

# Gases and the Kinetic–Molecular Theory

# 12





*Immersed in water, this green plant oxidizes the water to form bubbles of gaseous oxygen, O<sub>2</sub>.*

## OUTLINE

- |      |  |       |   |
|------|--|-------|---|
| 12-1 | Comparison of Solids, Liquids, and Gases   | 12-9  | Summary of Gas Laws: The Ideal Gas Equation                                     |
| 12-2 | Composition of the Atmosphere and Some Common Properties of Gases                  | 12-10 | Determination of Molecular Weights and Molecular Formulas of Gaseous Substances |
| 12-3 | Pressure   | 12-11 | Dalton's Law of Partial Pressures   |
| 12-4 | Boyle's Law: The Volume–Pressure Relationship                                      | 12-12 | Mass–Volume Relationships in Reactions Involving Gases                          |
| 12-5 | Charles's Law: The Volume–Temperature Relationship; The Absolute Temperature Scale | 12-13 | The Kinetic–Molecular Theory  |
| 12-6 | Standard Temperature and Pressure  | 12-14 | Diffusion and Effusion of Gases   |
| 12-7 | The Combined Gas Law Equation  | 12-15 | Real Gases: Deviations from Ideality  |
| 12-8 | Avogadro's Law and the Standard Molar Volume                                       |       |   |

## OBJECTIVES

*After you have studied this chapter, you should be able to*

- *List the properties of gases and compare gases, liquids, and solids*
- *Describe how pressure is measured*
- *Use and understand the absolute (Kelvin) temperature scale*
- *Describe the relationships among pressure, volume, temperature, and amount of gas (Boyle's Law, Charles's Law, Avogadro's Law, and the Combined Gas Law), and the limitations of each*
- *Use Boyle's Law, Charles's Law, Avogadro's Law, and the Combined Gas Law, as appropriate, to calculate changes in pressure, volume, temperature, and amount of gas*
- *Calculate gas densities and the standard molar volume*
- *Use the ideal gas equation to do pressure, volume, temperature, and mole calculations as related to gas samples*
- *Determine molecular weights and formulas of gaseous substances from measured properties of gases*
- *Describe how mixtures of gases behave and predict their properties (Dalton's Law of Partial Pressures)*
- *Carry out calculations about the gases involved in chemical reactions*
- *Apply the kinetic–molecular theory of gases and describe how this theory is consistent with the observed gas laws*
- *Describe molecular motion, diffusion, and effusion of gases*
- *Describe the molecular features that are responsible for nonideal behavior of real gases and explain when this nonideal behavior is important*



**TABLE 12-1** Densities and Molar Volumes of Three Substances at Atmospheric Pressure\*

Substance	Solid		Liquid (20°C)		Gas (100°C)	
	Density (g/mL)	Molar volume (mL/mol)	Density (g/mL)	Molar volume (mL/mol)	Density (g/mL)	Molar volume (mL/mol)
water (H <sub>2</sub> O)	0.917 (0°C)	19.6	0.998	18.0	0.000588	30,600
benzene (C <sub>6</sub> H <sub>6</sub> )	0.899 (0°C)	86.9	0.876	89.2	0.00255	30,600
carbon tetrachloride (CCl <sub>4</sub> )	1.70 (-25°C)	90.5	1.59	96.8	0.00503	30,600

\*The molar volume of a substance is the volume occupied by one mole of that substance.

## 12-1 COMPARISON OF SOLIDS, LIQUIDS, AND GASES


Matter exists in three physical states: solids, liquids, and gases. In the solid state H<sub>2</sub>O is known as ice, in the liquid state it is called water, and in the gaseous state it is known as steam or water vapor. Most, but not all, substances can exist in all three states. Most solids change to liquids and most liquids change to gases as they are heated. Liquids and gases are known as **fluids** because they flow freely. Solids and liquids are referred to as **condensed states** because they have much higher densities than gases. Table 12-1 displays the densities of a few common substances in different physical states.

As the data in Table 12-1 indicate, solids and liquids are many times denser than gases. The molecules must be very far apart in gases and much closer together in liquids and solids. For example, the volume of one mole of liquid water is about 18 milliliters, whereas one mole of steam occupies about 30,600 milliliters at 100°C and atmospheric pressure. Gases are easily compressed, and they completely fill any container in which they are present. This tells us that the molecules in a gas are far apart relative to their sizes and that interactions among them are weak. The possibilities for interaction among gaseous molecules would be minimal (because they are so far apart) were it not for their rapid motion.

All substances that are gases at room temperature may be liquefied by cooling and compressing them. Volatile liquids are easily converted to gases at room temperature or slightly above. The term **vapor** refers to a gas that is formed by evaporation of a liquid or sublimation of a solid. We often use this term when some of the liquid or solid remains in contact with the gas.

Some compounds decompose before melting or boiling.

Ice is less dense than liquid water. This behavior is quite unusual; most substances are denser in the solid state than in the liquid state.

 See the Saunders Interactive General Chemistry CD-ROM, Screen 1.3, States of Matter.

Volatile liquids evaporate readily. They have low boiling points.

## 12-2 COMPOSITION OF THE ATMOSPHERE AND SOME COMMON PROPERTIES OF GASES

Many important chemical substances are gases at ambient conditions. The earth's atmosphere is a mixture of gases and particles of liquids and solids (Table 12-2). The major gaseous components are N<sub>2</sub> (bp -195.79°C) and O<sub>2</sub> (bp -182.98°C), with smaller concentrations of other gases. All gases are *miscible*; that is, they mix completely *unless* they react with one another.

Several scientists, notably Torricelli (1643), Boyle (1660), Charles (1787), and Graham (1831), laid an experimental foundation on which our present understanding of gases is based. For example, their investigations showed that

Gas	% by Volume
N <sub>2</sub>	78.09
O <sub>2</sub>	20.94
Ar	0.93
CO <sub>2</sub>	0.03*
He, Ne, Kr, Xe	0.002
CH <sub>4</sub>	0.00015*
H <sub>2</sub>	0.00005
All others combined†	< 0.00004

\*Variable.

†Atmospheric moisture varies.




Diffusion of bromine vapor in air. Some liquid bromine (*dark reddish brown*) was placed in the small inner bottle. As the liquid evaporated, the resulting reddish brown gas diffused.

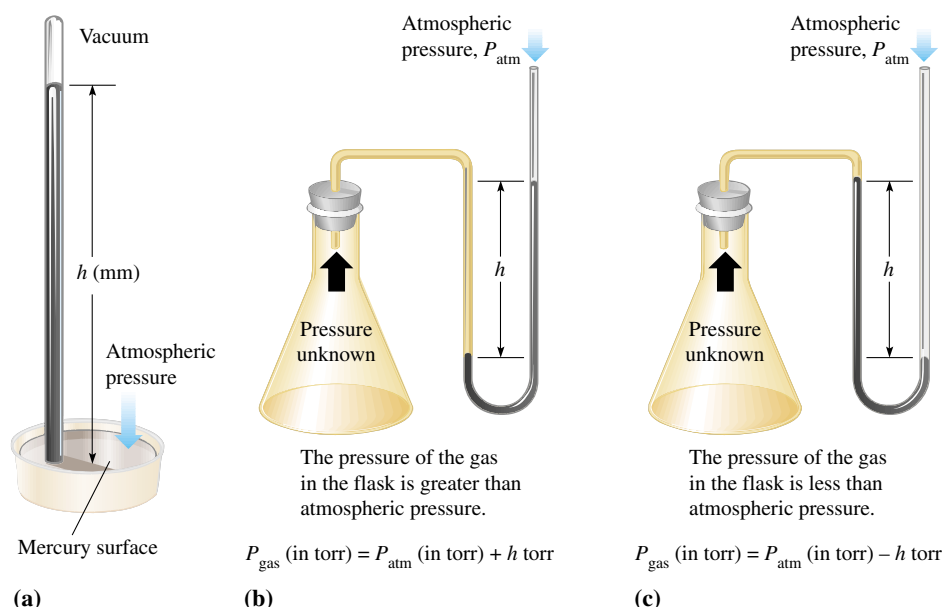
1. Gases can be compressed into smaller volumes; that is, their densities can be increased by applying increased pressure.
2. Gases exert pressure on their surroundings; in turn, pressure must be exerted to confine gases.
3. Gases expand without limits, and so gas samples completely and uniformly occupy the volume of any container.
4. Gases diffuse into one another, and so samples of gas placed in the same container mix completely. Conversely, different gases in a mixture do not separate on standing.
5. The amounts and properties of gases are described in terms of temperature, pressure, the volume occupied, and the number of molecules present. For example, a sample of gas occupies a greater volume when hot than it does when cold at the same pressure, but the number of molecules does not change.

Investigating four variables at once is difficult. In Sections 12-4 through 12-8 we shall see how to study these variables two at a time. Section 12-9 will consolidate these descriptions into a single relationship, the ideal gas equation.

### 12-3 PRESSURE

**Pressure** is defined as force per unit area—for example, pounds per square inch ( $\text{lb/in.}^2$ ), commonly known as *psi*. Pressure may be expressed in many different units, as we shall see. The mercury **barometer** is a simple device for measuring atmospheric pressures. Figure 12-1a illustrates the “heart” of the mercury barometer. A glass tube (about 800 mm long) is sealed at one end, filled with mercury, and then carefully inverted into a dish of mercury without air being allowed to enter. The mercury in the tube falls to the level at which the pressure of the air on the surface of the mercury in the dish equals the gravitational pull downward on the mercury in the tube. The air pressure is measured in terms

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.2, Properties of Gases: Pressure.



**Figure 12-1** Some laboratory devices for measuring pressure. (a) Schematic diagram of a closed-end barometer. At the level of the lower mercury surface, the pressure both inside and outside the tube must be equal to that of the atmosphere. There is no air inside the tube, so the pressure is exerted only by the mercury column  $h$  mm high. Hence, the atmospheric pressure must equal the pressure exerted by  $h$  mm Hg, or  $h$  torr. (b) The two-arm mercury barometer is called a manometer. In this sample, the pressure of the gas inside the flask is *greater than* the external atmospheric pressure. At the level of the lower mercury surface, the total pressure on the mercury in the left arm must equal the total pressure on the mercury in the right arm. The pressure exerted by the gas is equal to the external pressure *plus* the pressure exerted by the mercury column of height  $h$  mm, or  $P_{\text{gas}} \text{ (in torr)} = P_{\text{atm}} \text{ (in torr)} + h \text{ torr}$ . (c) When the gas pressure measured by the manometer is *less than* the external atmospheric pressure, the pressure exerted by the atmosphere is equal to the gas pressure *plus* the pressure exerted by the mercury column, or  $P_{\text{atm}} = P_{\text{gas}} + h$ . We can rearrange this to write  $P_{\text{gas}} \text{ (in torr)} = P_{\text{atm}} \text{ (in torr)} - h \text{ torr}$ .

of the height of the mercury column, that is, the vertical distance between the surface of the mercury in the open dish and that inside the closed tube. The pressure exerted by the atmosphere is equal to the pressure exerted by the column of mercury.

Mercury barometers are simple and well known, so gas pressures are frequently expressed in terms of millimeters of mercury (mm Hg, or just mm). In recent years the unit **torr** has been used to indicate pressure; it is defined as  $1 \text{ torr} = 1 \text{ mm Hg}$ .

A mercury **manometer** consists of a glass U-tube partially filled with mercury. One arm is open to the atmosphere, and the other is connected to a container of gas (see Figure 12-1b,c).

Atmospheric pressure varies with atmospheric conditions and distance above sea level. The atmospheric pressure decreases with increasing elevation because there is a decreasing mass of air above it. Approximately one half of the matter in the atmosphere is less than 20,000 feet above sea level. Thus, atmospheric pressure is only about one half as great at

*(text continues on page 440)*

The unit *torr* was named for Evangelista Torricelli (1608–1647), who invented the mercury barometer.



## The Environment

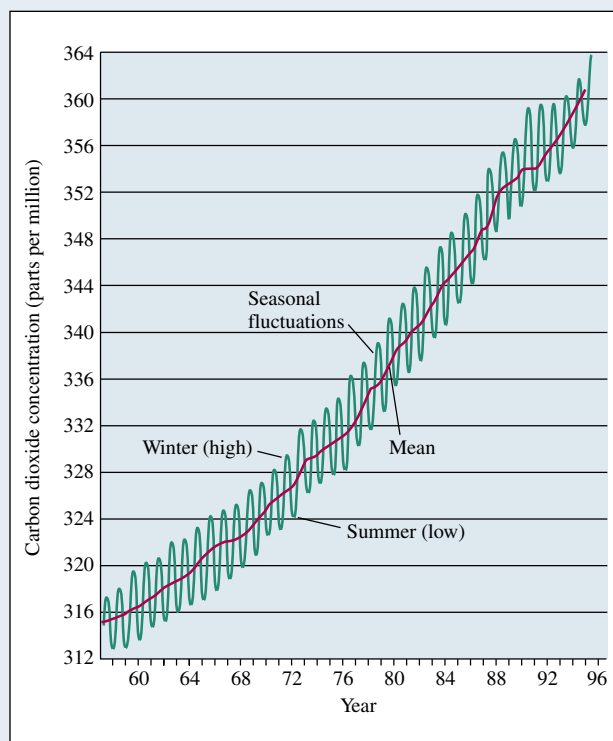
### The Greenhouse Effect

During the twentieth century, the great increase in our use of fossil fuels caused a significant rise in the concentration of carbon dioxide,  $\text{CO}_2$ , in the atmosphere. Scientists believe that the concentration of atmospheric  $\text{CO}_2$  could double by early in the 21st century, compared with its level just before the Industrial Revolution. During the last 100 to 200 years, the  $\text{CO}_2$  concentration has increased by 25%. The curve in Figure (a) shows the recent steady rise in atmospheric  $\text{CO}_2$  concentration.

Energy from the sun reaches the earth in the form of light. Neither  $\text{CO}_2$  nor  $\text{H}_2\text{O}$  vapor absorbs the visible light in sunlight, so they do not prevent it from reaching the surface of the earth. The energy given off by the earth in the form of lower-energy infrared (heat) radiation, however, is readily absorbed by both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (as it is by the glass or plastic of greenhouses). Thus, some of the heat the earth must lose to stay in thermal equilibrium can become trapped in the atmosphere, causing the temperature to rise (Figure b). This phenomenon, called the **greenhouse effect**, has been the subject of much discussion among scientists and the topic of many articles in the popular press. The anticipated rise in average global temperature by the year 2050 due to increased  $\text{CO}_2$  concentration is predicted to be 2 to 5°C.

An increase of 2 to 5°C may not seem like much. However, this is thought to be enough to cause a dramatic change in climate, transforming now productive land into desert and altering the habitats of many animals and plants beyond their ability to adapt. Another drastic consequence of even this small temperature rise would be the partial melting of the polar ice caps. The resulting rise in sea level, though only a few feet, would mean that water would inundate coastal cities such as Los Angeles, New York, and Houston, and low-lying coastal areas such as southern Florida and Louisiana. On a global scale, the effects would be devastating.

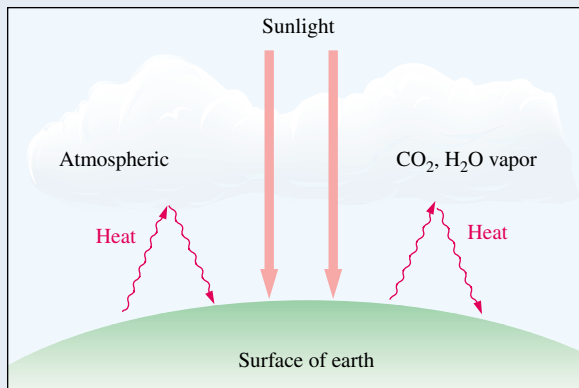
The earth's forests and jungles play a crucial role in maintaining the balance of gases in the atmosphere, removing  $\text{CO}_2$  and supplying  $\text{O}_2$ . The massive destruction, for economic reasons, of heavily forested areas such as the Amazon rain forest in South America is cited as another long-term contributor to global environmental problems. Worldwide, more than 3 million square miles of once-forested land is now barren for some reason; at least 60% of this land is now unused.



(a) A plot of the monthly average  $\text{CO}_2$  concentration in parts per million (ppm), measured at Mauna Loa Observatory, Hawaii, far from significant sources of  $\text{CO}_2$  from human activities. Annual fluctuations occur because plants in the Northern Hemisphere absorb  $\text{CO}_2$  in the spring and release it as they decay in the fall.

Environmental scientists estimate that if even one quarter of this land could be reforested, the vegetation would absorb 1.1 billion tons of  $\text{CO}_2$  annually.

Some scientists are more skeptical than others about the role of human-produced  $\text{CO}_2$  in climate changes and, indeed,



(b) The greenhouse effect. Visible light passes through atmospheric H<sub>2</sub>O and CO<sub>2</sub>, but heat radiated from the surface of the earth is absorbed by these gases.

about whether global warming is a significant phenomenon or simply another of the recognized warm–cold cycles that have occurred throughout the earth’s history. Such skeptics point out an unexplained increase in atmospheric CO<sub>2</sub> dur-



ing an extended period in the seventeenth century, and an even higher and more prolonged peak about 130,000 years ago. Even the most skeptical observers, however, seem to agree that responsible stewardship of the planet requires that we do something in a reasoned fashion to reduce production of greenhouse gases, primarily CO<sub>2</sub>, and that this will involve decreasing our dependence on energy from fossil fuels. Despite the technical and political problems of waste disposal, an essentially all-electric economy based on nuclear power may someday be a usable solution.

Much CO<sub>2</sub> is eventually absorbed by the vast amount of water in the oceans, where the carbonate–bicarbonate buffer system almost entirely counteracts any adverse effects of ocean water acidity. Ironically, there is also evidence to suggest that other types of air pollution in the form of particulate matter may partially counteract the greenhouse effect. The particles reflect visible (sun) radiation rather than absorbing it, blocking some light from entering the atmosphere. It seems foolish, however, to depend on one form of pollution to help rescue us from the effects of another! Real solutions to current environmental problems such as the greenhouse effect are not subject to quick fixes, but depend on long-term cooperative international efforts that are based on the firm knowledge resulting from scientific research.

Tropical rain forests are important in maintaining the balance of CO<sub>2</sub> and O<sub>2</sub> in the earth’s atmosphere. In recent years a portion of the South American forests (by far the world’s largest) larger than France has been destroyed, either by flooding caused by hydroelectric dams or by clearing of forest land for agricultural or ranching use. Such destruction continues at a rate of more than 20,000 square kilometers per year. If current trends continue, many of the world’s rain forests will be severely reduced or even obliterated in the next few years. The fundamental question—“What are the long-term consequences of the destruction of tropical rain forests?”—remains unanswered.



**Figure 12-2** Some commercial pressure-measuring devices. (a) A commercial mercury barometer. (b) Portable barometers. This type is called an *aneroid* (“not wet”) barometer. Some of the air has been removed from the airtight box, which is made of thin, flexible metal. When the pressure of the atmosphere changes, the remaining air in the box expands or contracts (Boyle’s Law), moving the flexible box surface and an attached pointer along a scale. (c) A tire gauge. This kind of gauge registers “relative” pressure, that is, the *difference* between internal pressure and the external atmospheric pressure. For instance, when the gauge reads 30 psi (pounds per square inch), the total gas pressure in the tire is 30 psi + 1 atm, or about 45 psi. In engineering terminology, this is termed “psig” (g = gauge).



