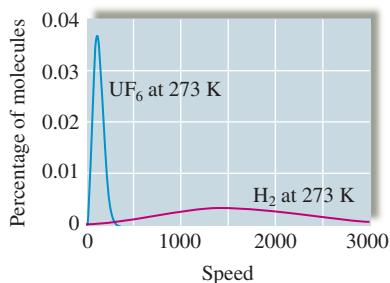
Diffusion is the term used to describe the mixing of gases. When a small amount of pungent-smelling ammonia is released at the front of a classroom, it takes some time before everyone in the room can smell it, because time is required for the ammonia to mix with the air. The rate of diffusion is the rate of the mixing of gases. **Effusion** is the term used to describe the passage of a gas through a tiny orifice into an evacuated chamber, as shown in Fig. 5.22. The rate of effusion measures the speed at which the gas is transferred into the chamber.

Effusion

Thomas Graham (1805–1869), a Scottish chemist, found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. Stated in another way, the relative rates of effusion of two gases at the same temperature and pressure are given by the inverse ratio of the square roots of the masses of the gas particles:

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

where M_1 and M_2 represent the molar masses of the gases. This equation is called **Graham's law of effusion**.

**FIGURE 5.23**

Relative molecular speed distribution of H_2 and UF_6 .

Solution

First we need to compute the molar masses: Molar mass of $\text{H}_2 = 2.016 \text{ g/mol}$, and molar mass of $\text{UF}_6 = 352.02 \text{ g/mol}$. Using Graham's law,

$$\frac{\text{Rate of effusion for } \text{H}_2}{\text{Rate of effusion for } \text{UF}_6} = \frac{\sqrt{M_{\text{UF}_6}}}{\sqrt{M_{\text{H}_2}}} = \sqrt{\frac{352.02}{2.016}} = 13.2$$

The effusion rate of the very light H_2 molecules is about 13 times that of the massive UF_6 molecules.

See Exercises 5.85 through 5.88.

Does the kinetic molecular model for gases correctly predict the relative effusion rates of gases summarized by Graham's law? To answer this question, we must recognize that the effusion rate for a gas depends directly on the average velocity of its particles. The faster the gas particles are moving, the more likely they are to pass through the effusion orifice. This reasoning leads to the following *prediction* for two gases at the same pressure and temperature (T):

$$\frac{\text{Effusion rate for gas 1}}{\text{Effusion rate for gas 2}} = \frac{u_{\text{rms}} \text{ for gas 1}}{u_{\text{rms}} \text{ for gas 2}} = \frac{\sqrt{\frac{3RT}{M_1}}}{\sqrt{\frac{3RT}{M_2}}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

This equation is identical to Graham's law. Thus the kinetic molecular model does fit the experimental results for the effusion of gases.



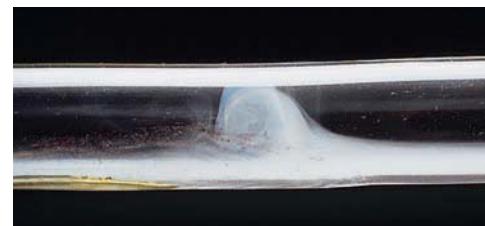
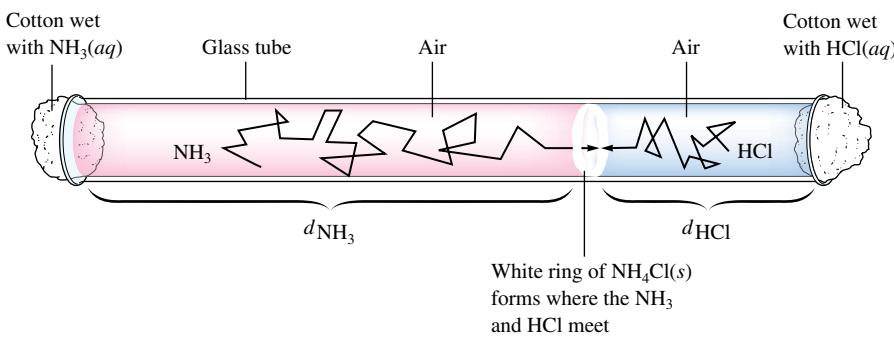
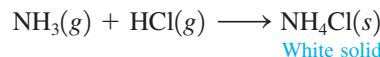
Visualization: Diffusion of Gases



Visualization: Gaseous Ammonia and Hydrochloric Acid

Diffusion

Diffusion is frequently illustrated by the lecture demonstration represented in Fig. 5.24, in which two cotton plugs soaked in ammonia and hydrochloric acid are simultaneously placed at the ends of a long tube. A white ring of ammonium chloride (NH_4Cl) forms where the NH_3 and HCl molecules meet several minutes later:

**FIGURE 5.24**

(above right) When $\text{HCl}(g)$ and $\text{NH}_3(g)$ meet in the tube, a white ring of $\text{NH}_4\text{Cl}(s)$ forms. (above left) A demonstration of the relative diffusion rates of NH_3 and HCl molecules through air. Two cotton plugs, one dipped in $\text{HCl}(aq)$ and one dipped in $\text{NH}_3(aq)$, are simultaneously inserted into the ends of the tube. Gaseous NH_3 and HCl vaporizing from the cotton plugs diffuse toward each other and, where they meet, react to form $\text{NH}_4\text{Cl}(s)$.

As a first approximation we might expect that the distances traveled by the two gases are related to the relative velocities of the gas molecules:

$$\frac{\text{Distance traveled by NH}_3}{\text{Distance traveled by HCl}} = \frac{u_{\text{rms}} \text{ for NH}_3}{u_{\text{rms}} \text{ for HCl}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} = \sqrt{\frac{36.5}{17}} = 1.5$$

However, careful experiments produce an observed ratio of less than 1.5, indicating that a quantitative analysis of diffusion requires a more complex analysis.

The diffusion of the gases through the tube is surprisingly slow in light of the fact that the velocities of HCl and NH₃ molecules at 25°C are about 450 and 660 meters per second, respectively. Why does it take several minutes for the NH₃ and HCl molecules to meet? The answer is that the tube contains air and thus the NH₃ and HCl molecules undergo many collisions with O₂ and N₂ molecules as they travel through the tube. Because so many collisions occur when gases mix, diffusion is quite complicated to describe theoretically.

5.8 Real Gases

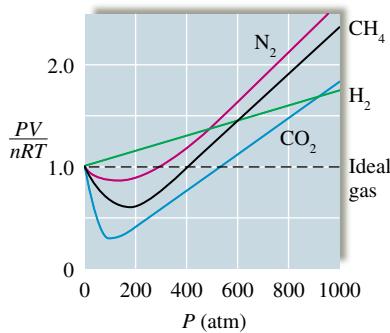


FIGURE 5.25
Plots of PV/nRT versus P for several gases (200 K). Note the significant deviations from ideal behavior ($PV/nRT = 1$). The behavior is close to ideal only at low pressures (less than 1 atm).