(a)



(b)



(c)

20,000 feet as it is at sea level. Mountain climbers and pilots use portable barometers to determine their altitudes (Figure 12-2). At sea level, at a latitude of 45°, the average atmospheric pressure supports a column of mercury 760 mm high in a simple mercury barometer when the mercury is at 0°C. This average sea-level pressure of 760 mm Hg is called **one atmosphere of pressure**.

$$1 \text{ atmosphere (atm)} = 760 \text{ mm Hg at } 0^\circ\text{C} = 760 \text{ torr}$$

The SI unit of pressure is the **pascal** (Pa), defined as the pressure exerted by a force of one newton acting on an area of one square meter. By definition, one **newton** (N) is the force required to give a mass of one kilogram an acceleration of one meter per second per second. Symbolically we represent one newton as

$$1 \text{ N} = \frac{1 \text{ kg} \cdot \text{m}}{\text{s}^2} \quad \text{so} \quad 1 \text{ Pa} = \frac{1 \text{ N}}{\text{m}^2} = \frac{1 \text{ kg}}{\text{m} \cdot \text{s}^2}$$

One atmosphere of pressure =  $1.01325 \times 10^5$  Pa, or 101.325 kPa.

Acceleration is the change in velocity (m/s) per unit time (s),  $\text{m/s}^2$ .



### 12-4 BOYLE'S LAW: THE VOLUME–PRESSURE RELATIONSHIP

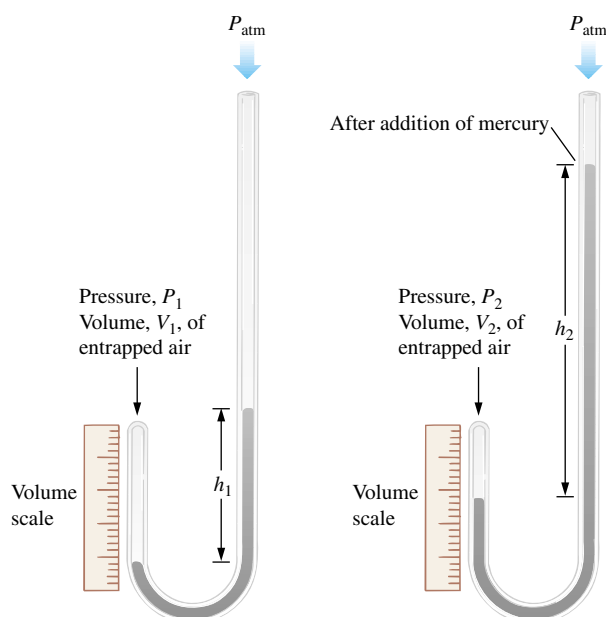
Early experiments on the behavior of gases were carried out by Robert Boyle (1627–1691) in the seventeenth century. In a typical experiment (Figure 12-3), a sample of a gas was trapped in a U-tube and allowed to come to constant temperature. Then its volume and the difference in the heights of the two mercury columns were recorded. This difference in height plus the pressure of the atmosphere represents the pressure on the gas. Addition of more mercury to the tube increases the pressure by changing the height of the mercury column. As a result, the gas volume decreases. The results of several such experiments are tabulated in Figure 12-4a.

Boyle showed that for a given sample of gas at constant temperature, the product of pressure and volume,  $P \times V$ , was always the same number.

At a given temperature, the product of pressure and volume of a definite mass of gas is constant.

$$PV = k \quad (\text{constant } n, T)$$

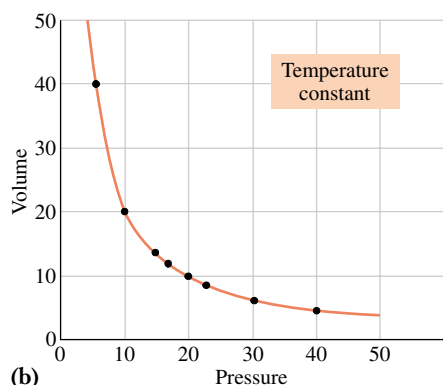
This relationship is **Boyle's Law**. The value of  $k$  depends on the amount (number of moles,  $n$ ) of gas present and on the temperature,  $T$ . Units for  $k$  are determined by the units used to express the volume ( $V$ ) and pressure ( $P$ ).



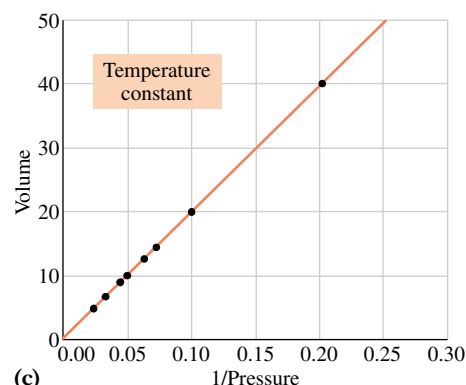
**Figure 12-3** A representation of Boyle's experiment. A sample of air is trapped in a tube in such a way that the pressure on the air can be changed and the volume of the air measured.  $P_{\text{atm}}$  is the atmospheric pressure, measured with a barometer.  $P_1 = h_1 + P_{\text{atm}}$ ,  $P_2 = h_2 + P_{\text{atm}}$ .

$P$	$V$	$P \times V$	$1/P$
5.0	40.0	200	0.20
10.0	20.0	200	0.10
15.0	13.3	200	0.0667
17.0	11.8	201	0.0588
20.0	10.0	200	0.0500
22.0	9.10	200	0.0455
30.0	6.70	201	0.0333
40.0	5.00	200	0.0250

(a)



(b)



(c)

**Figure 12-4** (a) Some typical data from an experiment such as that shown in Figure 12-3. Measured values of  $P$  and  $V$  are presented in the first two columns, on an arbitrary scale. (b, c) Graphical representations of Boyle's Law, using the data of part (a). (b)  $V$  versus  $P$ . (c)  $V$  versus  $1/P$ .

When the volume of a gas is plotted against its pressure at constant temperature, the resulting curve is one branch of a hyperbola. Figure 12-4b is a graphic illustration of this inverse relationship. When volume is plotted versus the reciprocal of the pressure,  $1/P$ , a straight line results (Figure 12-4c). In 1662, Boyle summarized the results of his experiments on various samples of gases in an alternative statement of Boyle's Law:

At constant temperature the volume,  $V$ , occupied by a definite mass of a gas is inversely proportional to the applied pressure,  $P$ .

$$V \propto \frac{1}{P} \quad \text{or} \quad V = k \left( \frac{1}{P} \right) \quad (\text{constant } n, T)$$

The symbol  $\propto$  reads "is proportional to." A proportionality is converted into an equality by introducing a proportionality constant,  $k$ .

At normal temperatures and pressure, most gases obey Boyle's Law rather well. We call this *ideal behavior*. Deviations from ideality are discussed in Section 12-15.

Let us think about a fixed mass of gas at constant temperature, but at two different conditions of pressure and volume (see Figure 12-3). For the first condition we can write

$$P_1 V_1 = k \quad (\text{constant } n, T)$$

and for the second condition we can write

$$P_2 V_2 = k \quad (\text{constant } n, T)$$

Because the right-hand sides of these two equations are the same, the left-hand sides must be equal, or

$$P_1 V_1 = P_2 V_2 \quad (\text{for a given amount of a gas at constant temperature})$$

This form of Boyle's Law is useful for calculations involving pressure and volume changes, as the following examples demonstrate.

**EXAMPLE 12-1** *Boyle's Law Calculation*

A sample of gas occupies 12 L under a pressure of 1.2 atm. What would its volume be if the pressure were increased to 2.4 atm?

**Plan**

We know the volume at one pressure and want to find the volume at another pressure (constant temperature). This suggests that we use Boyle's Law. We tabulate what is known and what is asked for, and then solve the Boyle's Law equation for the unknown quantity,  $V_2$ .

**Solution**

We have

$$\begin{array}{ll} V_1 = 12 \text{ L} & P_1 = 1.2 \text{ atm} \\ V_2 = ? & P_2 = 2.4 \text{ atm} \end{array}$$

Solving Boyle's Law,  $P_1V_1 = P_2V_2$ , for  $V_2$  and substituting gives

$$V_2 = \frac{P_1V_1}{P_2} = \frac{(1.2 \text{ atm})(12 \text{ L})}{2.4 \text{ atm}} = 6.0 \text{ L}$$

Pressure and volume are inversely proportional. Doubling the pressure halves the volume of a sample of gas at constant temperature.

It is often helpful to tabulate what is given and what is asked for in a problem.

**Problem-Solving Tip: Units in Boyle's Law Calculations**

Which units for volume and pressure are appropriate for Boyle's Law calculations? Boyle's Law in the form  $P_1V_1 = P_2V_2$  can be written as  $V_1/V_2 = P_2/P_1$ . This involves a ratio of volumes, so they can be expressed in any volume units—liters, milliliters, cubic feet—as long as the *same* units are used for both volumes. Likewise, because Boyle's Law involves a ratio of pressures, you can use any units for pressures—atmospheres, torr, pascals—as long as the *same* units are used for both pressures.

**EXAMPLE 12-2** *Boyle's Law Calculation*

A sample of oxygen occupies 10.0 L under a pressure of 790. torr (105 kPa). At what pressure would it occupy 13.4 L if the temperature did not change?

**Plan**

We know the pressure at one volume and wish to find the pressure at another volume (at constant temperature). We can solve Boyle's Law for the second pressure and substitute.

**Solution**

We have  $P_1 = 790.$  torr;  $V_1 = 10.0$  L;  $P_2 = ?$ ;  $V_2 = 13.4$  L. Solving Boyle's Law,  $P_1V_1 = P_2V_2$ , for  $P_2$  and substituting yields

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(790. \text{ torr})(10.0 \text{ L})}{13.4 \text{ L}} = 590. \text{ torr} \quad \left( \times \frac{101.3 \text{ kPa}}{760. \text{ torr}} = 78.6 \text{ kPa} \right)$$

You should now work Exercises 16 and 17.


**Problem-Solving Tip:** Use What You Can Predict About the Answer

In Example 12-1 the calculated volume decrease is consistent with the increase in pressure. We can use this reasoning in another method for solving that problem, that is, by setting up a “Boyle’s Law factor” to change the volume in the direction required by the pressure change. We reason that the pressure increases from 1.2 atm to 2.4 atm, so the volume *decreases* by the factor (1.2 atm/2.4 atm). The solution then becomes

$$\begin{aligned} \underline{?} \text{ L} &= 12 \text{ L} \times (\text{Boyle's Law factor that would decrease the volume}) \\ &= 12 \text{ L} \times \left( \frac{1.2 \text{ atm}}{2.4 \text{ atm}} \right) = 6.0 \text{ L} \end{aligned}$$

Now solve Example 12-2 using a Boyle’s Law factor.



An artist’s representation of Jacques Charles’s first ascent in a hydrogen balloon at the Tuileries, Paris, December 1, 1783.

Lord Kelvin (1824–1907) was born William Thompson. At the age of ten he was admitted to Glasgow University. Because its new appliance was based on Kelvin’s theories, a refrigerator company named its product the Kelvinator.

Recall that temperatures on the Kelvin scale are expressed in kelvins (not degrees Kelvin) and represented by K, not °K.

Absolute zero may be thought of as the limit of thermal contraction for an ideal gas.

## 12-5 CHARLES’S LAW: THE VOLUME–TEMPERATURE RELATIONSHIP; THE ABSOLUTE TEMPERATURE SCALE

In his pressure–volume studies on gases, Robert Boyle noticed that heating a sample of gas caused some volume change, but he did not follow up on this observation. About 1800, two French scientists—Jacques Charles (1746–1823) and Joseph Gay-Lussac (1778–1850), pioneer balloonists at the time—began studying the expansion of gases with increasing temperature. Their studies showed that the rate of expansion with increased temperature was constant and was the same for all the gases they studied as long as the pressure remained constant. The implications of their discovery were not fully recognized until nearly a century later. Then scientists used this behavior of gases as the basis of a new temperature scale, the absolute temperature scale.

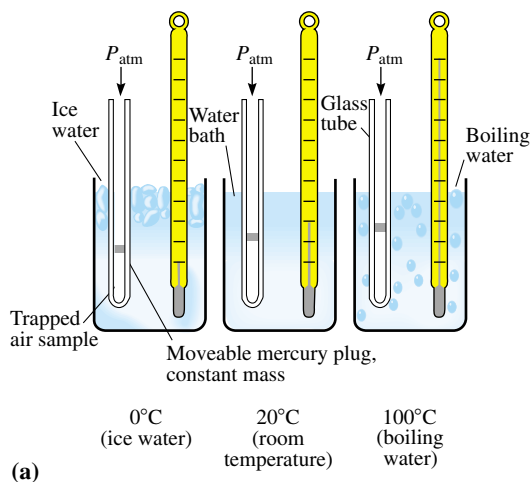
The change of volume with temperature, at constant pressure, is illustrated in Figure 12-5. From the table of typical data in Figure 12-5b, we see that volume ( $V$ , mL) increases as temperature ( $t$ , °C) increases, but the quantitative relationship is not yet obvious. These data are plotted in Figure 12-5c (line A), together with similar data for the same gas sample at different pressures (lines B and C).

Lord Kelvin, a British physicist, noticed that an extension of the different temperature–volume lines back to zero volume (dashed line) yields a common intercept at  $-273.15^\circ\text{C}$  on the temperature axis. Kelvin named this temperature **absolute zero**. The degrees are the same size over the entire scale, so  $0^\circ\text{C}$  becomes 273.15 degrees above absolute zero. In honor of Lord Kelvin’s work, this scale is called the Kelvin temperature scale. As pointed out in Section 1-12, the relationship between the Celsius and Kelvin temperature scales is  $\text{K} = ^\circ\text{C} + 273.15^\circ$ .

If we convert temperatures ( $^\circ\text{C}$ ) to absolute temperatures (K), the green scale in Figure 12-5c, the volume–temperature relationship becomes obvious. This relationship is known as **Charles’s Law**.

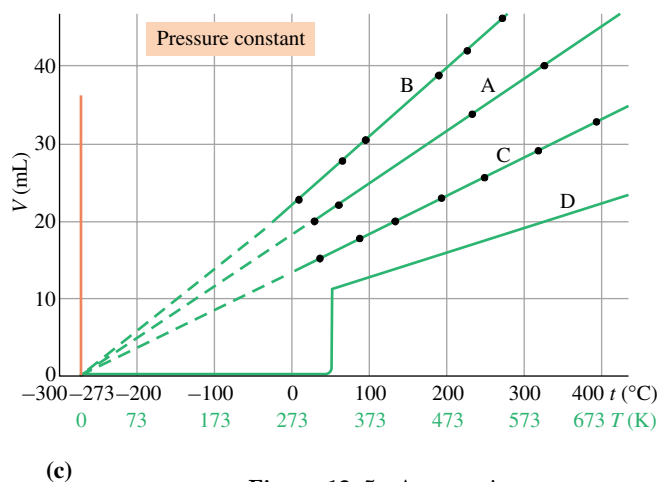
At constant pressure, the volume occupied by a definite mass of a gas is directly proportional to its absolute temperature.





$t$ (°C)	$V$ (mL)	$T$ (K)
27	20.0	300
54	21.8	327
100	24.9	373
127	26.7	400
227	33.3	500
327	40.0	600
427	46.7	700

(b)



**Figure 12-5** An experiment showing that the volume of an ideal gas increases as the temperature is increased at constant pressure. (a) A mercury plug of constant weight, plus atmospheric pressure, maintains a constant pressure on the trapped air. (b) Some representative volume–temperature data at constant pressure. The relationship becomes clear when  $t$  (°C) is converted to  $T$  (K) by adding 273°C. (c) A graph in which volume is plotted versus temperature on two different scales. Lines A, B, and C represent the same mass of the same ideal gas at different pressures. Line A represents the data tabulated in part (b). Graph D shows the behavior of a gas that condenses to form a liquid (in this case, at 50°C) as it is cooled.

We can express Charles’s Law in mathematical terms as

$$V \propto T \quad \text{or} \quad V = kT \quad (\text{constant } n, P)$$

Rearranging the expression gives  $V/T = k$ , a concise statement of Charles’s Law. As the temperature increases, the volume must increase proportionally. If we let subscripts 1 and 2 represent values for the same sample of gas at two different temperatures, we obtain

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{for a definite mass of gas at constant pressure})$$

which is the more useful form of Charles’s Law. This relationship is valid *only* when temperature,  $T$ , is expressed on an absolute (usually the Kelvin) scale.



When balloons filled with air are cooled in liquid nitrogen (bp  $-196^\circ\text{C}$ ), each shrinks to a small fraction of its original volume. Because the boiling points of the other components of air, except He and Ne, are higher than  $-196^\circ\text{C}$ , they condense to form liquids. When the balloons are removed from the liquid nitrogen, the liquids vaporize to form gases again. As the air warms to room temperature, the balloons expand to their original volume (Charles’s Law).

**EXAMPLE 12-3** Charles's Law Calculation

A sample of nitrogen occupies 117 mL at 100.°C. At what temperature in °C would it occupy 234 mL if the pressure did not change?

**Plan**

We know the volume of the sample at one temperature and wish to know its temperature corresponding to a second volume (constant pressure). We can solve Charles's Law for the second temperature. We must remember to carry out calculations with all temperatures expressed on the Kelvin scale, converting to or from Celsius as necessary.

**Solution**

$$\begin{aligned}
 V_1 &= 117 \text{ mL} & V_2 &= 234 \text{ mL} \\
 T_1 &= 100.^\circ\text{C} + 273^\circ = 373 \text{ K} & T_2 &= ? \\
 \frac{V_1}{T_1} &= \frac{V_2}{T_2} & \text{and} & T_2 = \frac{V_2 T_1}{V_1} = \frac{(234 \text{ mL})(373 \text{ K})}{(117 \text{ mL})} = 746 \text{ K} \\
 & & & ^\circ\text{C} = 746 \text{ K} - 273^\circ = 473^\circ\text{C}
 \end{aligned}$$

The temperature doubles on the Kelvin scale, from 373 K to 746 K, so the volume doubles.

*You should now work Exercise 24.*



**Problem-Solving Tip:** *Be Careful of Units in Charles's Law Calculations*

Which units for volume and temperature are appropriate for Charles's Law calculations?

The equation  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$  can be written as  $\frac{V_1}{V_2} = \frac{T_1}{T_2}$ . This involves a ratio of volumes, so they can be expressed in any volume units—liters, milliliters, cubic feet—as long as the *same* units are used for both volumes. But the relationship *does not apply at all* unless the temperatures are both expressed on an absolute scale. Remember to express all temperatures in kelvins for Charles's Law calculations.

## 12-6 STANDARD TEMPERATURE AND PRESSURE

We have seen that both temperature and pressure affect the volumes (and therefore the densities) of gases. It is often convenient to choose some “standard” temperature and pressure as a reference point for discussing gases. **Standard temperature and pressure (STP)** are, by international agreement, exactly 0°C (273.15 K) and one atmosphere of pressure (760. torr).

## 12-7 THE COMBINED GAS LAW EQUATION

Boyle's Law relates the pressures and volumes of a sample of gas at constant temperature,  $P_1V_1 = P_2V_2$ . Charles's Law relates the volumes and temperatures at constant pressure,

$V_1/T_1 = V_2/T_2$ . Combination of Boyle's Law and Charles's Law into a single expression gives the **combined gas law equation**.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad (\text{constant amount of gas})$$

When any five of the variables in the equation are known, the sixth variable can be calculated.

Notice that the combined gas law equation becomes

1.  $P_1V_1 = P_2V_2$  (Boyle's Law) when  $T$  is constant;
2.  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$  (Charles's Law) when  $P$  is constant; and
3.  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$  when  $V$  is constant.

### EXAMPLE 12-4 Combined Gas Law Calculation

A sample of neon occupies 105 liters at 27°C under a pressure of 985 torr. What volume would it occupy at standard temperature and pressure (STP)?

#### Plan

A sample of gas is changing in all three quantities  $P$ ,  $V$ , and  $T$ . This suggests that we use the combined gas law equation. We tabulate what is known and what is asked for, solve the combined gas law equation for the unknown quantity,  $V_2$ , and substitute known values.

#### Solution

$$\begin{array}{lll} V_1 = 105 \text{ L} & P_1 = 985 \text{ torr} & T_1 = 27^\circ\text{C} + 273^\circ = 300. \text{ K} \\ V_2 = \underline{?} & P_2 = 760. \text{ torr} & T_2 = 273 \text{ K} \end{array}$$

Solving for  $V_2$ ,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{so} \quad V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{(985 \text{ torr})(105 \text{ L})(273 \text{ K})}{(760. \text{ torr})(300. \text{ K})} = 124 \text{ L}$$

Alternatively, we can multiply the original volume by a Boyle's Law factor and a Charles's Law factor. As the pressure decreases from 985 torr to 760. torr, the volume increases, so the Boyle's Law factor is 985 torr/760. torr. As the temperature decreases from 300. K to 273 K, the volume decreases, so the Charles's Law factor is 273 K/300. K. Multiplication of the original volume by these factors gives the same result.

$$\underline{?} \text{ L} = 105 \text{ L} \times \frac{985 \text{ torr}}{760. \text{ torr}} \times \frac{273 \text{ K}}{300. \text{ K}} = 124 \text{ L}$$

The temperature decrease (from 300. K to 273 K) alone would give only a small *decrease* in the volume of neon, by a factor of 273 K/300. K, or 0.910. The pressure decrease (from 985 torr to 760. torr) alone would result in a greater *increase* in the volume, by a factor of 985 torr/760. torr, or 1.30. The result of the two changes is that the volume increases from 105 liters to 124 liters.

### EXAMPLE 12-5 Combined Gas Law Calculation

A sample of gas occupies 12.0 liters at 240.°C under a pressure of 80.0 kPa. At what temperature would the gas occupy 15.0 liters if the pressure were increased to 107 kPa?

#### Plan

The approach is the same as for Example 12-4 except that the unknown quantity is now the temperature,  $T_2$ .

**Solution**

$$V_1 = 12.0 \text{ L} \quad P_1 = 80.0 \text{ kPa} \quad T_1 = 240.^\circ\text{C} + 273^\circ = 513 \text{ K}$$

$$V_2 = 15.0 \text{ L} \quad P_2 = 107 \text{ kPa} \quad T_2 = ?$$

We solve the combined gas law equation for  $T_2$ .

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{so} \quad T_2 = \frac{P_2 V_2 T_1}{P_1 V_1} = \frac{(107 \text{ kPa})(15.0 \text{ L})(513 \text{ K})}{(80.0 \text{ kPa})(12.0 \text{ L})} = 858 \text{ K}$$

$$\text{K} = ^\circ\text{C} + 273^\circ \quad \text{so} \quad ^\circ\text{C} = 858 \text{ K} - 273^\circ = 585^\circ\text{C}$$

You should now work Exercises 32 and 33.

**Problem-Solving Tip: Units in Combined Gas Law Calculations**

The combined gas law equation is derived by combining Boyle's and Charles's Laws, so the comments in earlier Problem-Solving Tips also apply to this equation. Remember to express all temperatures in kelvins. Volumes can be expressed in any units as long as both are in the same units. Similarly, any pressure units can be used, so long as both are in the same units. Example 12-4 uses torr for both pressures; Example 12-5 uses kPa for both pressures.

## 12-8 AVOGADRO'S LAW AND THE STANDARD MOLAR VOLUME

In 1811, Amedeo Avogadro postulated that

at the same temperature and pressure, equal volumes of all gases contain the same number of molecules.

Many experiments have demonstrated that Avogadro's hypothesis is accurate to within about  $\pm 2\%$ , and the statement is now known as **Avogadro's Law**.

Avogadro's Law can also be stated as follows.

At constant temperature and pressure, the volume,  $V$ , occupied by a gas sample is directly proportional to the number of moles,  $n$ , of gas.

$$V \propto n \quad \text{or} \quad V = kn \quad \text{or} \quad \frac{V}{n} = k \quad (\text{constant } P, T)$$

For two samples of gas at the same temperature and pressure, the relation between volumes and numbers of moles can be represented as

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (\text{constant } T, P)$$



**TABLE 12-3** *Standard Molar Volumes and Densities of Some Gases*

Gas	Formula	(g/mol)	Standard Molar Volume (L/mol)	Density at STP (g/L)
hydrogen	H <sub>2</sub>	2.02	22.428	0.090
helium	He	4.003	22.426	0.178
neon	Ne	20.18	22.425	0.900
nitrogen	N <sub>2</sub>	28.01	22.404	1.250
oxygen	O <sub>2</sub>	32.00	22.394	1.429
argon	Ar	39.95	22.393	1.784
carbon dioxide	CO <sub>2</sub>	44.01	22.256	1.977
ammonia	NH <sub>3</sub>	17.03	22.094	0.771
chlorine	Cl <sub>2</sub>	70.91	22.063	3.214

Deviations in standard molar volume indicate that gases do not behave ideally.

The volume occupied by a mole of gas at *standard temperature and pressure*, STP, is referred to as the standard molar volume. It is nearly constant for all gases (Table 12-3).

The volume percentages given in Table 12-2 are also equal to mole percentages.

The **standard molar volume** of an ideal gas is taken to be 22.414 liters per mole at STP.

Gas densities depend on pressure and temperature; however, the number of moles of gas in a given sample does not change with temperature or pressure. Pressure changes affect volumes of gases according to Boyle's Law, and temperature changes affect volumes of gases according to Charles's Law. We can use these laws to convert gas densities at various temperatures and pressures to *standard temperature and pressure*. Table 12-3 gives the experimentally determined densities of several gases at standard temperature and pressure.

Density is defined as mass per unit volume.

### EXAMPLE 12-6 *Molecular Weight, Density*

One (1.00) mole of a gas occupies 27.0 liters, and its density is 1.41 g/L at a particular temperature and pressure. What is its molecular weight? What is the density of the gas at STP?

#### Plan

We can use dimensional analysis to convert the density, 1.41 g/L, to molecular weight, g/mol. To calculate the density at STP, we recall that the volume occupied by one mole would be 22.4 L.

#### Solution

We multiply the density under the original conditions by the unit factor 27.0 L/1.00 mol to generate the appropriate units, g/mol.


$$\frac{? \text{ g}}{\text{mol}} = \frac{1.41 \text{ g}}{\text{L}} \times \frac{27.0 \text{ L}}{\text{mol}} = 38.1 \text{ g/mol}$$

At STP, 1.00 mol of the gas, 38.1 g, would occupy 22.4 L, and its density would be

$$\text{Density} = \frac{38.1 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 1.70 \text{ g/L at STP}$$

You should now work Exercises 40 and 42.

**12-9** SUMMARY OF GAS LAWS: THE IDEAL GAS EQUATION

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.4, The Ideal Gas Law.

Let us summarize what we have learned about gases. Any sample of gas can be described in terms of its pressure, temperature (in kelvins), volume, and the number of moles,  $n$ , present. Any three of these variables determine the fourth. The gas laws we have studied give several relationships among these variables. An **ideal gas** is one that exactly obeys these gas laws. Many real gases show slight deviations from ideality, but at normal temperatures and pressures the deviations are usually small enough to be ignored. We will do so for the present and discuss deviations later.

We can summarize the behavior of ideal gases as follows.

Boyle's Law	$V \propto \frac{1}{P}$	(at constant $T$ and $n$ )
Charles's Law	$V \propto T$	(at constant $P$ and $n$ )
Avogadro's Law	$V \propto n$	(at constant $T$ and $P$ )
Summarizing	$V \propto \frac{nT}{P}$	(no restrictions)

As before, a proportionality can be written as an equality by introducing a proportionality constant, for which we'll use the symbol  $R$ . This gives

$$V = R \left( \frac{nT}{P} \right) \quad \text{or, rearranging,} \quad PV = nRT$$

This equation takes into account the values of  $n$ ,  $T$ ,  $P$ , and  $V$ . Restrictions that apply to the individual gas laws are therefore not needed for the ideal gas equation.

This relationship is called the **ideal gas equation** or the *ideal gas law*. The numerical value of  $R$ , the **universal gas constant**, depends on the choices of the units for  $P$ ,  $V$ , and  $T$ . One mole of an ideal gas occupies 22.414 liters at 1.0000 atmosphere and 273.15 K (STP). Solving the ideal gas law for  $R$  gives

$$R = \frac{PV}{nT} = \frac{(1.0000 \text{ atm})(22.414 \text{ L})}{(1.0000 \text{ mol})(273.15 \text{ K})} = 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

In working problems, we often round  $R$  to 0.0821 L·atm/mol·K. We can express  $R$  in other units, as shown inside the back cover of this text.

**EXAMPLE 12-7** Units of  $R$ 

$R$  can have any *energy* units per mole per kelvin. Calculate  $R$  in terms of joules per mole per kelvin and in SI units of kPa·dm<sup>3</sup>/mol·K.

**Plan**

We apply dimensional analysis to convert to the required units.

**Solution**

Appendix C shows that 1 L·atm = 101.325 joules.

$$R = \frac{0.082057 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{101.325 \text{ J}}{1 \text{ L} \cdot \text{atm}} = 8.3144 \text{ J/mol} \cdot \text{K}$$

Now evaluate  $R$  in SI units. One atmosphere pressure is 101.325 kilopascals, and the molar volume at STP is 22.414 dm<sup>3</sup>.

Recall that 1 dm<sup>3</sup> = 1 L.

$$R = \frac{PV}{nT} = \frac{101.325 \text{ kPa} \times 22.414 \text{ dm}^3}{1 \text{ mol} \times 273.15 \text{ K}} = 8.3145 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}$$

You should now work Exercise 43.

We can now express  $R$ , the universal gas constant, to four digits in three different sets of units.

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} = 8.314 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}$$

The usefulness of the ideal gas equation is that it relates the four variables,  $P$ ,  $V$ ,  $n$ , and  $T$ , that describe a sample of gas at *one set of conditions*. If any three of these variables are known, the fourth can be calculated.

### EXAMPLE 12-8 Ideal Gas Equation

What pressure, in atm, is exerted by 54.0 grams of Xe in a 1.00-liter flask at 20.°C?

#### Plan

We list the variables with the proper units. Then we solve the ideal gas equation for  $P$  and substitute values.

#### Solution

$$V = 1.00 \text{ L} \qquad n = 54.0 \text{ g Xe} \times \frac{1 \text{ mol}}{131.3 \text{ g Xe}} = 0.411 \text{ mol}$$

$$T = 20.^\circ\text{C} + 273^\circ = 293 \text{ K} \qquad P = ?$$

Solving  $PV = nRT$  for  $P$  and substituting gives

$$P = \frac{nRT}{V} = \frac{(0.411 \text{ mol}) \left( \frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (293 \text{ K})}{1.00 \text{ L}} = 9.89 \text{ atm}$$

### EXAMPLE 12-9 Ideal Gas Equation

What is the volume of a gas balloon filled with 4.00 moles of He when the atmospheric pressure is 748 torr and the temperature is 30.°C?

#### Plan

We first list the variables with the proper units. Then we solve the ideal gas equation for  $V$  and substitute known values.

#### Solution

$$P = 748 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.984 \text{ atm} \qquad n = 4.00 \text{ mol}$$

$$T = 30.^\circ\text{C} + 273^\circ = 303 \text{ K} \qquad V = ?$$

Solving  $PV = nRT$  for  $V$  and substituting gives

$$V = \frac{nRT}{P} = \frac{(4.00 \text{ mol}) \left( 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (303 \text{ K})}{0.984 \text{ atm}} = 101 \text{ L}$$

You should now work Exercise 46.

You may wonder why pressures are given in torr or mm Hg and temperatures in °C. This is because pressures are often measured with mercury barometers, and temperatures are measured with Celsius thermometers.



A helium-filled weather balloon.

### EXAMPLE 12-10 Ideal Gas Equation

A helium-filled weather balloon has a volume of 7240 cubic feet. How many grams of helium would be required to inflate this balloon to a pressure of 745 torr at 21°C? (1 ft<sup>3</sup> = 28.3 L)

#### Plan

We use the ideal gas equation to find  $n$ , the number of moles required, and then convert to grams. We must convert each quantity to one of the units stated for  $R$ . ( $R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ )

#### Solution

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm} \quad T = 21^\circ\text{C} + 273^\circ = 294 \text{ K}$$

$$V = 7240 \text{ ft}^3 \times \frac{28.3 \text{ L}}{1 \text{ ft}^3} = 2.05 \times 10^5 \text{ L} \quad n = ?$$

Solving  $PV = nRT$  for  $n$  and substituting gives

$$n = \frac{PV}{RT} = \frac{(0.980 \text{ atm})(2.05 \times 10^5 \text{ L})}{\left( 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (294 \text{ K})} = 8.32 \times 10^3 \text{ mol He}$$

$$? \text{ g He} = (8.32 \times 10^3 \text{ mol He}) \left( 4.00 \frac{\text{g}}{\text{mol}} \right) = 3.33 \times 10^4 \text{ g He}$$

You should now work Exercise 47.



#### Problem-Solving Tip: Watch Out for Units in Ideal Gas Law Calculations

The units of  $R$  that are appropriate for ideal gas law calculations are those that involve units of volume, pressure, moles, and temperature. When you use the value  $R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ , remember to express all quantities in a calculation in these units. Pressures should be expressed in atmospheres, volumes in liters, temperature in kelvins, and amount of gas in moles. In Examples 12-9 and 12-10 we converted pressures from torr to atm. In Example 12-10 the volume was converted from ft<sup>3</sup> to L.



**Summary of the ideal gas laws**

1. The individual gas laws are usually used to calculate the *changes* in conditions for a sample of gas (subscripts can be thought of as “before” and “after”).

$$\text{Boyle's Law} \quad P_1V_1 = P_2V_2 \quad (\text{for a given amount of a gas at constant temperature})$$

$$\text{Charles's Law} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{for a given amount of a gas at constant pressure})$$

$$\text{Combined Gas Law} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad (\text{for a given amount of a gas})$$

$$\text{Avogadro's Law} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (\text{for gas samples at the same temperature and pressure})$$

2. The ideal gas equation is used to calculate one of the four variables  $P$ ,  $V$ ,  $n$ , and  $T$ , which describe a sample of gas at *any single set of conditions*.

$$PV = nRT$$

The ideal gas equation can also be used to calculate the densities of gases.

**EXAMPLE 12-11 Ideal Gas Equation**

Nitric acid, a very important industrial chemical, is made by dissolving the gas nitrogen dioxide,  $\text{NO}_2$ , in water. Calculate the density of  $\text{NO}_2$  gas, in  $\text{g/L}$ , at 1.24 atm and  $50.^\circ\text{C}$ .

**Plan**

We use the ideal gas equation to find the number of moles,  $n$ , in any volume,  $V$ , at the specified pressure and temperature. Then we convert moles to grams. Because we want to express density in  $\text{g/L}$ , we choose a volume of one liter.

**Solution**

$$\begin{aligned} V &= 1.00 \text{ L} & n &= ? \\ T &= 50.^\circ\text{C} + 273^\circ = 323 \text{ K} & P &= 1.24 \text{ atm} \end{aligned}$$


Solving  $PV = nRT$  for  $n$  and substituting gives

$$n = \frac{PV}{RT} = \frac{(1.24 \text{ atm})(1.00 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(323 \text{ K})} = 0.0468 \text{ mol}$$


So there is 0.0468 mol  $\text{NO}_2/\text{L}$  at the specified  $P$  and  $T$ . Converting this to grams of  $\text{NO}_2$  per liter, we obtain

$$\text{Density} = \frac{? \text{ g}}{\text{L}} = \frac{0.0468 \text{ mol NO}_2}{\text{L}} \times \frac{46.0 \text{ g NO}_2}{\text{mol NO}_2} = 2.15 \text{ g/L}$$

You should now work Exercise 40.

 See the Saunders Interactive General Chemistry CD-ROM, Screen 12.5, Gas Density.

### 12-10 DETERMINATION OF MOLECULAR WEIGHTS AND MOLECULAR FORMULAS OF GASEOUS SUBSTANCES

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.6, Using Gas Laws: Determining Molar Mass.

In Section 2-10 we distinguished between simplest and molecular formulas of compounds. We showed how simplest formulas can be calculated from percent compositions of compounds. The molecular weight must be known to determine the molecular formula of a compound. For compounds that are gases at convenient temperatures and pressures, the ideal gas law provides a basis for determining molecular weights.

#### EXAMPLE 12-12 *Molecular Weight*

A 0.109-gram sample of a pure gaseous compound occupies 112 mL at 100.°C and 750. torr. What is the molecular weight of the compound?

##### Plan

We first use the ideal gas law,  $PV = nRT$ , to find the number of moles of gas. Then, knowing the mass of that number of moles of gas, we calculate the mass of one mole, the molecular weight.

##### Solution

$$V = 0.112 \text{ L} \quad T = 100.^{\circ}\text{C} + 273^{\circ} = 373 \text{ K} \quad P = 750. \text{ torr} \times \frac{1 \text{ atm}}{760. \text{ torr}} = 0.987 \text{ atm}$$

$$n = \frac{PV}{RT} = \frac{(0.987 \text{ atm})(0.112 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(373 \text{ K})} = 0.00361 \text{ mol}$$

The mass of 0.00361 mole of this gas is 0.109 g, so the mass of one mole is

$$\frac{? \text{ g}}{\text{mol}} = \frac{0.109 \text{ g}}{0.00361 \text{ mol}} = 30.2 \text{ g/mol}$$

The molecular weight of the gas is 30.2 amu. The gas could be ethane,  $\text{C}_2\text{H}_6$ , MW = 30.1 amu. Can you think of other possibilities? Could the gas have been NO,  $\text{CH}_3\text{OH}$ ,  $\text{O}_2$ , or  $\text{CH}_3\text{NH}_2$ ?

#### EXAMPLE 12-13 *Molecular Weight*

A 120.-mL flask contained 0.345 gram of a gaseous compound at 100.°C and 1.00 atm pressure. What is the molecular weight of the compound?

##### Plan

We use the ideal gas law,  $PV = nRT$ , to determine the number of moles of gas that filled the flask. Then, knowing the mass of this number of moles, we can calculate the mass of one mole.

##### Solution

$$V = 0.120 \text{ L} \quad P = 1.00 \text{ atm} \quad T = 100.^{\circ}\text{C} + 273^{\circ} = 373 \text{ K}$$

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(0.120 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(373 \text{ K})} = 0.00392 \text{ mol}$$

The mass of 0.00392 mol of gas is 0.345 g, so the mass of one mole is

$$\frac{? \text{ g}}{\text{mol}} = \frac{0.345 \text{ g}}{0.00392 \text{ mol}} = 88.0 \text{ g/mol}$$

You should now work Exercises 51 and 54.

Let's carry the calculation one step further in the next example.

### EXAMPLE 12-14 Molecular Formula

Additional analysis of the gaseous compound in Example 12-13 showed that it contained 54.5% carbon, 9.10% hydrogen, and 36.4% oxygen by mass. What is its molecular formula?

#### Plan

We first find the simplest formula for the compound as we did in Section 2-9 (Examples 2-12 and 2-13). Then we use the molecular weight that we determined in Example 12-13 to find the molecular formula. To find the molecular formula, we reason as in Example 2-16. We use the experimentally known molecular weight to find the ratio

$$n = \frac{\text{molecular weight}}{\text{simplest-formula weight}}$$

The molecular weight is  $n$  times the simplest-formula weight, so the molecular formula is  $n$  times the simplest formula.

#### Solution

Element	Relative Mass of Element	Relative Number of Atoms (divide mass by AW)	Divide by Smallest Number	Smallest Whole-Number Ratio of Atoms
C	54.5	$\frac{54.5}{12.0} = 4.54$	$\frac{4.54}{2.28} = 1.99$	2
H	9.10	$\frac{9.10}{1.01} = 9.01$	$\frac{9.01}{2.28} = 3.95$	4
O	36.4	$\frac{36.4}{16.0} = 2.28$	$\frac{2.28}{2.28} = 1.00$	1

$\text{C}_2\text{H}_4\text{O}$

The simplest formula is  $\text{C}_2\text{H}_4\text{O}$  and the simplest-formula weight is 44.0 amu.