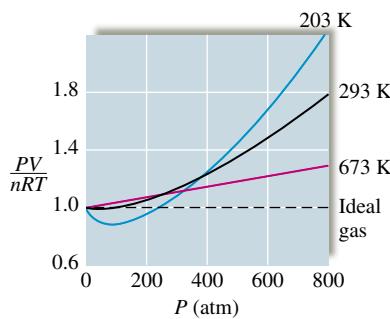


FIGURE 5.26
Plots of PV/nRT versus P for nitrogen gas at three temperatures. Note that although nonideal behavior is evident in each case, the deviations are smaller at the higher temperatures.

An ideal gas is a hypothetical concept. No gas *exactly* follows the ideal gas law, although many gases come very close at low pressures and/or high temperatures. Thus ideal gas behavior can best be thought of as the behavior *approached by real gases* under certain conditions.

We have seen that a very simple model, the kinetic molecular theory, by making some rather drastic assumptions (no interparticle interactions and zero volume for the gas particles), successfully explains ideal behavior. However, it is important that we examine real gas behavior to see how it differs from that predicted by the ideal gas law and to determine what modifications are needed in the kinetic molecular theory to explain the observed behavior. Since a model is an approximation and will inevitably fail, we must be ready to learn from such failures. In fact, we often learn more about nature from the failures of our models than from their successes.

We will examine the experimentally observed behavior of real gases by measuring the pressure, volume, temperature, and number of moles for a gas and noting how the quantity PV/nRT depends on pressure. Plots of PV/nRT versus P are shown for several gases in Fig. 5.25. For an ideal gas, PV/nRT equals 1 under all conditions, but notice that for real gases, PV/nRT approaches 1 only at very low pressures (typically below 1 atm). To illustrate the effect of temperature, PV/nRT is plotted versus P for nitrogen gas at several temperatures in Fig. 5.26. Note that the behavior of the gas appears to become more nearly ideal as the temperature is increased. The most important conclusion to be drawn from these figures is that a real gas typically exhibits behavior that is closest to ideal behavior at *low pressures and high temperatures*.

One of the most important procedures in science is correcting our models as we collect more data. We will understand more clearly how gases actually behave if we can figure out how to correct the simple model that explains the ideal gas law so that the new model fits the behavior we actually observe for gases. So the question is: How can we modify the assumptions of the kinetic molecular theory to fit the behavior of real gases? The first person to do important work in this area was Johannes van der Waals (1837–1923), a physics professor at the University of Amsterdam who in 1910 received a Nobel Prize for his work. To follow his analysis, we start with the ideal gas law,

$$P = \frac{nRT}{V}$$

Remember that this equation describes the behavior of a hypothetical gas consisting of volumeless entities that do not interact with each other. In contrast, a real gas consists of atoms or molecules that have finite volumes. Therefore, the volume available to a given particle in a real gas is less than the volume of the container because the gas particles themselves take up some of the space. To account for this discrepancy, van der Waals

represented the actual volume as the volume of the container V minus a correction factor for the volume of the molecules nb , where n is the number of moles of gas and b is an empirical constant (one determined by fitting the equation to the experimental results). Thus the volume *actually available* to a given gas molecule is given by the difference $V - nb$.

This modification of the ideal gas equation leads to the equation

$$P' = \frac{nRT}{V - nb}$$

The volume of the gas particles has now been taken into account.

The next step is to allow for the attractions that occur among the particles in a real gas. The effect of these attractions is to make the observed pressure P_{obs} smaller than it would be if the gas particles did not interact:

$$P_{\text{obs}} = (P' - \text{correction factor}) = \left(\frac{nRT}{V - nb} - \text{correction factor} \right)$$

P' is corrected for the finite volume of the particles. The attractive forces have not yet been taken into account.

The attractive forces among molecules will be discussed in Chapter 10.

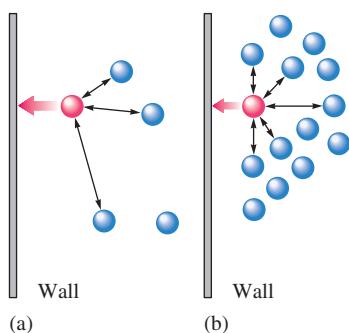


FIGURE 5.27

(a) Gas at low concentration—relatively few interactions between particles. The indicated gas particle exerts a pressure on the wall close to that predicted for an ideal gas.
 (b) Gas at high concentration—many more interactions between particles. The indicated gas particle exerts a much lower pressure on the wall than would be expected in the absence of interactions.

We have now corrected for both the finite volume and the attractive forces of the particles.

This effect can be understood using the following model. When gas particles come close together, attractive forces occur, which cause the particles to hit the wall very slightly less often than they would in the absence of these interactions (see Fig. 5.27).

The size of the correction factor depends on the concentration of gas molecules defined in terms of moles of gas particles per liter (n/V). The higher the concentration, the more likely a pair of gas particles will be close enough to attract each other. For large numbers of particles, the number of interacting pairs of particles depends on the square of the number of particles and thus on the square of the concentration, or $(n/V)^2$. This can be justified as follows: In a gas sample containing N particles, there are $N - 1$ partners available for each particle, as shown in Fig. 5.28. Since the $1 \cdots 2$ pair is the same as the $2 \cdots 1$ pair, this analysis counts each pair twice. Thus, for N particles, there are $N(N - 1)/2$ pairs. If N is a very large number, $N - 1$ approximately equals N , giving $N^2/2$ possible pairs. Thus the pressure, corrected for the attractions of the particles, has the form

$$P_{\text{obs}} = P' - a \left(\frac{n}{V} \right)^2$$

where a is a proportionality constant (which includes the factor of $\frac{1}{2}$ from $N^2/2$). The value of a for a given real gas can be determined from observing the actual behavior of that gas. Inserting the corrections for both the volume of the particles and the attractions of the particles gives the equation

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

Observed pressure Volume of the container Volume correction Pressure correction

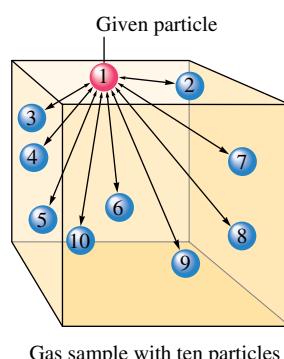
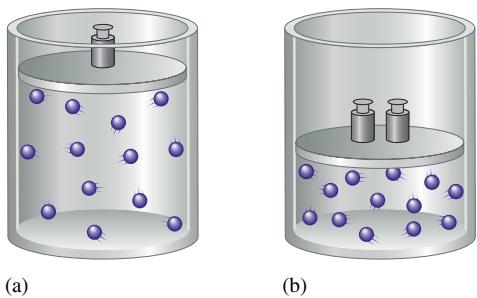


FIGURE 5.28

Illustration of pairwise interactions among gas particles. In a sample with 10 particles, each particle has 9 possible partners, to give $10(9)/2 = 45$ distinct pairs. The factor of $\frac{1}{2}$ arises because when particle 1 is the particle of interest we count the $(1 \cdots 2)$ pair, and when particle 2 is the particle of interest we count the $(2 \cdots 1)$ pair. However, $(1 \cdots 2)$ and $(2 \cdots 1)$ are the same pair that we have counted twice. Therefore, we must divide by 2 to get the actual number of pairs.

**FIGURE 5.29**

The volume taken up by the gas particles themselves is less important at (a) large container volume (low pressure) than at (b) small container volume (high pressure).

P_{obs} is usually called just P .

This equation can be rearranged to give the **van der Waals equation**:

$$\underbrace{\left[P_{\text{obs}} + a \left(\frac{n}{V} \right)^2 \right]}_{\text{Corrected pressure}} \times \underbrace{\left(V - nb \right)}_{\text{Corrected volume}} = nRT \underbrace{V_{\text{ideal}}}_{\text{P}_{\text{ideal}}}$$

The values of the weighting factors a and b are determined for a given gas by fitting experimental behavior. That is, a and b are varied until the best fit of the observed pressure is obtained under all conditions. The values of a and b for various gases are given in Table 5.3.

Experimental studies indicate that the changes van der Waals made in the basic assumptions of the kinetic molecular theory correct the major flaws in the model. First, consider the effects of volume. For a gas at low pressure (large volume), the volume of the container is very large compared with the volumes of the gas particles. That is, in this case the volume available to the gas is essentially equal to the volume of the container, and the gas behaves ideally. On the other hand, for a gas at high pressure (small container volume), the volume of the particles becomes significant so that the volume available to the gas is significantly less than the container volume. These cases are illustrated in Fig. 5.29. Note from Table 5.3 that the volume correction constant b generally increases with the size of the gas molecule, which gives further support to these arguments.

The fact that a real gas tends to behave more ideally at high temperatures also can be explained in terms of the van der Waals model. At high temperatures the particles are moving so rapidly that the effects of interparticle interactions are not very important.

The corrections to the kinetic molecular theory that van der Waals found necessary to explain real gas behavior make physical sense, which makes us confident that we understand the fundamentals of gas behavior at the particle level. This is significant because so much important chemistry takes place in the gas phase. In fact, the mixture of gases called the atmosphere is vital to our existence. In Section 5.10 we consider some of the important reactions that occur in the atmosphere.

5.9 Characteristics of Several Real Gases

We can understand gas behavior more completely if we examine the characteristics of several common gases. Note from Figure 5.25 that the gases H₂, N₂, CH₄, and CO₂ show different behavior when the compressibility ($\frac{PV}{nRT}$) is plotted versus P . For example, notice that the plot for H₂(g) never drops below the ideal value (1.0) in contrast to all the other gases. What is special about H₂ compared to these other gases? Recall from Section 5.8 that the reason that the compressibility of a real gas falls below 1.0 is that the actual (observed) pressure is lower than the pressure expected for an ideal gas due to the intermolecular attractions that occur in real gases. This must mean that H₂ molecules have very low attractive forces for each other. This idea is borne out by looking at the van der Waals

TABLE 5.3 Values of the van der Waals Constants for Some Common Gases

Gas	$a \left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \right)$	$b \left(\frac{\text{L}}{\text{mol}} \right)$
He	0.0341	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CO ₂	3.59	0.0427
CH ₄	2.25	0.0428
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

a value for H₂ in Table 5.3. Note that H₂ has the lowest value among the gases H₂, N₂, CH₄, and CO₂. Remember that the value of *a* reflects how much of a correction must be made to adjust the observed pressure up to the expected ideal pressure:

$$P_{\text{ideal}} = P_{\text{observed}} + a \left(\frac{n}{V} \right)^2$$

A low value for *a* reflects weak intermolecular forces among the gas molecules.

Also notice that although the compressibility for N₂ dips below 1.0, it does not show as much deviation as that for CH₄, which in turn does not show as much deviation as the compressibility for CO₂. Based on this behavior we can surmise that the importance of intermolecular interactions increases in this order:



This order is reflected by the relative *a* values for these gases in Table 5.3. In Section 10.1, we will see how these variations in intermolecular interactions can be explained. The main point to be made here is that real gas behavior can tell us about the relative importance of intermolecular attractions among gas molecules.

5.10 Chemistry in the Atmosphere

The most important gases to us are those in the **atmosphere** that surrounds the earth's surface. The principal components are N₂ and O₂, but many other important gases, such as H₂O and CO₂, are also present. The average composition of the earth's atmosphere near sea level, with the water vapor removed, is shown in Table 5.4. Because of gravitational effects, the composition of the earth's atmosphere is not constant; heavier molecules tend to be near the earth's surface, and light molecules tend to migrate to higher altitudes, with some eventually escaping into space. The atmosphere is a highly complex and dynamic system, but for convenience we divide it into several layers based on the way the temperature changes with altitude. (The lowest layer, called the *troposphere*, is shown in Fig. 5.30.) Note that in contrast to the complex temperature profile of the atmosphere, the pressure decreases in a regular way with increasing altitude.

The chemistry occurring in the higher levels of the atmosphere is mostly determined by the effects of high-energy radiation and particles from the sun and other sources in space. In fact, the upper atmosphere serves as an important shield to prevent this high-energy radiation from reaching the earth, where it would damage the relatively fragile molecules sustaining life. In particular, the ozone in the upper atmosphere helps prevent high-energy ultraviolet radiation from penetrating to the earth. Intensive research is in progress to determine the natural factors that control the ozone concentration and how it is affected by chemicals released into the atmosphere.

The chemistry occurring in the troposphere, the layer of atmosphere closest to the earth's surface, is strongly influenced by human activities. Millions of tons of gases and particulates are released into the troposphere by our highly industrial civilization. Actually, it is amazing that the atmosphere can absorb so much material with relatively small permanent changes (so far).

Significant changes, however, are occurring. Severe **air pollution** is found around many large cities, and it is probable that long-range changes in our planet's weather are taking place. We will discuss some of the long-range effects of pollution in Chapter 6. In this section we will deal with short-term, localized effects of pollution.