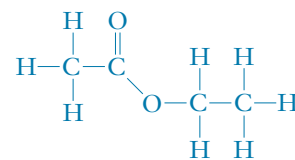
Division of the molecular weight by the simplest-formula weight gives

$$\frac{\text{molecular weight}}{\text{simplest-formula weight}} = \frac{88.0 \text{ amu}}{44.0 \text{ amu}} = 2$$

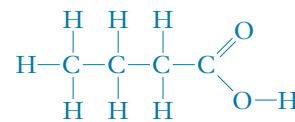
The molecular formula is therefore  $2 \times (\text{C}_2\text{H}_4\text{O}) = \text{C}_4\text{H}_8\text{O}_2$ .

The gas could be either ethyl acetate or butyric acid. Both have the formula  $\text{C}_4\text{H}_8\text{O}_2$ . They have very different odors, however. Ethyl acetate has the odor of nail polish remover. Butyric acid has the foul odor of rancid butter.

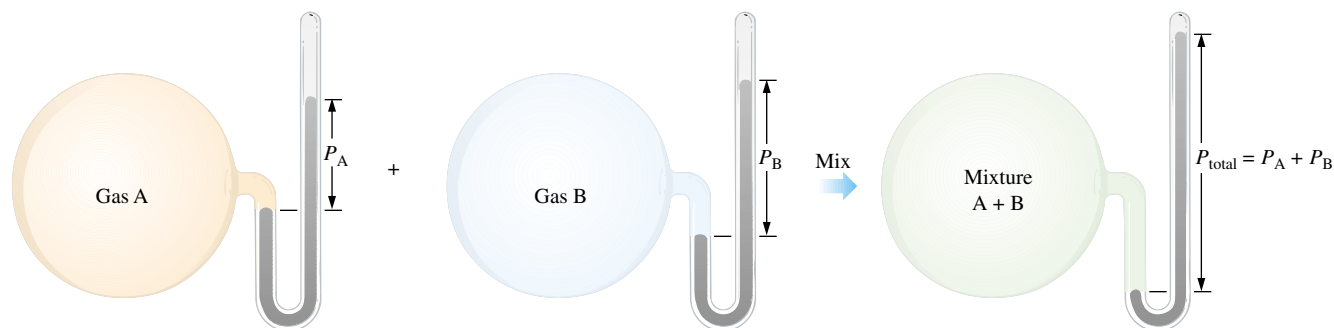
You should now work Exercise 52.



ethyl acetate



butyric acid



**Figure 12-6** An illustration of Dalton's Law. When the two gases *A* and *B* are mixed in the same container at the same temperature, they exert a total pressure equal to the sum of their partial pressures.

## 12-11 DALTON'S LAW OF PARTIAL PRESSURES

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.8, Gas Mixtures and Partial Pressures.

Many gas samples, including our atmosphere, are mixtures that consist of different kinds of gases. The total number of moles in a mixture of gases is

$$n_{\text{total}} = n_A + n_B + n_C + \dots$$

where  $n_A$ ,  $n_B$ , and so on represent the number of moles of each kind of gas present. Rearranging the ideal gas equation,  $P_{\text{total}}V = n_{\text{total}}RT$ , for the total pressure,  $P_{\text{total}}$ , and then substituting for  $n_{\text{total}}$  gives

$$P_{\text{total}} = \frac{n_{\text{total}}RT}{V} = \frac{(n_A + n_B + n_C + \dots)RT}{V}$$

Multiplying out the right-hand side gives

$$P_{\text{total}} = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} + \dots$$

Now  $n_A RT/V$  is the *partial pressure*  $P_A$  that the  $n_A$  moles of gas A alone would exert in the container at temperature  $T$ ; similarly,  $n_B RT/V = P_B$ , and so on. Substituting these into the equation for  $P_{\text{total}}$ , we obtain **Dalton's Law of Partial Pressures** (Figure 12-6).

$$P_{\text{total}} = P_A + P_B + P_C + \dots \quad (\text{constant } V, T)$$

The total pressure exerted by a mixture of ideal gases is the sum of the partial pressures of those gases.

Dalton's Law is useful in describing real gaseous mixtures at moderate pressures because it allows us to relate total measured pressures to the composition of mixtures.

John Dalton was the first to notice this effect. He did so in 1807 while studying the compositions of moist and dry air. The pressure that each gas exerts in a mixture is called its **partial pressure**. No way has been devised to measure the pressure of an individual gas in a mixture; it must be calculated from other quantities.

### EXAMPLE 12-15 Mixture of Gases

A 10.0-liter flask contains 0.200 mole of methane, 0.300 mole of hydrogen, and 0.400 mole of nitrogen at 25°C. (a) What is the pressure, in atmospheres, inside the flask? (b) What is the partial pressure of each component of the mixture of gases?



**Plan**

(a) We are given the number of moles of each component. The ideal gas law is then used to calculate the total pressure from the total number of moles. (b) The partial pressure of each gas in the mixture can be calculated by substituting the number of moles of each gas individually into  $PV = nRT$ .

**Solution**

(a)  $n = 0.200 \text{ mol CH}_4 + 0.300 \text{ mol H}_2 + 0.400 \text{ mol N}_2 = 0.900 \text{ mol of gas}$

$$V = 10.0 \text{ L} \quad T = 25^\circ\text{C} + 273^\circ = 298 \text{ K}$$

Solving  $PV = nRT$  for  $P$  gives  $P = nRT/V$ . Substitution gives

$$P = \frac{(0.900 \text{ mol})\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298 \text{ K})}{10.0 \text{ L}} = 2.20 \text{ atm}$$

(b) Now we find the partial pressures. For  $\text{CH}_4$ ,  $n = 0.200 \text{ mol}$ , and the values for  $V$  and  $T$  are the same as above.

$$P_{\text{CH}_4} = \frac{(n_{\text{CH}_4})RT}{V} = \frac{(0.200 \text{ mol})\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298 \text{ K})}{10.0 \text{ L}} = 0.489 \text{ atm}$$

Similar calculations for the partial pressures of hydrogen and nitrogen give

$$P_{\text{H}_2} = 0.734 \text{ atm} \quad \text{and} \quad P_{\text{N}_2} = 0.979 \text{ atm}$$

As a check, we use Dalton's Law:  $P_{\text{total}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \dots$ . Addition of the partial pressures in this mixture gives the total pressure.

$$P_{\text{total}} = P_{\text{CH}_4} + P_{\text{H}_2} + P_{\text{N}_2} = (0.489 + 0.734 + 0.979) \text{ atm} = 2.20 \text{ atm}$$

You should now work Exercises 58 and 59.



**Problem-Solving Tip:** *Amounts of Gases in Mixtures Can Be Expressed in Various Units*

In Example 12-15 we were given the number of moles of each gas. Sometimes the amount of a gas is expressed in other units that can be converted to number of moles. For instance, if we know the formula weight (or the formula), we can convert a given mass of gas to number of moles.

We can describe the composition of any mixture in terms of the mole fraction of each component. The **mole fraction**,  $X_{\text{A}}$ , of component A in a mixture is defined as

$$X_{\text{A}} = \frac{\text{no. mol A}}{\text{total no. mol of all components}}$$

Like any other fraction, mole fraction is a dimensionless quantity. For each component in a mixture, the mole fraction is

The sum of all mole fractions in a mixture is equal to 1.

$$X_A + X_B + \dots = 1 \text{ for any mixture}$$

We can use this relationship to check mole fraction calculations or to find a remaining mole fraction if we know all the others.

$$X_A = \frac{\text{no. mol A}}{\text{no. mol A} + \text{no. mol B} + \dots},$$
$$X_B = \frac{\text{no. mol B}}{\text{no. mol A} + \text{no. mol B} + \dots}, \quad \text{and so on}$$

For a gaseous mixture, we can relate the mole fraction of each component to its partial pressure as follows. From the ideal gas equation, the number of moles of each component can be written as

$$n_A = P_A V / RT, \quad n_B = P_B V / RT, \quad \text{and so on}$$

and the total number of moles is

$$n_{\text{total}} = P_{\text{total}} V / RT$$

Substituting into the definition of  $X_A$ ,

$$X_A = \frac{n_A}{n_A + n_B + \dots} = \frac{P_A V / RT}{P_{\text{total}} V / RT}$$

The quantities  $V$ ,  $R$ , and  $T$  cancel to give

$$X_A = \frac{P_A}{P_{\text{total}}}; \quad \text{similarly, } X_B = \frac{P_B}{P_{\text{total}}}; \quad \text{and so on}$$

We can rearrange these equations to give another statement of Dalton's Law of Partial Pressures.

$$P_A = X_A \times P_{\text{total}}; \quad P_B = X_B \times P_{\text{total}}; \quad \text{and so on}$$

The partial pressure of each gas is equal to its mole fraction in the gaseous mixture times the total pressure of the mixture.

---

### EXAMPLE 12-16 Mole Fraction, Partial Pressure

In Example 12-16 we see that, for a gas mixture, relative numbers of moles of components are the same as relative pressures of the components.

Calculate the mole fractions of the three gases in Example 12-15.

#### Plan

One way to solve this problem is to use the numbers of moles given in the problem. Alternatively we could use the partial pressures and the total pressure from Example 12-15.

#### Solution

Using the moles given in Example 12-15,

$$X_{\text{CH}_4} = \frac{n_{\text{CH}_4}}{n_{\text{total}}} = \frac{0.200 \text{ mol}}{0.900 \text{ mol}} = 0.222$$

$$X_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{total}}} = \frac{0.300 \text{ mol}}{0.900 \text{ mol}} = 0.333$$

$$X_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{total}}} = \frac{0.400 \text{ mol}}{0.900 \text{ mol}} = 0.444$$

Using the partial and total pressures calculated in Example 12-15,

$$X_{\text{CH}_4} = \frac{P_{\text{CH}_4}}{P_{\text{total}}} = \frac{0.489}{2.20 \text{ atm}} = 0.222$$

$$X_{\text{H}_2} = \frac{P_{\text{H}_2}}{P_{\text{total}}} = \frac{0.734 \text{ atm}}{2.20 \text{ atm}} = 0.334$$

$$X_{\text{N}_2} = \frac{P_{\text{N}_2}}{P_{\text{total}}} = \frac{0.979 \text{ atm}}{2.20 \text{ atm}} = 0.445$$

The difference between the two calculated results is due to rounding.

You should now work Exercise 60.

### EXAMPLE 12-17 Partial Pressure, Mole Fraction

The mole fraction of oxygen in the atmosphere is 0.2094. Calculate the partial pressure of  $\text{O}_2$  in air when the atmospheric pressure is 760. torr.

#### Plan

The partial pressure of each gas in a mixture is equal to its mole fraction in the mixture times the total pressure of the mixture.

#### Solution

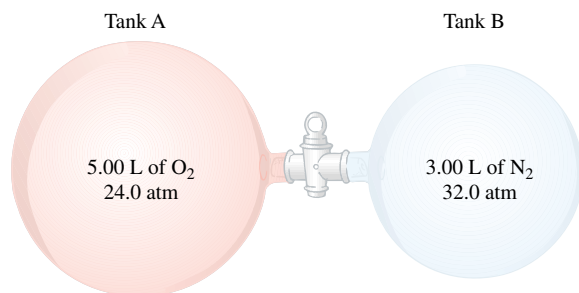
$$\begin{aligned} P_{\text{O}_2} &= X_{\text{O}_2} \times P_{\text{total}} \\ &= 0.2094 \times 760. \text{ torr} = 159 \text{ torr} \end{aligned}$$

Dalton's Law can be used in combination with other gas laws, as the following example shows.

### EXAMPLE 12-18 Mixture of Gases

Two tanks are connected by a closed valve. Each tank is filled with gas as shown, and both tanks are held at the same temperature. We open the valve and allow the gases to mix.

- (a) After the gases mix, what is the partial pressure of each gas, and what is the total pressure?  
 (b) What is the mole fraction of each gas in the mixture?



#### Plan

(a) Each gas expands to fill the available volume, 5.00 liters plus 3.00 liters or a total volume of 8.00 liters. We can use Boyle's Law to calculate the partial pressure that each gas would exert after it expands to fill 8.00 L. The total pressure is equal to the sum of the partial pressures of the two gases. (b) The mole fractions can be calculated from the ratio of the partial pressure of each gas to the total pressure.

**Solution**(a) For O<sub>2</sub>,

$$P_1V_1 = P_2V_2 \quad \text{or} \quad P_{2,\text{O}_2} = \frac{P_1V_1}{V_2} = \frac{24.0 \text{ atm} \times 5.00 \text{ L}}{8.00 \text{ L}} = 15.0 \text{ atm}$$

For N<sub>2</sub>,

$$P_1V_1 = P_2V_2 \quad \text{or} \quad P_{2,\text{N}_2} = \frac{P_1V_1}{V_2} = \frac{32.0 \text{ atm} \times 3.00 \text{ L}}{8.00 \text{ L}} = 12.0 \text{ atm}$$

The total pressure is the sum of the partial pressures.

$$P_{\text{total}} = P_{2,\text{O}_2} + P_{2,\text{N}_2} = 15.0 \text{ atm} + 12.0 \text{ atm} = 27.0 \text{ atm}$$

$$(b) \quad X_{\text{O}_2} = \frac{P_{2,\text{O}_2}}{P_{\text{total}}} = \frac{15.0 \text{ atm}}{27.0 \text{ atm}} = 0.556$$

$$X_{\text{N}_2} = \frac{P_{2,\text{N}_2}}{P_{\text{total}}} = \frac{12.0 \text{ atm}}{27.0 \text{ atm}} = 0.444$$

As a check, the sum of the mole fractions is 1.

*You should now work Exercise 62.*

Notice that this problem has been solved without calculating the number of moles of either gas.

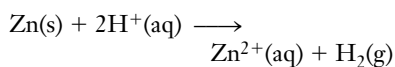
Gases that are soluble in water or that react with water cannot be collected by this method. Other liquids can be used.

The partial pressure exerted by the vapor above a liquid is called the vapor pressure of that liquid. A more extensive table of the vapor pressure of water appears in Appendix E.

Some gases can be collected over water. Figure 12-7 illustrates the collection of a sample of hydrogen by displacement of water. A gas produced in a reaction displaces the denser water from the inverted water-filled container. The pressure on the gas inside the collection container can be made equal to atmospheric pressure by raising or lowering the container until the water level inside is the same as that outside.

One complication arises, however. A gas in contact with water soon becomes saturated with water vapor. The pressure inside the container is the sum of the partial pressure of the gas itself *plus* the partial pressure exerted by the water vapor in the gas mixture (the **vapor pressure** of water). Every liquid shows a characteristic vapor pressure that varies only with temperature, and *not* with the volume of vapor present, so long as both liquid

**Figure 12-7** Apparatus for preparing hydrogen from zinc and sulfuric acid.



The hydrogen is collected by displacement of water.





and vapor are present. Table 12-4 displays the vapor pressure of water near room temperature.

The relevant point here is that a gas collected over water is “moist”; that is, it is saturated with water vapor. Measuring the atmospheric pressure at which the gas is collected, we can write

$$P_{\text{atm}} = P_{\text{gas}} + P_{\text{H}_2\text{O}} \quad \text{or} \quad P_{\text{gas}} = P_{\text{atm}} - P_{\text{H}_2\text{O}}$$

Example 12-19 provides a detailed illustration.

### EXAMPLE 12-19 Gas Collected Over Water

Hydrogen was collected over water (Figure 12-7) at 21°C on a day when the atmospheric pressure was 748 torr. The volume of the gas sample collected was 300. mL. (a) How many moles of H<sub>2</sub> were present? (b) How many moles of water vapor were present in the moist gas mixture? (c) What is the mole fraction of hydrogen in the moist gas mixture? (d) What would be the mass of the gas sample if it were dry?

#### Plan

(a) The vapor pressure of H<sub>2</sub>O,  $P_{\text{H}_2\text{O}} = 19$  torr at 21°C, is obtained from Table 12-4. Applying Dalton's Law,  $P_{\text{H}_2} = P_{\text{atm}} - P_{\text{H}_2\text{O}}$ . We then use the partial pressure of H<sub>2</sub> in the ideal gas equation to find the number of moles of H<sub>2</sub> present. (b) The partial pressure of water vapor (the vapor pressure of water at the stated temperature) is used in the ideal gas equation to find the number of moles of water vapor present. (c) The mole fraction of H<sub>2</sub> is the ratio of its partial pressure to the total pressure. (d) The number of moles found in part (a) can be converted to mass of H<sub>2</sub>.

#### Solution

$$(a) P_{\text{H}_2} = P_{\text{atm}} - P_{\text{H}_2\text{O}} = (748 - 19) \text{ torr} = 729 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.959 \text{ atm}$$

We also know

$$V = 300. \text{ mL} = 0.300 \text{ L} \quad \text{and} \quad T = 21^\circ\text{C} + 273^\circ = 294 \text{ K}$$

Solving the ideal gas equation for  $n_{\text{H}_2}$  gives

$$n_{\text{H}_2} = \frac{P_{\text{H}_2}V}{RT} = \frac{(0.959 \text{ atm})(0.300 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(294 \text{ K})} = 1.19 \times 10^{-2} \text{ mol H}_2$$

$$(b) P_{\text{H}_2\text{O}} = 19 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.025 \text{ atm}$$

$V$  and  $T$  have the same values as in part (a).

$$n_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}V}{RT} = \frac{(0.025 \text{ atm})(0.300 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(294 \text{ K})} = 3.1 \times 10^{-4} \text{ mol H}_2\text{O vapor}$$

$$(c) X_{\text{H}_2} = \frac{P_{\text{H}_2}}{P_{\text{total}}} = \frac{729 \text{ torr}}{748 \text{ torr}} = 0.974$$

$$(d) \underline{?} \text{ g H}_2 = 1.19 \times 10^{-2} \text{ mol} \times \frac{2.02 \text{ g}}{1 \text{ mol}} = 2.40 \times 10^{-2} \text{ g H}_2$$

You should now work Exercise 64.

**TABLE 12-4** Vapor Pressure of Water Near Room Temperature

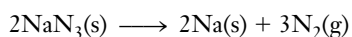
Temperature (°C)	Vapor Pressure of Water (torr)
19	16.48
20	17.54
21	18.65
22	19.83
23	21.07
24	22.38
25	23.76
26	25.21
27	26.74
28	28.35

Remember that *each* gas occupies the *total* volume of the container.

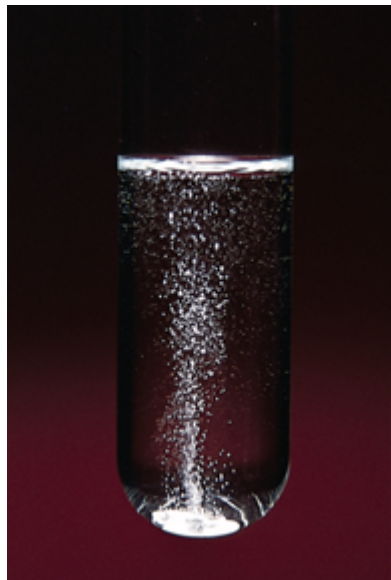
At STP, this dry hydrogen would occupy 267 mL. Can you calculate this?



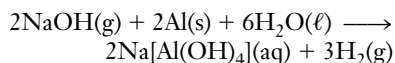
The nitrogen gas formed in the rapid reaction



fills an automobile air bag during a collision. The air bag fills within 1/20th of a second after a front collision.



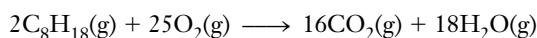
Production of a gas by a reaction.



This reaction is used in some solid drain cleaners.