The two main sources of pollution are transportation and the production of electricity. The combustion of petroleum in vehicles produces CO, CO₂, NO, and NO₂, along with unburned molecules from petroleum. When this mixture is trapped close to the ground in stagnant air, reactions occur producing chemicals that are potentially irritating and harmful to living systems.

TABLE 5.4 Atmospheric Composition Near Sea Level (Dry Air)*

Component	Mole Fraction
N ₂	0.78084
O ₂	0.20948
Ar	0.00934
CO ₂	0.000345
Ne	0.00001818
He	0.00000524
CH ₄	0.00000168
Kr	0.00000114
H ₂	0.0000005
NO	0.0000005
Xe	0.000000087

*The atmosphere contains various amounts of water vapor depending on conditions.

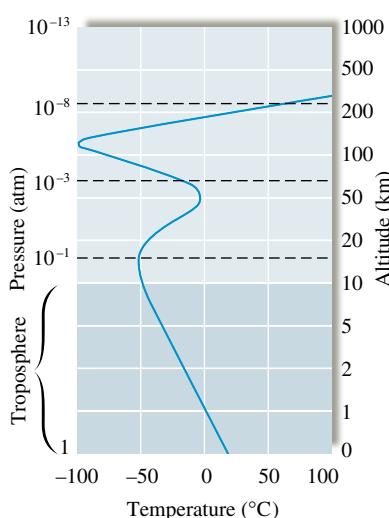


FIGURE 5.30

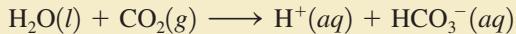
The variation of temperature (blue) and pressure (dashed lines) with altitude. Note that the pressure steadily decreases with altitude, but the temperature increases and decreases.



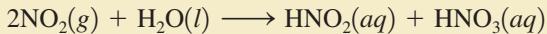
CHEMICAL IMPACT

Acid Rain: A Growing Problem

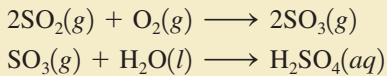
Rainwater, even in pristine wilderness areas, is slightly acidic because some of the carbon dioxide present in the atmosphere dissolves in the raindrops to produce H⁺ ions by the following reaction:



This process produces only very small concentrations of H⁺ ions in the rainwater. However, gases such as NO₂ and SO₂, which are by-products of energy use, can produce significantly higher H⁺ concentrations. Nitrogen dioxide reacts with water to give a mixture of nitrous acid and nitric acid:



Sulfur dioxide is oxidized to sulfur trioxide, which then reacts with water to form sulfuric acid:



The damage caused by the acid formed in polluted air is a growing worldwide problem. Lakes are dying in Norway,

the forests are under stress in Germany, and buildings and statues are deteriorating all over the world.

The Field Museum in Chicago contains more white Georgia marble than any other structure in the world. But nearly 70 years of exposure to the elements has taken such a toll on it that the building has recently undergone a multimillion-dollar renovation to replace the damaged marble with freshly quarried material.

What is the chemistry of the deterioration of marble by sulfuric acid? Marble is produced by geologic processes at high temperatures and pressures from limestone, a sedimentary rock formed by slow deposition of calcium carbonate from the shells of marine organisms. Limestone and marble are chemically identical (CaCO₃) but differ in physical properties; limestone is composed of smaller particles of calcium carbonate and is thus more porous and more workable. Although both limestone and marble are used for buildings, marble can be polished to a higher sheen and is often preferred for decorative purposes.

Both marble and limestone react with sulfuric acid to form calcium sulfate. The process can be represented most

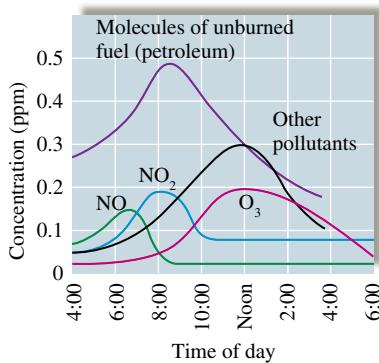


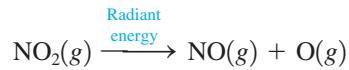
FIGURE 5.31

Concentration (in molecules per million molecules of "air") for some smog components versus time of day.

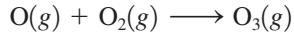
(From "Photochemistry of Air Pollution," by P. A. Leighton, in *Physical Chemistry: A Series of Monographs*, edited by Eric Hutchinson and P. Van Rysselberghe, copyright 1961 and renewed 1989, Elsevier Science (USA), reproduced by permission of the publisher.)

The OH radical has no charge [it has one fewer electron than the hydroxide ion (OH⁻)].

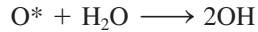
The complex chemistry of polluted air appears to center around the nitrogen oxides (NO_x). At the high temperatures found in the gasoline and diesel engines of cars and trucks, N₂ and O₂ react to form a small quantity of NO that is emitted into the air with the exhaust gases (see Fig. 5.31). This NO is immediately oxidized in air to NO₂, which, in turn, absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atoms:



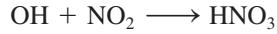
Oxygen atoms are very reactive and can combine with O₂ to form ozone:



Ozone is also very reactive and can react directly with other pollutants, or the ozone can absorb light and break up to form an energetically excited O₂ molecule (O₂^{*}) and an energetically excited oxygen atom (O^{*}). The latter species readily reacts with a water molecule to form two hydroxyl radicals (OH):

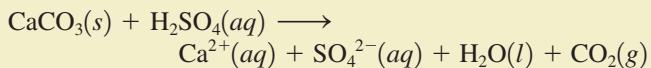


The hydroxyl radical is a very reactive oxidizing agent. For example, OH can react with NO₂ to form nitric acid:



The OH radical also can react with the unburned hydrocarbons in the polluted air to produce chemicals that cause the eyes to water and burn and are harmful to the respiratory system.

simply as



In this equation the calcium sulfate is represented by separate hydrated ions because calcium sulfate is quite water soluble and dissolves in rainwater. Thus, in areas bathed by rainwater, the marble slowly dissolves away.

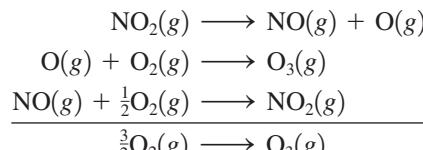
In areas of the building protected from the rain, the calcium sulfate can form the mineral gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The $\cdot 2\text{H}_2\text{O}$ in the formula of gypsum indicates the presence of two water molecules (called *waters of hydration*) for each CaSO_4 formula unit in the solid. The smooth surface of the marble is thus replaced by a thin layer of gypsum, a more porous material that binds soot and dust.

What can be done to protect limestone and marble structures from this kind of damage? Of course, one approach is to lower sulfur dioxide emissions from power plants (see Fig. 5.33). In addition, scientists are experimenting with coatings to protect marble from the acidic atmosphere. However, a coating can do more harm than good unless it “breathes.” If moisture trapped beneath the coating freezes, the expanding ice can fracture the marble. Needless to say, it is difficult to find a coating that will allow water, but not acid, to pass—but the search continues.



The damaging effects of acid rain can be seen by comparing these photos of a decorative statue on the Field Museum in Chicago. The first photo was taken about 1920, the second in 1990.

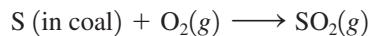
The end product of this whole process is often referred to as **photochemical smog**, so called because light is required to initiate some of the reactions. The production of photochemical smog can be understood more clearly by examining as a group the reactions discussed above:



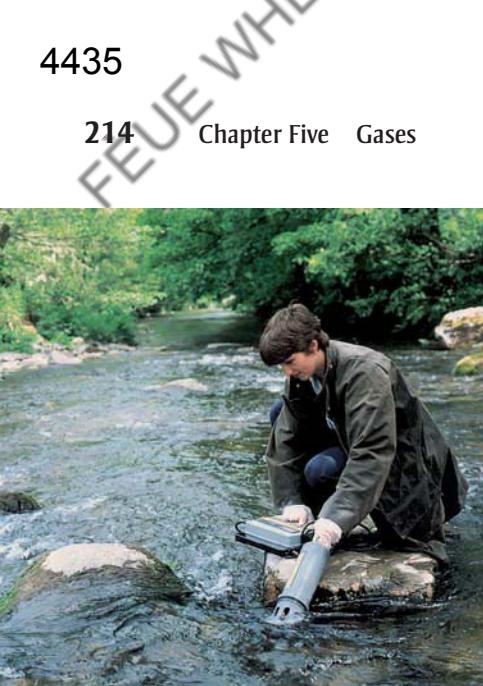
Note that the NO_2 molecules assist in the formation of ozone without being themselves used up. The ozone formed then leads to the formation of OH and other pollutants.

We can observe this process by analyzing polluted air at various times during a day (see Fig. 5.31). As people drive to work between 6 and 8 a.m., the amounts of NO, NO_2 , and unburned molecules from petroleum increase. Later, as the decomposition of NO_2 occurs, the concentration of ozone and other pollutants builds up. Current efforts to combat the formation of photochemical smog are focused on cutting down the amounts of molecules from unburned fuel in automobile exhaust and designing engines that produce less nitric oxide.

The other major source of pollution results from burning coal to produce electricity. Much of the coal found in the Midwest contains significant quantities of sulfur, which, when burned, produces sulfur dioxide:

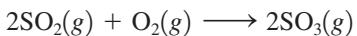


Although represented here as O_2 , the actual oxidant for NO is OH or an organic peroxide such as CH_3COO , formed by oxidation of organic pollutants.

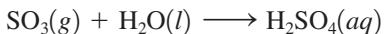
**FIGURE 5.32**

An environmental officer in Wales tests the pH of water.

A further oxidation reaction occurs when sulfur dioxide is changed to sulfur trioxide in the air:^{*}



The production of sulfur trioxide is significant because it can combine with droplets of water in the air to form sulfuric acid:

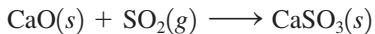


Sulfuric acid is very corrosive to both living things and building materials. Another result of this type of pollution is **acid rain**. In many parts of the northeastern United States and southeastern Canada, acid rain has caused some freshwater lakes to become too acidic to support any life (Fig. 5.32).

The problem of sulfur dioxide pollution is made more complicated by the energy crisis. As petroleum supplies dwindle and the price increases, our dependence on coal will probably grow. As supplies of low-sulfur coal are used up, high-sulfur coal will be utilized. One way to use high-sulfur coal without further harming the air quality is to remove the sulfur dioxide from the exhaust gas by means of a system called a *scrubber* before it is emitted from the power plant stack. A common method of scrubbing is to blow powdered limestone (CaCO_3) into the combustion chamber, where it is decomposed to lime and carbon dioxide:

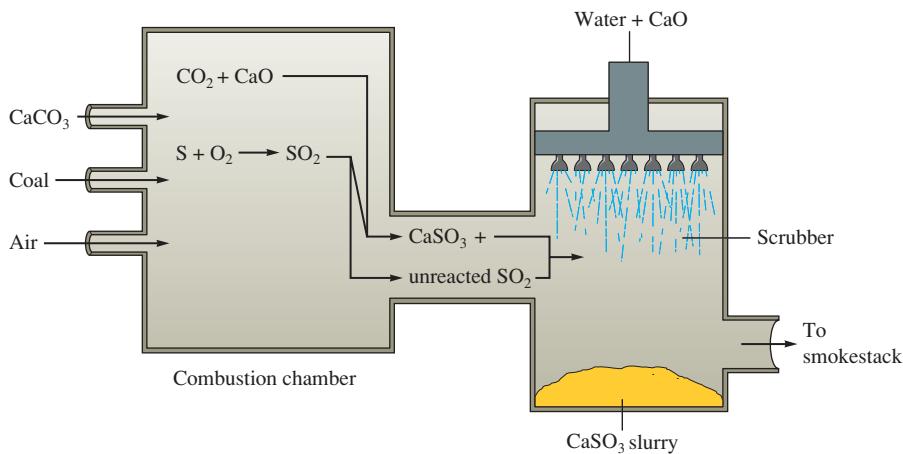


The lime then combines with the sulfur dioxide to form calcium sulfite:



To remove the calcium sulfite and any remaining unreacted sulfur dioxide, an aqueous suspension of lime is injected into the exhaust gases to produce a *slurry* (a thick suspension), as shown in Fig. 5.33.

Unfortunately, there are many problems associated with scrubbing. The systems are complicated and expensive and consume a great deal of energy. The large quantities of calcium sulfite produced in the process present a disposal problem. With a typical scrubber, approximately 1 ton of calcium sulfite per year is produced per person served by the power plant. Since no use has yet been found for this calcium sulfite, it is usually buried in a landfill. As a result of these difficulties, air pollution by sulfur dioxide continues to be a major problem, one that is expensive in terms of damage to the environment and human health as well as in monetary terms.

**FIGURE 5.33**

A schematic diagram of the process for scrubbing sulfur dioxide from stack gases in power plants.

^{*}This reaction is very slow unless solid particles are present. See Chapter 12 for a discussion.