## 12-12 MASS-VOLUME RELATIONSHIPS IN REACTIONS INVOLVING GASES

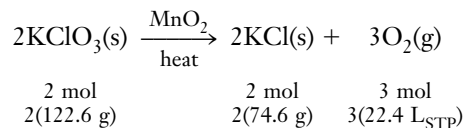
Many chemical reactions produce gases. For instance, the combustion of hydrocarbon in excess oxygen at high temperatures produces both carbon dioxide and water as gases, as illustrated for octane.



The  $\text{N}_2$  gas produced by the very rapid decomposition of sodium azide,  $\text{NaN}_3(\text{s})$ , inflates air bags used as safety devices in automobiles.

We know that one mole of gas, measured at STP, occupies 22.4 liters; we can use the ideal gas equation to find the volume of a mole of gas at any other conditions. This information can be utilized in stoichiometry calculations (Section 3-2).

Small amounts of oxygen can be produced in the laboratory by heating solid potassium chlorate,  $\text{KClO}_3$ , in the presence of a catalyst, manganese(IV) oxide,  $\text{MnO}_2$ . Solid potassium chloride,  $\text{KCl}$ , is also produced. (CAUTION: Heating  $\text{KClO}_3$  can be dangerous.)



Unit factors can be constructed using any two of these quantities.

### EXAMPLE 12-20 Gas Volume in a Chemical Reaction

What volume of  $\text{O}_2$  (STP) can be produced by heating 112 grams of  $\text{KClO}_3$ ?

#### Plan

The preceding equation shows that two moles of  $\text{KClO}_3$  produce three moles of  $\text{O}_2$ . We construct appropriate unit factors from the balanced equation and the standard molar volume of oxygen to solve the problem.

#### Solution

$$\begin{aligned} \underline{?} \text{ L}_{\text{STP}} \text{ O}_2 &= 112 \text{ g KClO}_3 \times \frac{1 \text{ mol KClO}_3}{122.6 \text{ g KClO}_3} \times \frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} \times \frac{22.4 \text{ L}_{\text{STP}} \text{ O}_2}{1 \text{ mol O}_2} \\ &= 30.7 \text{ L}_{\text{STP}} \text{ O}_2 \end{aligned}$$

This calculation shows that the thermal decomposition of 112 grams of  $\text{KClO}_3$  produces 30.7 liters of oxygen measured at standard conditions.

*You should now work Exercise 76.*

### EXAMPLE 12-21 Gas Volume in a Chemical Reaction

A 1.80-gram mixture of potassium chlorate,  $\text{KClO}_3$ , and potassium chloride,  $\text{KCl}$ , was heated until all of the  $\text{KClO}_3$  had decomposed. After being dried, the liberated oxygen occupied 405 mL at  $25^\circ\text{C}$  when the barometric pressure was 745 torr. (a) How many moles of  $\text{O}_2$  were produced? (b) What percentage of the mixture was  $\text{KClO}_3$ ?

**Plan**

(a) The number of moles of O<sub>2</sub> produced can be calculated from the ideal gas equation. (b) Then we use the balanced chemical equation to relate the known number of moles of O<sub>2</sub> formed and the mass of KClO<sub>3</sub> that decomposed to produce it.

**Solution**

$$(a) V = 405 \text{ mL} = 0.405 \text{ L}; P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$T = 25^\circ\text{C} + 273^\circ = 298 \text{ K}$$

Solving the ideal gas equation for  $n$  and evaluating gives

$$n = \frac{PV}{RT} = \frac{(0.980 \text{ atm})(0.405 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298 \text{ K})} = 0.0162 \text{ mol O}_2$$

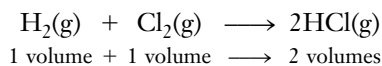
$$(b) \underline{?} \text{ g KClO}_3 = 0.0162 \text{ mol O}_2 \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} \times \frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} = 1.32 \text{ g KClO}_3$$

The sample contained 1.32 grams of KClO<sub>3</sub>. The percent of KClO<sub>3</sub> in the sample is

$$\% \text{ KClO}_3 = \frac{\text{g KClO}_3}{\text{g sample}} \times 100\% = \frac{1.32 \text{ g}}{1.80 \text{ g}} \times 100\% = 73.3\% \text{ KClO}_3$$

*You should now work Exercise 78.*

Our study of stoichiometry has shown that substances react in definite mole and mass proportions. Using previously discussed gas laws, we can show that gases also react in simple, definite proportions by volume. For example, *one* volume of hydrogen always combines (reacts) with *one* volume of chlorine to form *two* volumes of hydrogen chloride, if all volumes are measured at the same temperature and pressure



Volumes may be expressed in any units as long as the same unit is used for all. Gay-Lussac summarized several experimental observations on combining volumes of gases. The summary is known as **Gay-Lussac's Law of Combining Volumes:**

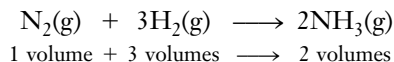
At constant temperature and pressure, the volumes of reacting gases can be expressed as a ratio of simple whole numbers.

The ratio is obtained from the coefficients in the balanced equation for the reaction. Clearly, the law applies only to *gaseous* substances at the same temperature and pressure. No generalizations can be made about the volumes of solids and liquids as they undergo chemical reactions. Consider the following examples, based on experimental observations at constant temperature and pressure. Hundreds more could be cited.

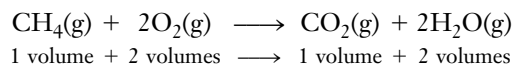


See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.7, Gas Laws and Chemical Reactions.

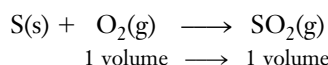
1. One volume of nitrogen can react with three volumes of hydrogen to form two volumes of ammonia



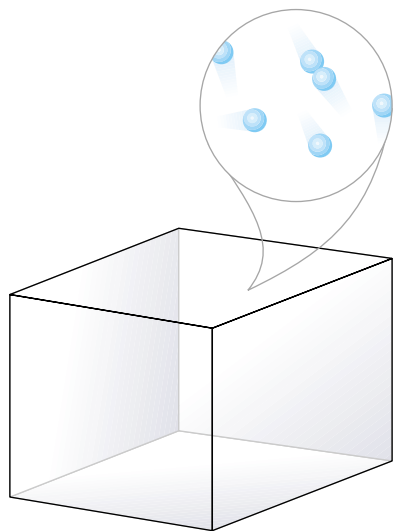
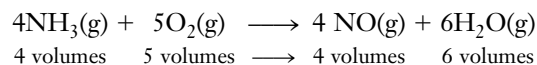
2. One volume of methane reacts with (burns in) two volumes of oxygen to give one volume of carbon dioxide and two volumes of steam



3. Sulfur (a solid) reacts with one volume of oxygen to form one volume of sulfur dioxide



4. Four volumes of ammonia burn in five volumes of oxygen to produce four volumes of nitric oxide and six volumes of steam



**Figure 12-8** A representation of molecular motion. Gaseous molecules, in constant motion, undergo collisions with one another and with the walls of the container.

## 12-13 THE KINETIC-MOLECULAR THEORY

As early as 1738, Daniel Bernoulli (1700–1782) envisioned gaseous molecules in ceaseless motion striking the walls of their container and thereby exerting pressure. In 1857, Rudolf Clausius (1822–1888) published a theory that attempted to explain various experimental observations that had been summarized by Boyle's, Dalton's, Charles's, and Avogadro's laws. The basic assumptions of the **kinetic-molecular theory** for an ideal gas follow.

1. The observation that gases can be easily compressed indicates that the molecules are far apart. At ordinary temperatures and pressures, the gas molecules themselves occupy an insignificant fraction of the total volume of the container.
2. Near temperatures and pressures at which a gas liquefies, the gas does not behave ideally (Section 12-15) and attractions or repulsions among gas molecules *are* significant.
3. At any given instant, only a small fraction of the molecules are involved in collisions.

1. Gases consist of discrete molecules. The individual molecules are very small and are very far apart relative to their own sizes.
2. The gas molecules are in continuous, random, straight-line motion with varying velocities (see Figure 12-8).
3. The collisions between gas molecules and with the walls of the container are elastic; the total energy is conserved during a collision; that is, there is no net energy gain or loss.
4. Between collisions, the molecules exert no attractive or repulsive forces on one another; instead, each molecule travels in a straight line with a constant velocity.

Kinetic energy is the energy a body possesses by virtue of its motion. It is  $\frac{1}{2}mu^2$ , where  $m$ , the body's mass, can be expressed in grams and  $u$ , its velocity, can be expressed in meters per second (m/s). The assumptions of the kinetic-molecular theory can be used to relate temperature and molecular kinetic energy (see the Enrichment section, pages 467–469).

The average kinetic energy of gaseous molecules is directly proportional to the absolute temperature of the sample. The average kinetic energies of molecules of different gases are equal at a given temperature.

For instance, in samples of  $\text{H}_2$ , He,  $\text{CO}_2$ , and  $\text{SO}_2$  at the same temperature, all the molecules have the same average kinetic energies. But the lighter molecules,  $\text{H}_2$  and He, have much higher average velocities than do the heavier molecules,  $\text{CO}_2$  and  $\text{SO}_2$ , at the same temperature.

We can summarize this very important result from the kinetic-molecular theory.

$$\text{Average molecular } KE = \overline{KE} \propto T$$


or

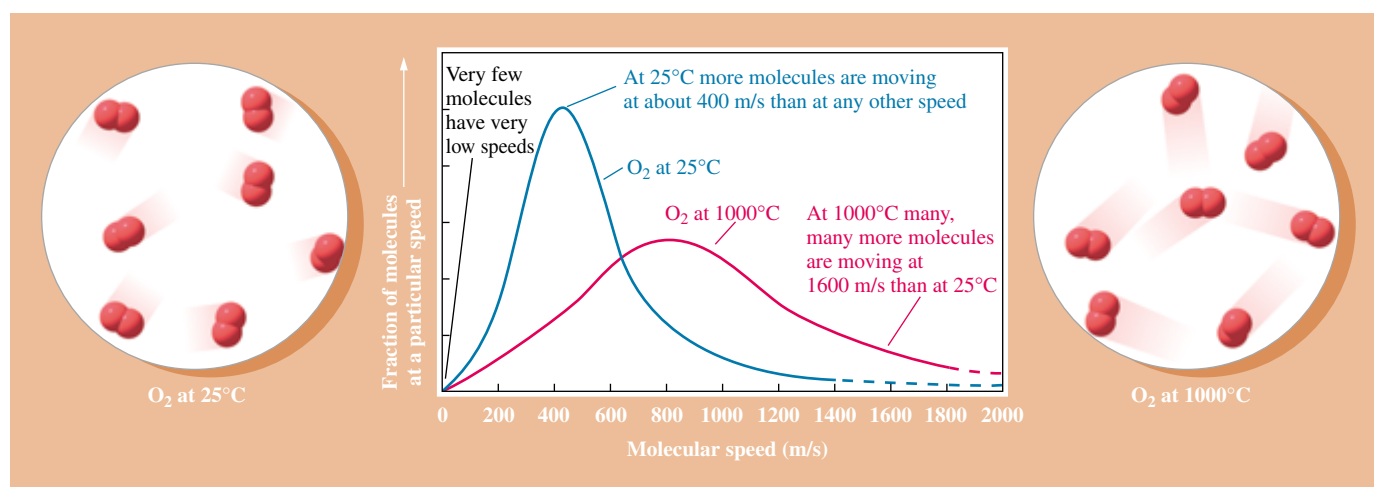
$$\text{Average molecular speed} = \bar{u} \propto \sqrt{\frac{T}{\text{molecular weight}}}$$

A bar over a quantity denotes an *average* of that quantity.

Molecular kinetic energies of gases increase with increasing temperature and decrease with decreasing temperature. We have referred only to the *average* kinetic energy; in a given sample, some molecules may be moving quite rapidly while others are moving more slowly. Figure 12-9 shows the distribution of speeds of gaseous molecules at two temperatures.

The kinetic-molecular theory satisfactorily explains most of the observed behavior of gases in terms of molecular behavior. Let's look at the gas laws in terms of the kinetic-molecular theory.

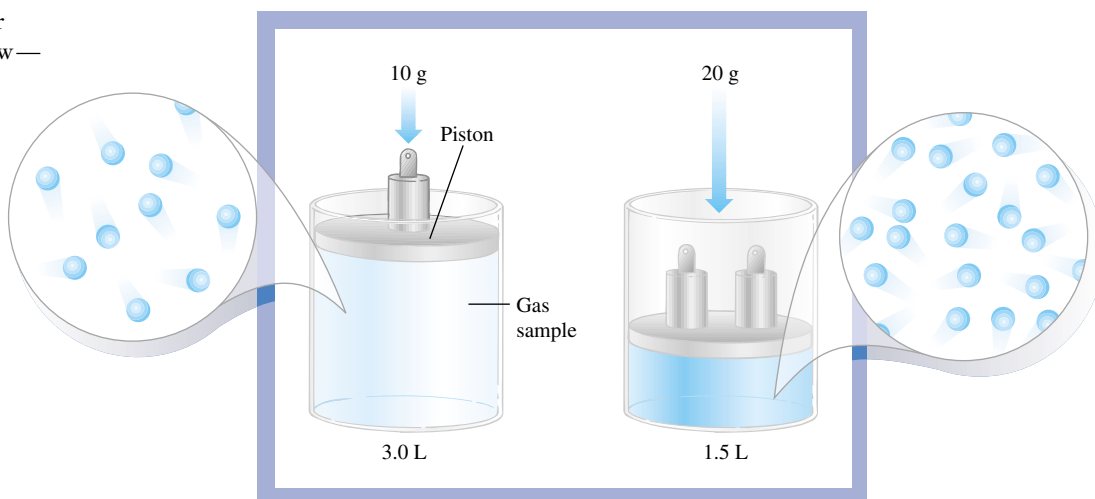
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.11, Distribution of Molecular Speeds.



**Figure 12-9** The Maxwellian distribution function for molecular speeds. This graph shows the relative numbers of  $\text{O}_2$  molecules having a given speed at  $25^\circ\text{C}$  and at  $1000^\circ\text{C}$ . At  $25^\circ\text{C}$ , most  $\text{O}_2$  molecules have speeds between 200 and 600 m/s (450–1350 miles per hour). Some of the molecules have very high speeds, so the distribution curve never reaches the horizontal axis.




**Figure 12-10** A molecular interpretation of Boyle's Law—the change in pressure of a gas with changes in volume (at constant temperature). The entire apparatus is enclosed in a vacuum. In the smaller volume, more molecules strike the walls per unit time to give a higher pressure.



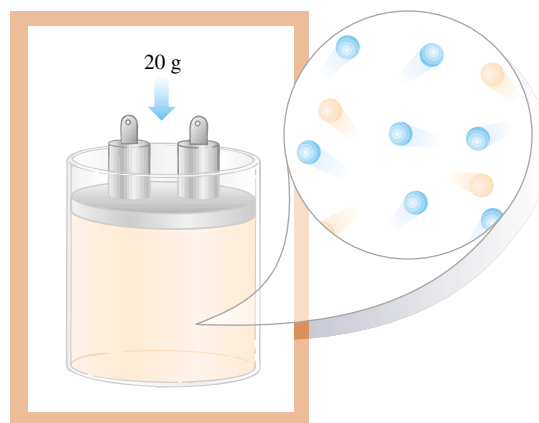
### Boyle's Law

The pressure exerted by a gas on the walls of its container is caused by gas molecules striking the walls. Clearly, pressure depends on two factors: (1) the number of molecules striking the walls per unit time and (2) how vigorously the molecules strike the walls. If the temperature is held constant, the average speed and the force of the collisions remain the same. But halving the volume of a sample of gas doubles the pressure because twice as many molecules strike a given area on the walls per unit time. Likewise, doubling the volume of a sample of gas halves the pressure because only half as many gas molecules strike a given area on the walls per unit time (Figure 12-10).

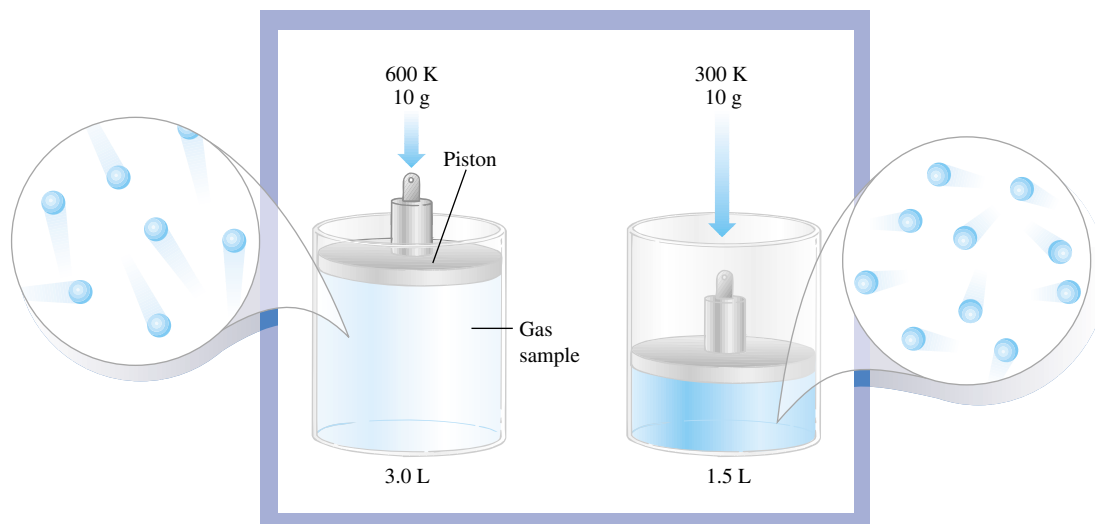
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.10, Gas Laws and the Kinetic-Molecular Theory.

### Dalton's Law


In a gas sample the molecules are very far apart and do not attract one another significantly. Each kind of gas molecule acts independently of the presence of the other kind. The molecules of each gas thus collide with the walls with a frequency and vigor that do not change even if other molecules are present (Figure 12-11). As a result, each gas exerts a partial pressure that is independent of the presence of the other gas, and the total pressure is due to the sum of all the molecule-wall collisions.



**Figure 12-11** A molecular interpretation of Dalton's Law. The molecules act independently, so each gas exerts its own partial pressure due to its molecular collisions with the walls.



**Figure 12-12** A molecular interpretation of Charles's Law—the change in volume of a gas with changes in temperature (at constant pressure). At the lower temperature, molecules strike the walls less often and less vigorously. Thus, the volume must be less to maintain the same pressure.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.9, Kinetic-Molecular Theory of Gases.

### Charles's Law

Recall that average kinetic energy is directly proportional to the absolute temperature. Doubling the *absolute* temperature of a sample of gas doubles the average kinetic energy of the gaseous molecules, and the increased force of the collisions of molecules with the walls doubles the volume at constant pressure. Similarly, halving the absolute temperature decreases kinetic energy to half its original value; at constant pressure, the volume decreases by half because of the reduced vigor of the collision of gaseous molecules with the container walls (Figure 12-12).

### Kinetic-Molecular Theory, the Ideal Gas Equation, and Molecular Speeds

In 1738, Daniel Bernoulli derived Boyle's Law from Newton's laws of motion applied to gas molecules. This derivation was the basis for an extensive mathematical development of the kinetic-molecular theory more than a century later by Clausius, Maxwell, Boltzmann, and others. Although we do not need to study the detailed mathematical presentation of this theory, we can gain some insight into its concepts from the reasoning behind Bernoulli's derivation. Here we present that reasoning based on proportionality arguments.