Key Terms

Section 5.1

barometer
manometer
mm Hg
torr
standard atmosphere
pascal

Section 5.2

Boyle's law
ideal gas
Charles's law
absolute zero
Avogadro's law

Section 5.3

universal gas constant
ideal gas law

Section 5.4

molar volume
standard temperature and pressure (STP)

Section 5.5

Dalton's law of partial pressures
partial pressure
mole fraction

Section 5.6

kinetic molecular theory (KMT)
root mean square velocity
joule

Section 5.7

diffusion
effusion
Graham's law of effusion

Section 5.8

real gas
van der Waals equation

Section 5.10

atmosphere
air pollution
photochemical smog
acid rain

For Review

State of a gas

- The state of a gas can be described completely by specifying its pressure (P), volume (V), temperature (T) and the amount (moles) of gas present (n)
- Pressure
 - Common units

$$1 \text{ torr} = 1 \text{ mm Hg}$$

$$1 \text{ atm} = 760 \text{ torr}$$

- SI unit: pascal

$$1 \text{ atm} = 101,325 \text{ Pa}$$

Gas laws

- Discovered by observing the properties of gases
- Boyle's law: $PV = k$
- Charles's law: $V = bT$
- Avogadro's law: $V = an$
- Ideal gas law: $PV = nRT$
- Dalton's law of partial pressures: $P_{\text{total}} = P_1 + P_2 + P_3 + \dots$, where P_n represents the partial pressure of component n in a mixture of gases

Kinetic molecular theory (KMT)

- Model that accounts for ideal gas behavior
- Postulates of the KMT:
 - Volume of gas particles is zero
 - No particle interactions
 - Particles are in constant motion, colliding with the container walls to produce pressure
 - The average kinetic energy of the gas particles is directly proportional to the temperature of the gas in kelvins

Gas properties

- The particles in any gas sample have a range of velocities
- The root mean square (rms) velocity for a gas represents the average of the squares of the particle velocities

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

- Diffusion: the mixing of two or more gases
- Effusion: the process in which a gas passes through a small hole into an empty chamber

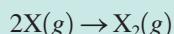
Real gas behavior

- Real gases behave ideally only at high temperatures and low pressures
- Understanding how the ideal gas equation must be modified to account for real gas behavior helps us understand how gases behave on a molecular level
- Van der Waals found that to describe real gas behavior we must consider particle interactions and particle volumes

REVIEW QUESTIONS

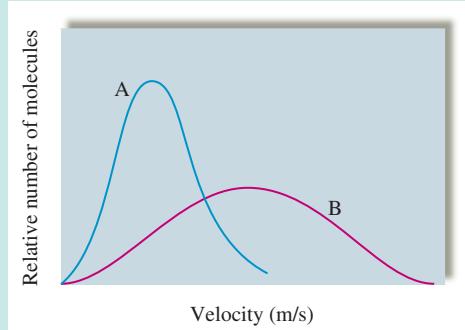
- Explain how a barometer and a manometer work to measure the pressure of the atmosphere or the pressure of a gas in a container.

2. What are Boyle's law, Charles's law, and Avogadro's law? What plots do you make to show a linear relationship for each law?
3. Show how Boyle's law, Charles's law, and Avogadro's law are special cases of the ideal gas law. Using the ideal gas law, determine the relationship between P and n (at constant V and T) and between P and T (at constant V and n).
4. Rationalize the following observations.
 - a. Aerosol cans will explode if heated.
 - b. You can drink through a soda straw.
 - c. A thin-walled can will collapse when the air inside is removed by a vacuum pump.
 - d. Manufacturers produce different types of tennis balls for high and low elevations.
5. Consider the following balanced equation in which gas X forms gas X₂:



Equal moles of X are placed in two separate containers. One container is rigid so the volume cannot change; the other container is flexible so the volume changes to keep the internal pressure equal to the external pressure. The above reaction is run in each container. What happens to the pressure and density of the gas inside each container as reactants are converted to products?

6. Use the postulates of the kinetic molecular theory (KMT) to explain why Boyle's law, Charles's law, Avogadro's law, and Dalton's law of partial pressures hold true for ideal gases. Use the KMT to explain the P versus n (at constant V and T) relationship and the P versus T (at constant V and n) relationship.
7. Consider the following velocity distribution curves A and B.

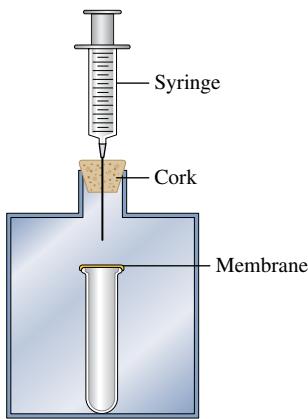


- a. If the plots represent the velocity distribution of 1.0 L of He(g) at STP versus 1.0 L of Cl₂(g) at STP, which plot corresponds to each gas? Explain your reasoning.
- b. If the plots represent the velocity distribution of 1.0 L of O₂(g) at temperatures of 273 K versus 1273 K, which plot corresponds to each temperature? Explain your reasoning. Under which temperature condition would the O₂(g) sample behave most ideally? Explain.
8. Briefly describe two methods one might use to find the molar mass of a newly synthesized gas for which a molecular formula was not known.
9. In the van der Waals equation, why is a term added to the observed pressure and why is a term subtracted from the container volume to correct for nonideal gas behavior?
10. Why do real gases not always behave ideally? Under what conditions does a real gas behave most ideally? Why?

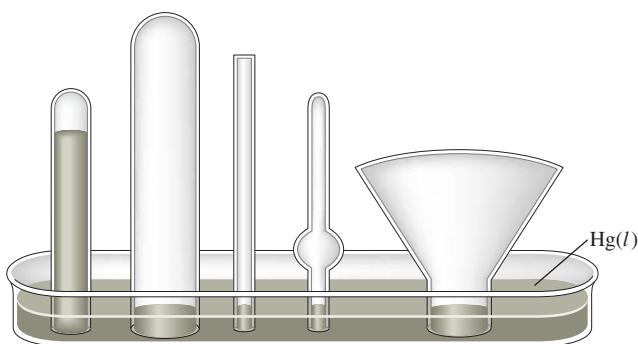
Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- Consider the following apparatus: a test tube covered with a non-permeable elastic membrane inside a container that is closed with a cork. A syringe goes through the cork.

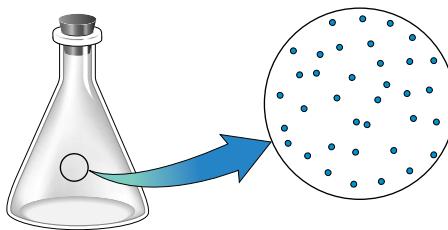


- As you push down on the syringe, how does the membrane covering the test tube change?
- You stop pushing the syringe but continue to hold it down. In a few seconds, what happens to the membrane?
- Figure 5.2 shows a picture of a barometer. Which of the following statements is the best explanation of how this barometer works?
 - Air pressure outside the tube causes the mercury to move in the tube until the air pressure inside and outside the tube is equal.
 - Air pressure inside the tube causes the mercury to move in the tube until the air pressure inside and outside the tube is equal.
 - Air pressure outside the tube counterbalances the weight of the mercury in the tube.
 - Capillary action of the mercury causes the mercury to go up the tube.
 - The vacuum that is formed at the top of the tube holds up the mercury.
 Justify your choice, and for the choices you did not pick, explain what is wrong with them. Pictures help!
- The barometer below shows the level of mercury at a given atmospheric pressure. Fill all the other barometers with mercury for that same atmospheric pressure. Explain your answer.



- As you increase the temperature of a gas in a sealed, rigid container, what happens to the density of the gas? Would the results be the same if you did the same experiment in a container with a piston at constant pressure? (See Figure 5.17.)

- A diagram in a chemistry book shows a magnified view of a flask of air as follows:



What do you suppose is between the dots (the dots represent air molecules)?

- air
 - dust
 - pollutants
 - oxygen
 - nothing
- If you put a drinking straw in water, place your finger over the opening, and lift the straw out of the water, some water stays in the straw. Explain.
 - A chemistry student relates the following story: I noticed my tires were a bit low and went to the gas station. As I was filling the tires, I thought about the kinetic molecular theory (KMT). I noticed the tires because the volume was low, and I realized that I was increasing both the pressure and volume of the tires. "Hmmm," I thought, "that goes against what I learned in chemistry, where I was told pressure and volume are inversely proportional." What is the fault in the logic of the chemistry student in this situation? Explain why we think pressure and volume to be inversely related (draw pictures and use the KMT).
 - Chemicals *X* and *Y* (both gases) react to form the gas *XY*, but it takes a bit of time for the reaction to occur. Both *X* and *Y* are placed in a container with a piston (free to move), and you note the volume. As the reaction occurs, what happens to the volume of the container? (See Fig. 5.18.)
 - Which statement best explains why a hot-air balloon rises when the air in the balloon is heated?
 - According to Charles's law, the temperature of a gas is directly related to its volume. Thus the volume of the balloon increases, making the density smaller. This lifts the balloon.
 - Hot air rises inside the balloon, and this lifts the balloon.
 - The temperature of a gas is directly related to its pressure. The pressure therefore increases, and this lifts the balloon.
 - Some of the gas escapes from the bottom of the balloon, thus decreasing the mass of gas in the balloon. This decreases the density of the gas in the balloon, which lifts the balloon.
 - Temperature is related to the root mean square velocity of the gas molecules. Thus the molecules are moving faster, hitting the balloon more, and thus lifting the balloon.
 Justify your choice, and for the choices you did not pick, explain what is wrong with them.

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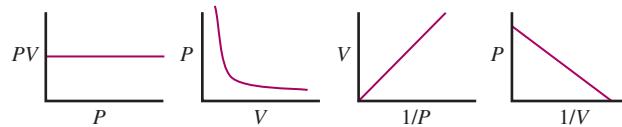
- 10.** Draw a highly magnified view of a sealed, rigid container filled with a gas. Then draw what it would look like if you cooled the gas significantly but kept the temperature above the boiling point of the substance in the container. Also draw what it would look like if you heated the gas significantly. Finally, draw what each situation would look like if you evacuated enough of the gas to decrease the pressure by a factor of 2.
- 11.** If you release a helium balloon, it soars upward and eventually pops. Explain this behavior.
- 12.** If you have any two gases in different containers that are the same size at the same pressure and same temperature, what is true about the moles of each gas? Why is this true?
- 13.** Explain the following seeming contradiction: You have two gases, A and B, in two separate containers of equal volume and at equal pressure and temperature. Therefore, you must have the same number of moles of each gas. Because the two temperatures are equal, the average kinetic energies of the two samples are equal. Therefore, since the energy given such a system will be converted to translational motion (that is, move the molecules), the root mean square velocities of the two are equal, and thus the particles in each sample move, on average, with the same relative speed. Since A and B are different gases, they each must have a different molar mass. If A has higher molar mass than B, the particles of A must be hitting the sides of the container with more force. Thus the pressure in the container of gas A must be higher than that in the container with gas B. However, one of our initial assumptions was that the pressures were equal.
- 14.** You have a balloon covering the mouth of a flask filled with air at 1 atm. You apply heat to the bottom of the flask until the volume of the balloon is equal to that of the flask.
- Which has more air in it, the balloon or the flask? Or do both have the same amount? Explain.
 - In which is the pressure greater, the balloon or the flask? Or is the pressure the same? Explain.
- 15.** How does Dalton's law of partial pressures help us with our model of ideal gases? That is, what postulates of the kinetic molecular theory does it support?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of the book and a solution appears in the *Solutions Guide*.

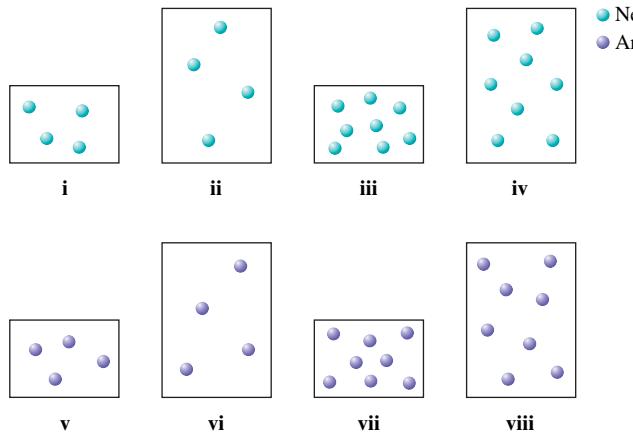
Questions

- 16.** At room temperature, water is a liquid with a molar volume of 18 mL. At 105°C and 1 atm pressure, water is a gas and has a molar volume of over 30 L. Explain the large difference in molar volumes.
- 17.** If a barometer were built using water ($d = 1.0 \text{ g/cm}^3$) instead of mercury ($d = 13.6 \text{ g/cm}^3$), would the column of water be higher than, lower than, or the same as the column of mercury at 1.00 atm? If the level is different, by what factor? Explain.
- 18.** A bag of potato chips is packed and sealed in Los Angeles, California, and then shipped to Lake Tahoe, Nevada, during ski season. It is noticed that the volume of the bag of potato chips has increased upon its arrival in Lake Tahoe. What external conditions would most likely cause the volume increase?