In the kinetic-molecular theory pressure is viewed as the result of collisions of gas molecules with the walls of the container. As each molecule strikes a wall, it exerts a small impulse. The pressure is the total force thus exerted on the walls divided by the area of the walls. The total force on the walls (and thus the pressure) is proportional to two factors: (1) the



**E**nrichment

(Enrichment, continued)

impulse exerted by each collision and (2) the rate of collisions (number of collisions in a given time interval).

$$P \propto (\text{impulse per collision}) \times (\text{rate of collisions})$$

Let us represent the mass of an individual molecule by  $m$  and its speed by  $u$ . The heavier the molecule is (greater  $m$ ) and the faster it is moving (greater  $u$ ), the harder it pushes on the wall when it collides. The impulse due to each molecule is proportional to its *momentum*,  $mu$ .

$$\text{Impulse per collision} \propto mu$$

The rate of collisions, in turn, is proportional to two factors. First, the rate of collision must be proportional to the molecular speed; the faster the molecules move, the more often they reach the wall to collide. Second, this collision rate must be proportional to the number of molecules per unit volume,  $N/V$ . The greater the number of molecules,  $N$ , in a given volume, the more molecules collide in a given time interval.

$$\text{Rate of collisions} \propto (\text{molecular speed}) \times (\text{molecules per unit volume})$$

or

$$\text{Rate of collisions} \propto (u) \times \left(\frac{N}{V}\right)$$

We can introduce these proportionalities into the one describing pressure, to conclude that

$$P \propto (mu) \times u \times \frac{N}{V} \quad \text{or} \quad P \propto \frac{Nmu^2}{V} \quad \text{or} \quad PV \propto Nmu^2$$

$\overline{u^2}$  is the average of the squares of the molecular speeds. It is proportional to the square of the average speed, but the two quantities are not equal.

At any instant not all molecules are moving at the same speed,  $u$ . We should reason in terms of the *average* behavior of the molecules, and express the quantity  $u^2$  in average terms as  $\overline{u^2}$ , the **mean-square speed**.

$$PV \propto Nmu^2$$

Not all molecules collide with the walls at right angles, so we must average (using calculus) over all the trajectories. This gives a proportionality constant of  $\frac{1}{3}$ , and

$$PV = \frac{1}{3}Nmu^2$$

This describes the quantity  $PV$  (pressure  $\times$  volume) in terms of *molecular quantities*—number of molecules, molecular masses, and molecular speeds. The number of molecules,  $N$ , is given by the number of moles,  $n$ , times Avogadro's number,  $N_{\text{Av}}$ , or  $N = nN_{\text{Av}}$ . Making this substitution, we obtain

$$PV = \frac{1}{3}nN_{\text{Av}}\overline{mu^2}$$

The ideal gas equation describes (pressure  $\times$  volume) in terms of *measurable quantities*—number of moles and absolute temperature.

$$PV = nRT$$

So we see that the ideas of the kinetic-molecular theory lead to an equation of the same form as the macroscopic ideal gas equation. Thus, the molecular picture of the theory is consistent with the ideal gas equation and gives support to the theory. Equating the right-hand sides of these last two equations and canceling  $n$  gives

$$\frac{1}{3}N_{\text{Av}}\overline{mu^2} = RT$$

This equation can also be written as

$$\frac{1}{3}N_{\text{Av}} \times (2 \times \frac{1}{2}\overline{mu^2}) = RT$$

From physics we know that the *kinetic energy* of a particle of mass  $m$  moving at speed  $u$  is  $\frac{1}{2}mu^2$ . So we can write

$$\frac{2}{3}N_{\text{Av}} \times (\text{avg } KE \text{ per molecule}) = RT$$

or

$$N_{\text{Av}} \times (\text{avg } KE \text{ per molecule}) = \frac{3}{2}RT$$

This equation shows that the absolute temperature is directly proportional to the average molecular kinetic energy, as postulated by the kinetic-molecular theory. Because there are  $N_{\text{Av}}$  molecules in a mole, the left-hand side of this equation is equal to the total kinetic energy of a mole of molecules.

$$\text{Total kinetic energy per mole of gas} = \frac{3}{2}RT$$

With this interpretation, the total molecular-kinetic energy of a mole of gas depends *only* on the temperature, and not on the mass of the molecules or the gas density.

We can also obtain some useful equations for molecular speeds from the previous reasoning. Solving the equation

$$\frac{1}{3}N_{\text{Av}}\overline{mu^2} = RT$$

for root-mean-square speed,  $u_{\text{rms}} = \sqrt{\overline{u^2}}$ , we obtain

$$u_{\text{rms}} = \sqrt{\frac{3RT}{N_{\text{Av}}m}}$$

We recall that  $m$  is the mass of a single molecule. So  $N_{\text{Av}}m$  is the mass of Avogadro's number of molecules, or one mole of substance; this is equal to the *molecular weight*,  $M$ , of the gas.

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

### EXAMPLE 12-22 Molecular Speed

Calculate the root-mean-square speed of  $\text{H}_2$  molecules in meters per second at  $20^\circ\text{C}$ . Recall that

$$1 \text{ J} = 1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

#### Plan

We substitute the appropriate values into the equation relating  $u_{\text{rms}}$  to temperature and molecular weight. Remember that  $R$  must be expressed in the appropriate units.

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 8.314 \frac{\text{kg} \cdot \text{m}^2}{\text{mol} \cdot \text{K} \cdot \text{s}^2}$$

## Solution

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \frac{\text{kg}\cdot\text{m}^2}{\text{mol}\cdot\text{K}\cdot\text{s}^2} \times 293 \text{ K}}{2.016 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}}}}$$

$$u_{\text{rms}} = \sqrt{3.62 \times 10^6 \text{ m}^2/\text{s}^2} = 1.90 \times 10^3 \text{ m/s} \quad (\text{about } 4250 \text{ mph})$$

You should now work Exercise 86.

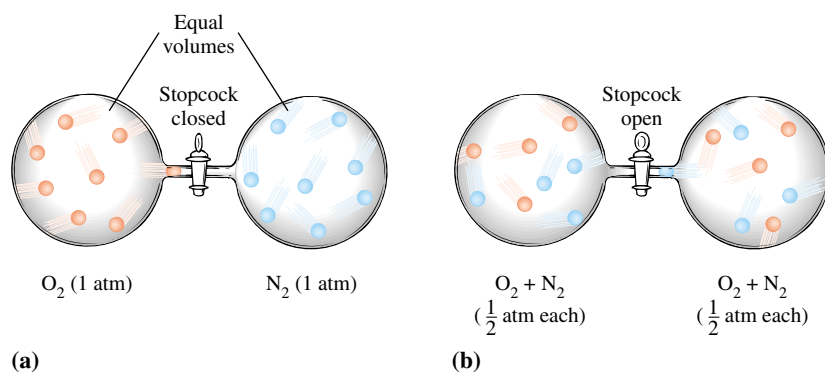
### 12-14 DIFFUSION AND EFFUSION OF GASES

Scientists use the word “effusion” to describe the escape of a gas through a tiny hole, and the word “diffusion” to describe movement of a gas into a space or the mixing of one gas with another. The distinction made by scientists is somewhat sharper than that usually found in a dictionary.

Because gas molecules are in constant, rapid, random motion, they diffuse quickly throughout any container (Figure 12-13). For example, if hydrogen sulfide (the smell of rotten eggs) is released in a large room, the odor can eventually be detected throughout the room. If a mixture of gases is placed in a container with thin porous walls, the molecules effuse through the walls. Because they move faster, lighter gas molecules effuse through the tiny openings of porous materials faster than heavier molecules (Figure 12-14).

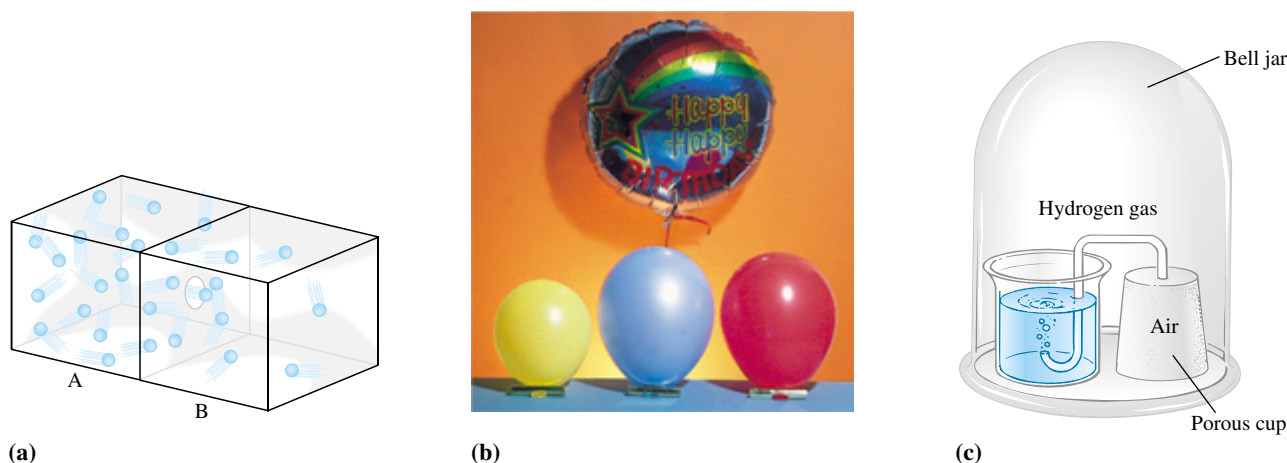
Although they are the most abundant elements in the universe, hydrogen and helium occur as gases only in trace amounts in our atmosphere. This is due to the high average molecular speeds resulting from their low molecular weights. At temperatures in our atmosphere, these molecules reach speeds exceeding the escape velocity required for them to break out of the earth’s gravitational pull and diffuse into interplanetary space. Thus, most of the gaseous hydrogen and helium that were probably present in large concentrations in the earth’s early atmosphere have long since diffused away. The same is true for the abundance of these gases on other small planets in our solar system, especially those with higher average temperatures than ours (Mercury and Venus). The Mariner 10 spacecraft in 1974 revealed measurable amounts of He in the atmosphere of Mercury; the source of this helium is unknown. Massive bodies such as stars (including our own sun) are mainly H and He.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 12.12, Applications of the Kinetic-Molecular Theory.



**Figure 12-13** A representation of diffusion of gases. The space between the molecules allows for ease of mixing one gas with another. Collisions of molecules with the walls of the container are responsible for the pressure of the gas.





**Figure 12-14** Effusion of gases. (a) A molecular interpretation of effusion. Molecules are in constant motion; occasionally they strike the opening and escape. (b) Latex balloons were filled with the same volume of He (yellow), N<sub>2</sub> (blue), and O<sub>2</sub> (red). Lighter molecules, such as He, effuse through the tiny pores of the latex balloons more rapidly than does N<sub>2</sub> or O<sub>2</sub>. The silver party balloon is made of a metal-coated polymer with pores that are too small to allow rapid He effusion. (c) If a bell jar full of hydrogen is brought down over a porous cup full of air, rapidly moving hydrogen diffuses into the cup faster than the oxygen and nitrogen in the air can effuse out of the cup. This causes an increase in pressure in the cup sufficient to produce bubbles in the water in the beaker.

## 12-15 REAL GASES: DEVIATIONS FROM IDEALITY

Until now our discussions have dealt with *ideal* behavior of gases. By this we mean that the identity of a gas does not affect how it behaves, and the same equations should work equally well for all gases. Under ordinary conditions most *real* gases do behave ideally; their  $P$  and  $V$  are predicted by the ideal gas laws, so they do obey the postulates of the kinetic-molecular theory. According to the kinetic-molecular model, (1) all but a negligible volume of a gas sample is empty space, and (2) the molecules of *ideal* gases do not attract one another because they are so far apart relative to their own sizes.

Under some conditions, however, most gases can have pressures and/or volumes that are *not* accurately predicted by the ideal gas laws. This tells us that they are not behaving entirely as postulated by the kinetic-molecular theory.

Nonideal gas behavior (deviation from the predictions of the ideal gas laws) is most significant at *high pressures* and/or *low temperatures*, that is, near the conditions under which the gas liquefies.

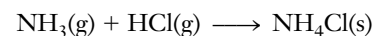
Johannes van der Waals (1837–1923) studied deviations of real gases from ideal behavior. In 1867, he empirically adjusted the ideal gas equation

$$P_{\text{ideal}}V_{\text{ideal}} = nRT$$

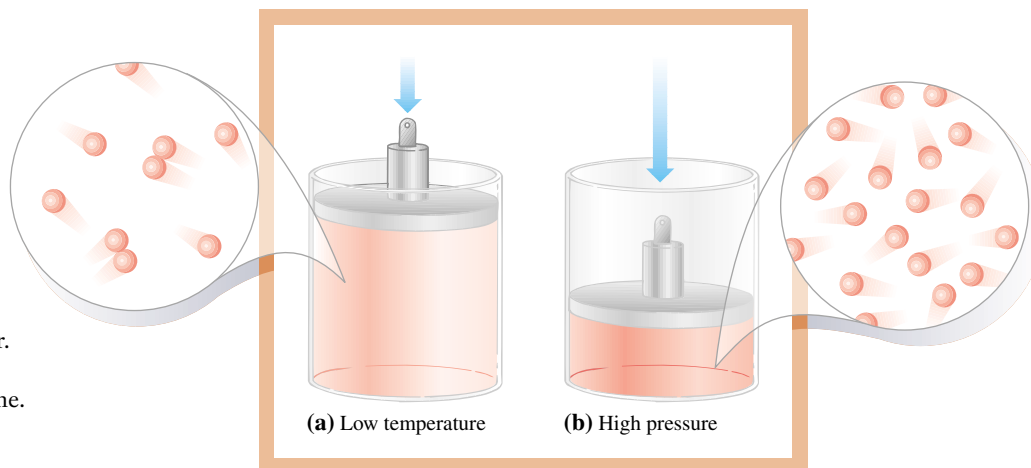
to take into account two complicating factors.



NH<sub>3</sub> gas (*left*) and HCl gas (*right*) escape from concentrated aqueous solutions. The white smoke (solid NH<sub>4</sub>Cl) shows where the gases mix and react.



**Figure 12-15** A molecular interpretation of deviations from ideal behavior. (a) A sample of gas at a low temperature. Each sphere represents a molecule. Because of their low kinetic energies, attractive forces between molecules can now cause a few molecules to “stick together.” (b) A sample of gas under high pressure. The molecules are quite close together. The free volume is now a much smaller fraction of the total volume.

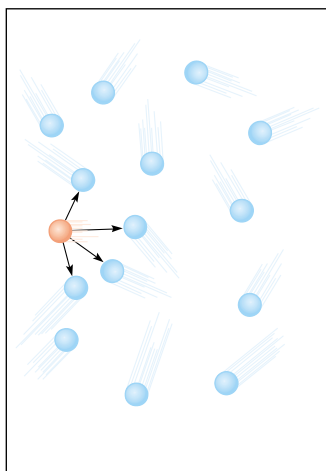


1. According to the kinetic–molecular theory, the molecules are so small, relative to the total volume of the gas, that each molecule can move through virtually the entire *measured volume* of the container,  $V_{\text{measured}}$  (Figure 12-15a). But under high pressures, a gas is compressed so that the volume of the molecules themselves becomes a significant fraction of the total volume occupied by the gas. As a result, the *available volume*,  $V_{\text{available}}$ , for any molecule to move in is less than the *measured volume* by an amount that depends on the volume excluded by the presence of the other molecules (Figure 12-15b). To account for this, we subtract a correction factor,  $nb$ .

$$V_{\text{ideally available}} = V_{\text{measured}} - nb$$

The factor  $nb$  corrects for the volume occupied by the molecules themselves. Larger molecules have greater values of  $b$ , and the greater the number of molecules in a sample (higher  $n$ ), the larger is the volume correction. The correction term becomes negligibly small, however, when the volume is large.

2. The kinetic–molecular theory describes pressure as resulting from molecular collisions with the walls of the container; this theory assumes that attractive forces between molecules are insignificant. For any real gas, the molecules can attract one another. But at higher temperatures, the potential energy due to intermolecular attractions is negligibly small compared with the high kinetic energy due to the rapid motion of the molecules and to the great distances between them. When the temperature is quite low (low kinetic energy), the molecules move so slowly that the potential energy due to even small attractive forces *does* become important. This perturbation becomes even more important when the molecules are very close together (at high pressure). As a result, the molecules deviate from their straight-line paths and take longer to reach the walls, so fewer collisions take place in a given time interval. Furthermore for a molecule about to collide with the wall, the attraction by its neighbors causes the collision to be less energetic than it would otherwise be (Figure 12-16). As a consequence, the pressure that the gas exerts,  $P_{\text{measured}}$ , is less than the pressure it would exert if attractions were truly negligible,  $P_{\text{ideally exerted}}$ . To correct for this, we subtract a correction factor,  $n^2a/V^2$ , from the ideal pressure.



**Figure 12-16** A gas molecule strikes the walls of a container with diminished force. The attractive forces between a molecule and its neighbors are significant.

$$P_{\text{measured}} = P_{\text{ideally exerted}} - \frac{n^2 a}{V_{\text{measured}}^2}$$

or

$$P_{\text{ideally exerted}} = P_{\text{measured}} + \frac{n^2 a}{V_{\text{measured}}^2}$$

In this correction term, large values of  $a$  indicate strong attractive forces. When more molecules are present (greater  $n$ ) and when the molecules are close together (smaller  $V^2$  in the denominator), the correction term becomes larger. The correction term becomes negligibly small, however, when the volume is large.

When we substitute these two expressions for corrections into the ideal gas equation, we obtain the equation

$$\left( P_{\text{measured}} + \frac{n^2 a}{V_{\text{measured}}^2} \right) (V_{\text{measured}} - nb) = nRT$$

or

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

The van der Waals equation, like the ideal gas equation, is known as an *equation of state*, that is, an equation that describes a state of matter.

This is the **van der Waals equation**. In this equation,  $P$ ,  $V$ ,  $T$ , and  $n$  represent the *measured* values of pressure, volume, temperature (expressed on the absolute scale), and number of moles, respectively, just as in the ideal gas equation. The quantities  $a$  and  $b$  are experimentally derived constants that differ for different gases (Table 12-5). When  $a$  and  $b$  are both zero, the van der Waals equation reduces to the ideal gas equation.

We can understand the relative values of  $a$  and  $b$  in Table 12-5 in terms of molecular properties. Note that  $a$  for helium is very small. This is the case for all noble gases and many other nonpolar molecules, because only very weak attractive forces, called dispersion forces, exist between them. **Dispersion forces** result from short-lived electrical dipoles produced by the attraction of one atom's nucleus for an adjacent atom's electrons. These forces exist for all molecules but are especially important for nonpolar molecules, which would never liquefy if dispersion forces did not exist. Polar molecules such as ammonia,  $\text{NH}_3$ , have permanent charge separations (dipoles), so they exhibit greater forces of attraction for one another. This explains the high value of  $a$  for ammonia. Dispersion forces and permanent dipole forces of attraction are discussed in more detail in Chapter 13.

Larger molecules have greater values of  $b$ . For instance,  $\text{H}_2$ , a first-row diatomic molecule, has a greater  $b$  value than the first-row monatomic He. The  $b$  value for  $\text{CO}_2$ , which contains three second-row atoms, is greater than that for  $\text{N}_2$ , which contains only two second-row atoms.

The following example illustrates the deviation of methane,  $\text{CH}_4$ , from ideal gas behavior under high pressure.

**TABLE 12-5** *van der Waals Constants*

Gas	$a$ ( $\text{L}^2 \cdot \text{atm} / \text{mol}^2$ )	$b$ ( $\text{L} / \text{mol}$ )
$\text{H}_2$	0.244	0.0266
He	0.034	0.0237
$\text{N}_2$	1.39	0.0391
$\text{NH}_3$	4.17	0.0371
$\text{CO}_2$	3.59	0.0427
$\text{CH}_4$	2.25	0.0428

### EXAMPLE 12-23 *van der Waals Equation*

Calculate the pressure exerted by 1.00 mole of methane,  $\text{CH}_4$ , in a 500.-mL vessel at  $25.0^\circ\text{C}$  assuming (a) ideal behavior and (b) nonideal behavior.

**Plan**

- (a) Ideal gases obey the ideal gas equation. We can solve this equation for  $P$ .  
 (b) To describe methane as a nonideal gas, we use the van der Waals equation and solve for  $P$ .

**Solution**

- (a) Using the ideal gas equation to describe ideal gas behavior,

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{(1.00 \text{ mol})\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}{0.500 \text{ L}} = 48.9 \text{ atm}$$

- (b) Using the van der Waals equation to describe nonideal gas behavior,

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

For  $\text{CH}_4$ ,  $a = 2.25 \text{ L}^2 \cdot \text{atm}/\text{mol}^2$  and  $b = 0.0428 \text{ L}/\text{mol}$  (see Table 12-5).

$$\left[P + \frac{(1.00 \text{ mol})^2(2.25 \text{ L}^2 \cdot \text{atm}/\text{mol}^2)}{(0.500 \text{ L})^2}\right]\left[0.500 \text{ L} - (1.00 \text{ mol})\left(0.0428 \frac{\text{L}}{\text{mol}}\right)\right] = (1.00 \text{ mol})\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})$$

Combining terms and canceling units, we get

$$P + 9.00 \text{ atm} = \frac{24.5 \text{ L} \cdot \text{atm}}{0.457 \text{ L}} = 53.6 \text{ atm}$$

$$P = 44.6 \text{ atm}$$

The pressure is 4.3 atm (8.8%) less than that calculated from the ideal gas law. A significant error would be introduced by assuming ideal behavior at this high pressure.

*You should now work Exercises 96 and 97.*

Repeating the calculations of Example 12-23 with the volume twenty times higher ( $V = 10.0 \text{ L}$ ) gives ideal and nonideal pressures, respectively, of 2.45 and 2.44 atm, a difference of only 0.4%.

Many other equations have been developed to describe the behavior of real gases. Each of these contains quantities that must be empirically derived for each gas.

## Key Terms

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**Absolute zero** The zero point on the absolute temperature scale;  $-273.15^\circ\text{C}$  or  $0 \text{ K}$ ; theoretically, the temperature at which molecular motion is a minimum.

**Atmosphere (atm)** A unit of pressure; the pressure that will support a column of mercury 760 mm high at  $0^\circ\text{C}$ ; 760 torr.

**Avogadro's Law** At the same temperature and pressure, equal volumes of all gases contain the same number of molecules.

**Barometer** A device for measuring atmospheric pressure. See Figures 12-1 and 12-2. The liquid is usually mercury.

**Boyle's Law** At constant temperature, the volume occupied by a given mass of a gas is inversely proportional to the applied pressure.

**Charles's Law** At constant pressure, the volume occupied by a definite mass of a gas is directly proportional to its absolute temperature.

**Condensed states** The solid and liquid states.

**Dalton's Law of Partial Pressures** The total pressure exerted by a mixture of gases is the sum of the partial pressures of the individual gases.

**Diffusion** The movement of a substance (e.g., a gas) into a space or the mixing of one substance (e.g., a gas) with another.

**Dispersion Forces** Weak, short-range attractive forces between short-lived temporary dipoles.

**Effusion** The escape of a gas through a tiny hole or a thin porous wall.

**Equation of state** An equation that describes the behavior of matter in a given state; for example, the van der Waals equation describes the behavior of the gaseous state.

**Fluids** Substances that flow freely; gases and liquids.

**Gay-Lussac's Law of Combining Volumes** At constant temperature and pressure, the volumes of reacting gases (and any gaseous products) can be expressed as ratios of small whole numbers.

**Ideal gas** A hypothetical gas that obeys exactly all postulates of the kinetic-molecular theory.

**Ideal Gas Equation** The product of the pressure and volume of an ideal gas is directly proportional to the number of moles of the gas and the absolute temperature.

**Kinetic-molecular theory** A theory that attempts to explain macroscopic observations on gases in microscopic or molecular terms.

**Manometer** A two-armed barometer. See Figure 12-1.

**Mole fraction** The number of moles of a component of a mixture divided by the total number of moles in the mixture.

**Partial pressure** The pressure exerted by one gas in a mixture of gases.

**Pascal (Pa)** The SI unit of pressure; it is defined as the pressure exerted by a force of one newton acting on an area of one square meter.

**Pressure** Force per unit area.

**Real gases** Gases that deviate from ideal gas behavior.

**Root-mean-square speed,  $u_{\text{rms}}$**  The square root of the mean-square speed,  $\sqrt{\overline{u^2}}$ . This is equal to  $\sqrt{\frac{3RT}{M}}$  for an ideal gas. The root-mean-square speed is slightly different from the average speed, but the two quantities are proportional.

**Standard molar volume** The volume occupied by one mole of an ideal gas under standard conditions; 22.414 liters.

**Standard temperature and pressure (STP)** Standard temperature 0°C (273.15 K), and standard pressure, one atmosphere, are standard conditions for gases.

**Torr** A unit of pressure; the pressure that will support a column of mercury 1 mm high at 0°C.

**Universal gas constant  $R$** , the proportionality constant in the ideal gas equation,  $PV = nRT$ .

**van der Waals equation** An equation of state that extends the ideal gas law to real gases by inclusion of two empirically determined parameters, which are different for different gases.

**Vapor** A gas formed by boiling or evaporation of a liquid or sublimation of a solid; a term commonly used when some of the liquid or solid remains in contact with the gas.

**Vapor pressure** The pressure exerted by a vapor in equilibrium with its liquid or solid.

## Exercises

You may assume *ideal gas behavior* unless otherwise indicated.

### Basic Ideas

1. Define pressure. Give a precise scientific definition—one that can be understood by someone without any scientific training.
2. State whether each property is characteristic of all gases, some gases, or no gas: (a) transparent to light; (b) colorless; (c) unable to pass through filter paper; (d) more difficult to compress than liquid water; (e) odorless; (f) settles on standing.
3. Describe the mercury barometer. How does it work?
4. What is a manometer? How does it work?
5. Express a pressure of 685 torr in the following units: (a) mm Hg; (b) atm; (c) Pa; (d) kPa.
6. A typical laboratory atmospheric pressure reading is 755 torr. Convert this value to (a) psi, (b) cm Hg, (c) inches Hg, (d) kPa, (e) atm, and (f) ft H<sub>2</sub>O.
7. Complete the following table.

	atm	torr	Pa	kPa
Standard atmosphere	1			
Partial pressure of nitrogen in the atmosphere		593		
A tank of compressed hydrogen			$1.61 \times 10^5$	
Atmospheric pressure at the summit of Mt. Everest				33.7

8. State whether each of the following samples of matter is a gas. If the information is insufficient for you to decide, write "insufficient information."
  - (a) A material is in a steel tank at 100. atm pressure. When the tank is opened to the atmosphere, the material immediately expands, increasing its volume many-fold.
  - (b) A material, on being emitted from an industrial

- smokestack, rises about 10 m into the air. Viewed against a clear sky, it has a white appearance.
- (c) 1.0 mL of material weighs 8.2 g.
- (d) When a material is released from a point 30 ft below the level of a lake at sea level (equivalent in pressure to about 76 cm of mercury), it rises rapidly to the surface, at the same time doubling its volume.
- (e) A material is transparent and pale green in color.
- (f) One cubic meter of a material contains as many molecules as  $1 \text{ m}^3$  of air at the same temperature and pressure.
- \*9. The densities of mercury and corn oil are 13.5 g/mL and 0.92 g/mL, respectively. If corn oil were used in a barometer, what would be the height of the column, in meters, at standard atmospheric pressure? (The vapor pressure of the oil is negligible.)
10. Steel tanks for storage of gases are capable of withstanding pressures greater than 125 atm. Express this pressure in psi.
11. Automobile tires are normally inflated to a pressure of 28 psi as measured by a tire gauge. (a) Express this pressure in atmospheres. (b) Assuming standard atmospheric pressure, calculate the internal pressure of the tire.

### Boyle's Law: The Pressure–Volume Relationship

12. (a) On what kinds of observations (measurements) is Boyle's Law based? State the law. (b) Use the statement of Boyle's Law to derive a simple mathematical expression for Boyle's Law.
13. Could the words "a fixed number of moles" be substituted for "a definite mass" in the statement of Boyle's Law? Explain.
14. A gas sample contained in a cylinder equipped with a moveable piston occupied 300. mL at a pressure of 2.00 atm. What would be the final pressure if the volume were increased to 500. mL at constant temperature?
15. A balloon that contains 1.50 liters of air at 1.00 atm is taken under water to a depth at which the pressure is 3.00 atm. Calculate the new volume of the balloon. Assume that the temperature remains constant.
16. A 50.-L sample of gas collected in the upper atmosphere at a pressure of 18.3 torr is compressed into a 150.-mL container at the same temperature. (a) What is the new pressure, in atmospheres? (b) To what volume would the original sample have had to be compressed to exert a pressure of 10.0 atm?
17. A sample of krypton gas occupies 75.0 mL at 0.400 atm. If the temperature remained constant, what volume would the krypton occupy at (a) 4.00 atm, (b) 0.00400 atm, (c) 765 torr, (d) 4.00 torr, and (e)  $3.5 \times 10^{-2}$  torr?
- \*18. A cylinder containing 15 L of helium gas at a pressure of 165 atm is to be used to fill toy balloons to a pressure of 1.1 atm. Each inflated balloon has a volume of 2.0 L. What is the maximum number of balloons that can be

inflated? (Remember that 15 L of helium at 1.1 atm will remain in the "exhausted" cylinder.)

19. (a) Can an absolute temperature scale based on Fahrenheit rather than Celsius degrees be developed? Why? (b) Can an absolute temperature scale that is based on a "degree" twice as large as a Celsius degree be developed? Why?
20. (a) What does "absolute temperature scale" mean? (b) Describe the experiments that led to the evolution of the absolute temperature scale. What is the relationship between the Celsius and Kelvin temperature scales? (c) What does "absolute zero" mean?
21. Complete the table by making the required temperature conversions. Pay attention to significant figures.

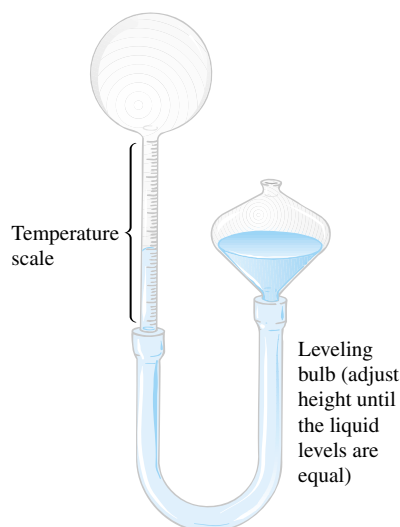
	Temperature	
	K	°C
Normal boiling point of water		100
Reference for thermodynamic data	298.15	
Dry ice becomes a gas at atmospheric pressure		-78.5
The center of the sun (estimated)	$1.53 \times 10^7$	

### Charles's Law: The Volume–Temperature Relationship

22. (a) Why is a plot of volume versus temperature at constant pressure a straight line (see Figure 12-5)? (b) On what kind of observations (measurements) is Charles's Law based? State the law.
23. A gas occupies a volume of 31.0 L at 17.0°C. If the gas temperature rises to 34.0°C at constant pressure, (a) would you expect the volume to double to 62.0 L? Explain. Calculate the new volume (b) at 34.0°C, (c) at 400. K, and (d) at 0.00°C.
24. Several balloons are inflated with helium to a volume of 0.75 L at 27°C. One of the balloons was found several hours later; the temperature had dropped to 22°C. What would be the volume of the balloon when found, if no helium has escaped?
25. Which of the following statements are true? Which are false? Why is each true or false? *Assume constant pressure* in each case.
- (a) If a sample of gas is heated from 100°C to 200°C, the volume will double.
- (b) If a sample of gas is heated from 0.°C to 273°C, the volume will double.
- (c) If a sample of gas is cooled from 1273°C to 500.°C, the volume will decrease by a factor of 2.



- (d) If a sample of gas is cooled from  $1000.^{\circ}\text{C}$  to  $200.^{\circ}\text{C}$ , the volume will decrease by a factor of 5.  
 (e) If a sample of gas is heated from  $473^{\circ}\text{C}$  to  $1219^{\circ}\text{C}$ , the volume will increase by a factor of 2.
- \*26. The device shown here is a gas thermometer. (a) At the ice point, the gas volume is 1.400 L. What would be the new volume if the gas temperature were raised from the ice point to  $8.0^{\circ}\text{C}$ ? (b) Assume the cross-sectional area of the graduated arm is  $1.0\text{ cm}^2$ . What would be the difference in height if the gas temperature changed from  $0^{\circ}\text{C}$  to  $8.0^{\circ}\text{C}$ ? (c) What modifications could be made to increase the sensitivity of the thermometer?



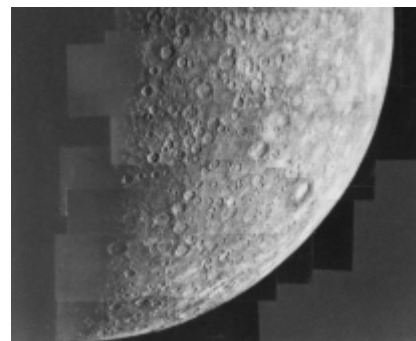
27. A weather balloon is filled to the volume of 150. L on a day when the temperature is  $19^{\circ}\text{C}$ . If no gases escaped, what would be the volume of the weather balloon after it rises to an altitude where the temperature is  $-8^{\circ}\text{C}$ ?  
 28. Calculate the volume of an ideal gas at the temperatures of dry ice ( $-78.5^{\circ}\text{C}$ ), liquid  $\text{N}_2$  ( $-195.8^{\circ}\text{C}$ ), and liquid He ( $-268.9^{\circ}\text{C}$ ) if it occupies 5.00 L at  $25.0^{\circ}\text{C}$ . Assume constant pressure. Plot your results, and extrapolate to zero volume. At what temperature would zero volume be theoretically reached?

### The Combined Gas Law

29. Classify the relationship between the variables (a)  $P$  and  $V$ , (b)  $V$  and  $T$ , and (c)  $P$  and  $T$  as either (i) directly proportional or (ii) inversely proportional.  
 30. Prepare sketches of plots of (a)  $P$  vs.  $V$ , (b)  $P$  vs.  $1/V$ , (c)  $V$  vs.  $T$ , and (d)  $P$  vs.  $T$  for an ideal gas.  
 31. A sample of gas occupies 400. mL at STP. Under what pressure would this sample occupy 200. mL if the temperature were increased to  $819^{\circ}\text{C}$ ?  
 32. A 280.-mL sample of neon exerts a pressure of 660. torr at  $26^{\circ}\text{C}$ . At what temperature in  $^{\circ}\text{C}$  would it exert a pressure of 940. torr in a volume of 440. mL?
33. A 247-mL sample of a gas exerts a pressure of 3.13 atm at  $16.0^{\circ}\text{C}$ . What volume would it occupy at  $100.^{\circ}\text{C}$  and 1.00 atm?  
 34. Show how Boyle's and Charles's gas laws can be obtained from the combined gas law equation.

### STP, Standard Molar Volume, and Gas Densities

35. How many molecules of an ideal gas are contained in a 2.00-L flask at STP?  
 36. (a) What is Avogadro's Law? What does it mean? (b) What does "standard molar volume" mean? (c) Are there conditions other than STP at which 1 mole of an ideal gas would occupy 22.4 L? Explain.  
 37. Sodium vapor has been detected recently as a major component of the thin atmosphere of Mercury using a ground-based telescope and a spectrometer. Its concentration is estimated to be about  $1.0 \times 10^5$  atoms per  $\text{cm}^3$ . (a) Express this in moles per liter. (b) The maximum temperature of the atmosphere was measured by Mariner 10 to be about  $970.^{\circ}\text{C}$ . What is the approximate partial pressure of sodium vapor at that temperature?



The surface of the planet Mercury.

38. The limit of sensitivity for the analysis of carbon monoxide, CO, in air is 1 ppb (ppb = parts per billion) by volume. What is the smallest number of CO molecules that can be detected in 10. L of air at STP?  
 39. A lab instructor asked a student to calculate the number of moles of gas contained in a 320.-mL bulb in the laboratory. The student determined that the pressure and temperature of the gas were 732 torr and  $23.3^{\circ}\text{C}$ . The student calculated the following:

$$\underline{\quad} \text{ mol} = 0.320 \text{ L} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 0.0143 \text{ mol}$$

Was the student correct? Why?

40. Ethylene dibromide (EDB) was formerly used as a fumigant for fruits and grains, but now it is banned because it is a potential health hazard. EDB is a liquid that boils at  $109^{\circ}\text{C}$ . Its molecular weight is 188 g/mol. Calculate the density of its vapor at  $180^{\circ}\text{C}$  and 1.00 atm.

- \*41. A 503-mL flask contains 0.0243 mol of an ideal gas at a given temperature and pressure. Another flask contains 0.0388 mol of the gas at the same temperature and pressure. What is the volume of the second flask?
42. A laboratory technician forgot what the color coding on some commercial cylinders of gas meant, but remembered that each of two specific tanks contained one of the following gases: He, Ne, Ar, or Kr. Measurements at STP made on samples of the gases from the two cylinders showed the gas densities to be 3.74 g/L and 0.178 g/L. (a) Determine by calculation which of these gases was present in each tank. (b) Could this determination be made if the densities had been at a temperature and pressure different from STP?

### The Ideal Gas Equation

43. Calculate  $R$  in  $\text{L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ , in  $\text{kPa}\cdot\text{dm}^3/\text{mol}\cdot\text{K}$ , in  $\text{J}/\text{mol}\cdot\text{K}$ , and in  $\text{kJ}/\text{mol}\cdot\text{K}$ .
44. (a) What is an ideal gas? (b) What is the ideal gas equation? (c) Outline the logic used to obtain the ideal gas equation. (d) What is  $R$ ? How is it obtained?
45. (a) A chemist is preparing to carry out a reaction at high pressure that requires 36.0 mol of hydrogen gas. The chemist pumps the hydrogen into a 12.3-L rigid steel container at 25°C. To what pressure (in atmospheres) must the hydrogen be compressed? (b) What would be the density of the high-pressure hydrogen?
46. Calculate the pressure needed to contain 2.44 mol of an ideal gas at 45°C in a volume of 3.70 L.
47. (a) How many molecules are in a 1.00-L container of gaseous oxygen if the pressure is  $2.50 \times 10^{-9}$  torr and the temperature is 1225 K? (b) How many grams of oxygen are in the container?
- \*48. A barge containing 580. tons of liquid chlorine was involved in an accident. (a) What volume would this amount of chlorine occupy if it were all converted to a gas at 750. torr and 18°C? (b) Assume that the chlorine is confined to a width of 0.500 mile and an average depth of 60. ft. What would be the length, in feet, of this chlorine “cloud”?

### Molecular Weights and Formulas for Gaseous Compounds

49. Analysis of a volatile liquid shows that it contains 37.23% carbon, 7.81% hydrogen, and 54.96% chlorine by mass. At 150.°C and 1.00 atm, 500. mL of the vapor has a mass of 0.922 g. (a) What is the molecular weight of the compound? (b) What is its molecular formula?
- \*50. A student was given a container of ethane,  $\text{C}_2\text{H}_6$ , that had been closed at STP. By making appropriate measurements, the student found that the mass of the sample of ethane was 0.244 g and the volume of the container was 185 mL. Use the student’s data to calculate the molecular weight of ethane. What percent error is obtained? Suggest some possible sources of the error.
51. Calculate the molecular weight of a gaseous element if 0.480 g of the gas occupies 367 mL at 365 torr and 45°C. Suggest the identity of the element.
52. A cylinder was found in a storeroom of a manufacturing plant. The label on the cylinder was gone and no one remembered what the cylinder held. A 0.00500-gram sample was found to occupy 4.13 mL at 23°C and 745 torr. The sample was also found to be composed of only carbon and hydrogen. Identify the gas.
53. A sample of porous rock was brought back from the planet Farout on the other side of the galaxy. Trapped in the rock was a carbon–oxygen gas. The unknown gas was extracted and evaluated. A volume of 3.70 mL of the gas was collected under the conditions of STP. The mass of the gas sample was determined to be 0.00726 grams. Additional analysis proved that there was only one compound present in the sample. What was the most probable identity of the gas based on these analyses?
- \*54. A highly volatile liquid was allowed to vaporize completely into a 250.-mL flask immersed in boiling water. From the following data, calculate the molecular weight (in amu per molecule) of the liquid. Mass of empty flask = 65.347 g; mass of flask filled with water at room temperature = 327.4 g; mass of flask and condensed liquid = 65.739 g; atmospheric pressure = 743.3 torr; temperature of boiling water = 99.8°C; density of water at room temperature = 0.997 g/mL.
55. A pure gas contains 85.63% carbon and 14.37% hydrogen by mass. Its density is 2.50 g/L at STP. What is its molecular formula?