- 19.** Boyle's law can be represented graphically in several ways. Which of the following plots does *not* correctly represent Boyle's law (assuming constant T and n)? Explain.



- 20.** As weather balloons rise from the earth's surface, the pressure of the atmosphere becomes less, tending to cause the volume of the balloons to expand. However, the temperature is much lower in the upper atmosphere than at sea level. Would this temperature effect tend to make such a balloon expand or contract? Weather balloons do, in fact, expand as they rise. What does this tell you?
- 21.** Which noble gas has the smallest density at STP? Explain.
- 22.** Consider two different containers, each filled with 2 moles of Ne(g) . One of the containers is rigid and has constant volume. The other container is flexible (like a balloon) and is capable of changing its volume to keep the external pressure and internal pressure equal to each other. If you raise the temperature in both containers, what happens to the pressure and density of the gas inside each container? Assume a constant external pressure.
- 23.** Do all the molecules in a 1-mol sample of $\text{CH}_4(\text{g})$ have the same kinetic energy at 273 K? Do all molecules in a 1-mol sample of $\text{N}_2(\text{g})$ have the same velocity at 546 K? Explain.
- 24.** Consider the following samples of gases at the same temperature.



Arrange each of these samples in order from lowest to highest:

- pressure
- average kinetic energy
- density
- root mean square velocity

Note: Some samples of gases may have equal values for these attributes. Assume the larger containers have a volume twice the volume of the smaller containers and assume the mass of an argon atom is twice the mass of a neon atom.

- 25.** As $\text{NH}_3(\text{g})$ is decomposed into nitrogen gas and hydrogen gas at constant pressure and temperature, the volume of the product gases collected is twice the volume of NH_3 reacted. Explain. As $\text{NH}_3(\text{g})$

is decomposed into nitrogen gas and hydrogen gas at constant volume and temperature, the total pressure increases by some factor. Why the increase in pressure and by what factor does the total pressure increase when reactants are completely converted into products? How do the partial pressures of the product gases compare to each other and to the initial pressure of NH_3 ?

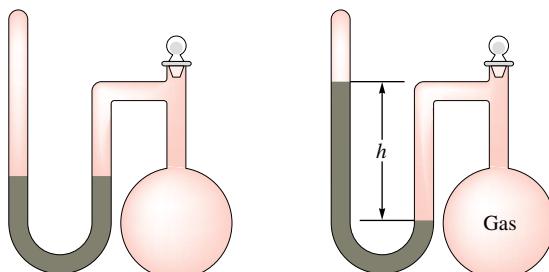
- 26.** Which of the following statements is (are) true? For the false statements, correct them.
- At constant temperature, the lighter the gas molecules, the faster the average velocity of the gas molecules.
 - At constant temperature, the heavier the gas molecules, the larger the average kinetic energy of the gas molecules.
 - A real gas behaves most ideally when the container volume is relatively large and the gas molecules are moving relatively quickly.
 - As temperature increases, the effect of interparticle interactions on gas behavior is increased.
 - At constant V and T , as gas molecules are added into a container, the number of collisions per unit area increases resulting in a higher pressure.
 - The kinetic molecular theory predicts that pressure is inversely proportional to temperature at constant volume and mol of gas.

Exercises

In this section similar exercises are paired.

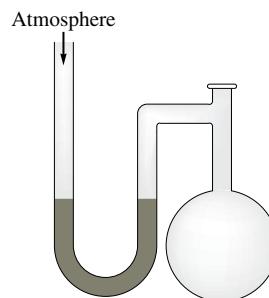
Pressure

- 27.** Freon-12 (CF_2Cl_2) is commonly used as the refrigerant in central home air conditioners. The system is initially charged to a pressure of 4.8 atm. Express this pressure in each of the following units (1 atm = 14.7 psi).
- mm Hg
 - torr
 - Pa
 - psi
- 28.** A gauge on a compressed gas cylinder reads 2200 psi (pounds per square inch; 1 atm = 14.7 psi). Express this pressure in each of the following units.
- standard atmospheres
 - megapascals (MPa)
 - torr
-
- 29.** A sealed-tube manometer (as shown below) can be used to measure pressures below atmospheric pressure. The tube above the mercury is evacuated. When there is a vacuum in the flask, the mercury levels in both arms of the U-tube are equal. If a gaseous sample is introduced into the flask, the mercury levels are different. The difference h is a measure of the pressure of the gas inside the flask. If h is equal to 6.5 cm, calculate the pressure in the flask in torr, pascals, and atmospheres.

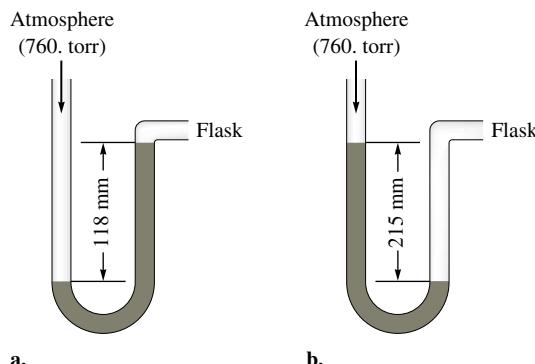


- 30.** If the sealed-tube manometer in Exercise 29 had a height difference of 20.0 inches between the mercury levels, what is the pressure in the flask in torr and atmospheres?

- 31.** A diagram for an open-tube manometer is shown below.



If the flask is open to the atmosphere, the mercury levels are equal. For each of the following situations where a gas is contained in the flask, calculate the pressure in the flask in torr, atmospheres, and pascals.



- c.** Calculate the pressures in the flask in parts a and b (in torr) if the atmospheric pressure is 635 torr.

- 32.** **a.** If the open-tube manometer in Exercise 31 contains a non-volatile silicone oil (density = 1.30 g/cm^3) instead of mercury (density = 13.6 g/cm^3), what are the pressures in the flask as shown in parts a and b in torr, atmospheres, and pascals?
b. What advantage would there be in using a less dense fluid than mercury in a manometer used to measure relatively small differences in pressure?

Gas Laws

- 33.** A particular balloon is designed by its manufacturer to be inflated to a volume of no more than 2.5 L. If the balloon is filled with 2.0 L of helium at sea level, is released, and rises to an altitude at which the atmospheric pressure is only 500. mm Hg, will the balloon burst? (Assume temperature is constant.)
- 34.** A balloon is filled to a volume of $7.00 \times 10^2 \text{ mL}$ at a temperature of 20.0°C . The balloon is then cooled at constant pressure to a temperature of $1.00 \times 10^2 \text{ K}$. What is the final volume of the balloon?