### Gas Mixtures and Dalton’s Law

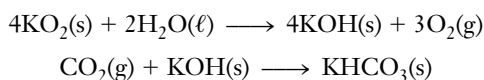
56. (a) What are partial pressures of gases? (b) State Dalton’s Law. Express it symbolically.
57. A sample of oxygen of mass 30.0 g is confined in a vessel at 0°C and 1000. torr. Then 8.00 g of hydrogen is pumped into the vessel at constant temperature. What will be the final pressure in the vessel (assuming only mixing with no reaction)?
58. A gaseous mixture contains 5.23 g of chloroform,  $\text{CHCl}_3$ , and 1.66 g of methane,  $\text{CH}_4$ . What pressure is exerted by the mixture inside a 50.0-mL metal container at 275°C? What pressure is contributed by the  $\text{CHCl}_3$ ?
59. A cyclopropane–oxygen mixture can be used as an anesthetic. If the partial pressures of cyclopropane and oxygen are 140. torr and 560. torr, respectively, what is the ratio of the number of moles of cyclopropane to the number of moles of oxygen in this mixture? What is the corresponding ratio of molecules?
60. What is the mole fraction of each gas in a mixture having the partial pressures of 0.267 atm of He, 0.317 atm of Ar, and 0.277 atm of Xe?

- \*61. Assume that unpolluted air has the composition shown in Table 12-2. (a) Calculate the number of molecules of  $N_2$ , of  $O_2$ , and of Ar in 1.00 L of air at  $21^\circ\text{C}$  and 1.00 atm. (b) Calculate the mole fractions of  $N_2$ ,  $O_2$ , and Ar in the air.
62. Individual samples of  $O_2$ ,  $N_2$ , and He are present in three 2.25-L vessels. Each exerts a pressure of 1.50 atm. (a) If all three gases are forced into the same 1.00-L container with no change in temperature, what will be the resulting pressure? (b) What is the partial pressure of  $O_2$  in the mixture? (c) What are the partial pressures of  $N_2$  and He?
63. Hydrogen was collected over water at  $20^\circ\text{C}$  and 755 torr. The volume of this gas sample was 45.3 mL. What volume would the dry hydrogen occupy at STP?
64. A nitrogen sample occupies 447 mL at STP. If the same sample were collected over water at  $25^\circ\text{C}$  and 750. torr, what would be the volume of the gas sample?
- \*65. A study of climbers who reached the summit of Mt. Everest without supplemental oxygen revealed that the partial pressures of  $O_2$  and  $CO_2$  in their lungs were 35 torr and 7.5 torr, respectively. The barometric pressure at the summit was 253 torr. Assume that the lung gases are saturated with moisture at a body temperature of  $37^\circ\text{C}$ . Calculate the partial pressure of inert gas (mostly nitrogen) in the climbers' lungs.
66. A 4.00-L flask containing He at 6.00 atm is connected to a 3.00-L flask containing  $N_2$  at 3.00 atm and the gases are allowed to mix. (a) Find the partial pressures of each gas after they are allowed to mix. (b) Find the total pressure of the mixture. (c) What is the mole fraction of helium?
67. A 3.46-liter sample of a gas was collected over water on a day when the temperature was  $21^\circ\text{C}$  and the barometric pressure was 718 torr. The dry sample of gas had a mass of 4.20 g. What is the molecular weight of the gas? At  $21^\circ\text{C}$  the vapor pressure of water is 18.65 torr.
71. Calculate the volume of methane,  $CH_4$ , measured at 300. K and 815 torr, that can be produced by the bacterial breakdown of 1.00 kg of a simple sugar.
- $$C_6H_{12}O_6 \longrightarrow 3CH_4 + 3CO_2$$
- \*72. A common laboratory preparation of oxygen is
- $$2KClO_3(s) \xrightarrow[\text{heat}]{MnO_2} 2KCl(s) + 3O_2(g)$$
- If you were designing an experiment to generate four bottles (each containing 250. mL) of  $O_2$  at  $25^\circ\text{C}$  and 755 torr and allowing for 25% waste, what mass of potassium chlorate would be required?
73. Many campers use small propane stoves to cook meals. What volume of air (see Table 12-2) will be required to burn 11.5 L of propane,  $C_3H_8$ ? Assume all gas volumes are measured at the same temperature and pressure.
- $$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$
- \*74. If 2.00 L of nitrogen and 5.00 L of hydrogen were allowed to react, how many liters of  $NH_3(g)$  could form? Assume all gases are at the same temperature and pressure, and that the limiting reactant is used up.
- $$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
- \*75. We burn 15.00 L of ammonia in 20.00 L of oxygen at  $500^\circ\text{C}$ . What volume of nitric oxide,  $NO$ , gas can form? What volume of steam,  $H_2O(g)$ , is formed? Assume all gases are at the same temperature and pressure, and that the limiting reactant is used up.
- $$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$
76. What mass of  $KNO_3$  would have to be decomposed to produce 21.1 L of oxygen measured at STP?
- $$2KNO_3(s) \xrightarrow{\text{heat}} 2KNO_2(s) + O_2(g)$$

### Stoichiometry in Reactions Involving Gases

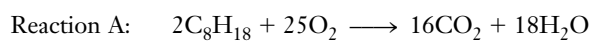
68. During a collision, automobile air bags are inflated by the  $N_2$  gas formed by the explosive decomposition of sodium azide,  $NaN_3$ .
- $$2NaN_3 \longrightarrow 2Na + 3N_2$$
- What mass of sodium azide would be needed to inflate a 30.0-L bag to a pressure of 1.40 atm at  $25^\circ\text{C}$ ?
69. Assuming the volumes of all gases in the reaction are measured at the same temperature and pressure, calculate the volume of water vapor obtainable by the explosive reaction of a mixture of 440. mL of hydrogen gas and 325 mL of oxygen gas.
- \*70. One liter of sulfur vapor,  $S_8(g)$ , at  $600^\circ\text{C}$  and 1.00 atm is burned in excess pure oxygen to give sulfur dioxide gas,  $SO_2$ , measured at the same temperature and pressure. What mass of  $SO_2$  gas is obtained?
77. Refer to Exercise 76. An impure sample of  $KNO_3$  that had a mass of 50.3 g was heated until all of the  $KNO_3$  had decomposed. The liberated oxygen occupied 4.22 L at STP. What percentage of the sample was  $KNO_3$ ? Assume that no impurities decompose to produce oxygen.
- \*78. Heating a 5.913-g sample of an ore containing a metal sulfide, in the presence of excess oxygen, produces 1.177 L of dry  $SO_2$ , measured at  $35.0^\circ\text{C}$  and 755 torr. Calculate the percentage by mass of sulfur in the ore.
- \*79. The following reactions occur in a gas mask (a self-contained breathing apparatus) sometimes used by underground miners. The  $H_2O$  and  $CO_2$  come from exhaled air, and  $O_2$  is inhaled as it is produced.  $KO_2$  is potassium superoxide. The  $CO_2$  is converted to the solid salt

$\text{KHCO}_3$ , potassium hydrogen carbonate, so that  $\text{CO}_2$  is not inhaled in significant amounts.

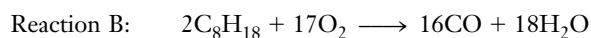


(a) What volume of  $\text{O}_2$ , measured at STP, is produced by the complete reaction of 1.00 g of  $\text{KO}_2$ ? (b) What is this volume at body temperature,  $37^\circ\text{C}$ , and 1.00 atm? (c) What mass of  $\text{KOH}$  is produced in part (a)? (d) What volume of  $\text{CO}_2$ , measured at STP, will react with the mass of  $\text{KOH}$  of part (c)? (e) What is the volume of  $\text{CO}_2$  in part (d) measured at  $37^\circ\text{C}$  and 1.00 atm?

- \*80. Let us represent gasoline as octane,  $\text{C}_8\text{H}_{18}$ . When hydrocarbon fuels burn in the presence of sufficient oxygen,  $\text{CO}_2$  is formed.



But when the supply of oxygen is limited, the poisonous gas carbon monoxide,  $\text{CO}$ , is formed.



Any automobile engine, no matter how well tuned, burns its fuel by some combination of these two reactions. Suppose an automobile engine is running at idle speed in a closed garage with air volume  $97.5 \text{ m}^3$ . This engine burns 95.0% of its fuel by reaction A, and the remainder by reaction B. (a) How many liters of octane, density  $0.702 \text{ g/mL}$ , must be burned for the  $\text{CO}$  to reach a concentration of  $2.00 \text{ g/m}^3$ ? (b) If the engine running at idle speed burns fuel at the rate of  $1.00 \text{ gal/h}$  ( $0.0631 \text{ L/min}$ ), how long does it take to reach the  $\text{CO}$  concentration in (a)?

### The Kinetic—Molecular Theory and Molecular Speeds

81. Outline the kinetic–molecular theory.
82. The radius of a typical molecule of a gas is  $2.00 \text{ \AA}$ . (a) Find the volume of a molecule assuming it to be spherical. For a sphere,  $V = 4/3 \pi r^3$ . (b) Calculate the volume actually occupied by 1.00 mol of these molecules. (c) If 1.0 mol of this gas occupies 22.4 L, find the fraction of the volume actually occupied by the molecules. (d) Comment on your answer to part (c) in view of the first statement summarizing the kinetic–molecular theory of an ideal gas.
83. How does the kinetic–molecular theory explain (a) Boyle’s Law? (b) Dalton’s Law? (c) Charles’s Law?
84.  $\text{SiH}_4$  molecules are heavier than  $\text{CH}_4$  molecules; yet, according to kinetic–molecular theory, the average kinetic energies of the two gases at the same temperature are equal. How can this be?
- \*85. At  $22^\circ\text{C}$ ,  $\text{Cl}_2$  molecules have some rms speed (which we need not calculate). At what temperature would the rms speed of  $\text{F}_2$  molecules be the same?
- \*86. (a) How do average speeds of gaseous molecules vary with temperature? (b) Calculate the ratio of the rms speed of  $\text{N}_2$  molecules at  $100^\circ\text{C}$  to the rms speed of the same molecules at  $0^\circ\text{C}$ .
87. How do the average kinetic energies and average speeds of each gas in a mixture compare?
88. (a) If you heat a gaseous sample in a fixed volume container, the pressure increases. Use the kinetic–molecular theory to explain the increased pressure. (b) If the volume of a gaseous sample is reduced at constant temperature, the pressure increases. Use the kinetic–molecular theory to explain the increase in pressure.

### Real Gases and Deviations from Ideality

89. What is the van der Waals equation? How does it differ from the ideal gas equation?
90. Which of the following gases would be expected to behave most nearly ideally under the same conditions?  $\text{H}_2$ ,  $\text{F}_2$ ,  $\text{HF}$ . Which one would be expected to deviate from ideal behavior the most? Explain both answers.
91. Does the effect of intermolecular attraction on the properties of a gas become more significant or less significant if (a) the gas is compressed to a smaller volume at constant temperature? (b) more gas is forced into the same volume at the same temperature? (c) the temperature of the gas is raised at constant pressure?
92. Does the effect of molecular volume on the properties of a gas become more significant or less significant if (a) the gas is compressed to a smaller volume at constant temperature? (b) more gas is forced into the same volume at the same temperature? (c) the temperature of the gas is raised at constant pressure?
93. A sample of gas has a molar volume of 10.1 L at a pressure of 745 torr and a temperature of  $-138^\circ\text{C}$ . Is the gas behaving ideally?
94. Calculate the compressibility factor,  $(P_{\text{real}})(V_{\text{real}})/RT$ , for a 1.00-mol sample of  $\text{NH}_3$  under the following conditions: in a 500.-mL vessel at  $-10.0^\circ\text{C}$  it exerts a pressure of 30.0 atm. What would be the *ideal* pressure for 1.00 mol of  $\text{NH}_3$  at  $-10.0^\circ\text{C}$  in a 500.-mL vessel? Compare this with the real pressure and account for the difference.
95. (a) How do “real” and “ideal” gases differ? (b) Under what kinds of conditions are deviations from ideality most important? Why?
96. Find the pressure of a sample of carbon tetrachloride,  $\text{CCl}_4$ , if 1.00 mol occupies 35.0 L at  $77.0^\circ\text{C}$  (slightly above its normal boiling point). Assume that  $\text{CCl}_4$  obeys (a) the ideal gas law; (b) the van der Waals equation. The van der Waals constants for  $\text{CCl}_4$  are  $a = 20.39 \text{ L}^2\cdot\text{atm/mol}^2$  and  $b = 0.1383 \text{ L/mol}$ .
97. Repeat the calculations of Exercise 96 using a 3.10-mol gas sample confined to 6.15 L at  $135^\circ\text{C}$ .

## Mixed Exercises

98. A student is to perform a laboratory experiment that requires the evolution and collection of 75 mL of dry oxygen gas at one atmosphere and 25°C. What is the minimum mass of water required to generate the oxygen by electrolysis of water?
99. A tilting McLeod gauge is used to measure very low pressures of gases in glass vacuum lines in the laboratory. It operates by compressing a large volume of gas at low pressure to a much smaller volume so that the pressure is more easily measured. What is the pressure of a gas in a vacuum line if a 53.3-mL volume of the gas, when compressed to 0.133 mL, supports a 16.9-mm column of mercury?



A McLeod gauge.

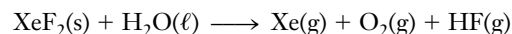
100. Imagine that you live in a cabin with an interior volume of 150. m<sup>3</sup>. On a cold morning your indoor air temperature is 10.°C, but by the afternoon the sun has warmed the cabin air to 18°C. The cabin is not sealed; therefore, the pressure inside is the same as it is outdoors. Assume that the pressure remains constant during the day. How many cubic meters of air would have been forced out of the cabin by the sun's warming? How many liters?
101. A particular tank can safely hold gas up to a pressure of 44.3 atm. When the tank contains 38.1 g of N<sub>2</sub> at 25°C, the gas exerts a pressure of 10.1 atm. What is the highest temperature to which the gas sample can be heated safely?
102. Find the molecular weight of Freon-12 (a chlorofluorocarbon) if 8.29 L of vapor at 200.°C and 790. torr has a mass of 26.8 g.
103. A flask of unknown volume was filled with air to a pressure of 3.25 atm. This flask was then attached to an evacuated flask with a known volume of 5.00 L, and the air was allowed to expand into the flask. The final pressure of the air (in both flasks) was 2.40 atm. Calculate the volume of the first flask.
- \*104. Relative humidity is the ratio of the pressure of water vapor in the air to the pressure of water vapor in air that is saturated with water vapor at the same temperature.

Relative humidity

$$= \frac{\text{actual partial pressure of H}_2\text{O vapor}}{\text{partial pressure of H}_2\text{O vapor if sat'd}}$$

Often this quantity is multiplied by 100 to give the percent relative humidity. Suppose the percent relative humidity is 80.0% at 91.4°F (33.0°C) in a house with volume 245 m<sup>3</sup>. Then an air conditioner is turned on. Due to the condensation of water vapor on the cold coils of the air conditioner, water vapor is also removed from the air as it cools. After the air temperature has reached 77.0°F (25.0°C), the percent relative humidity is measured to be 15.0%. (a) What mass of water has been removed from the air in the house? (*Reminder:* Take into account the difference in saturated water vapor pressure at the two temperatures.) (b) What volume would this liquid water occupy at 25°C? (Density of liquid water at 25.0°C = 0.997 g/cm<sup>3</sup>.)

105. A 450.-mL flask contains 0.500 g of nitrogen gas at a pressure of 744 torr. Are these data sufficient to allow you to calculate the temperature of the gas? If not, what is missing? If so, what is the temperature in °C?
106. Use both the ideal gas law and the van der Waals equation to calculate the pressure exerted by a 10.0-mol sample of ammonia in a 60.0-L container at 100.°C. By what percentage do the two results differ?
107. What volume of hydrogen fluoride at 743 torr and 24°C will be released by the reaction of 38.3 g of xenon difluoride with a stoichiometric amount of water? The *unbalanced* equation is



What volumes of oxygen and xenon will be released under these conditions?

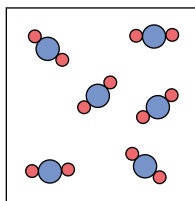
108. Cyanogen is 46.2% carbon and 53.8% nitrogen by mass. At a temperature of 25°C and a pressure of 750. torr, 1.00 g of cyanogen gas occupies 0.476 L. Determine the empirical formula and the molecular formula of cyanogen.
109. Incandescent light bulbs contain noble gases, such as argon, so that the filament will last longer. The approximate volume of a 100.-watt bulb is 130. cm<sup>3</sup>, and the bulb contains 0.125 g of argon. How many grams of argon would be contained in a 150.-watt bulb under the same pressure and temperature conditions if the volume of the larger wattage bulb is 180. cm<sup>3</sup>?

## CONCEPTUAL EXERCISES

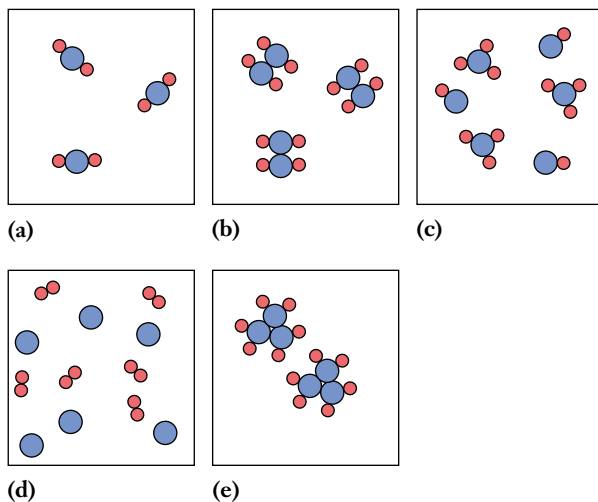
110. An attempt was made to collect carbon dioxide, isolated from the decomposition of a carbonate-containing mineral, by first bubbling the gas through pure liquid acetic acid. The experiment yielded 500. mL of a gaseous mixture of acetic acid and carbon dioxide at 1.00 atm and

16.0°C. The vapor pressure of pure acetic acid at 16.0°C is 400. torr. What should be the total mass of the collected sample?

111. The ideal gas equation deals with one set of volume, temperature, and pressure conditions; the combined gas law equation deals with two sets of conditions. Derive the combined gas law equation from the ideal gas equation.
112. Redraw Figure 12-12 so that it not only depicts the decrease in space between molecules as the system is cooled from 600. K to 300. K but also emphasizes the change in kinetic energy.
113. Suppose you were asked to supply a particular mass of a specified gas in a container of fixed volume at a specified pressure and temperature. Is it likely that you could fulfill the request? Explain.
114. The gas molecules in the box undergo a reaction at constant temperature and pressure.



If the initial volume is 1.8 L and the final volume is 0.9 L, which of the following boxes could be the products of the reaction? Explain your reasoning.



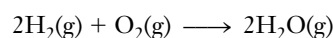
115. Use Dalton's Law of Partial Pressures to illustrate the changes that take place in the partial pressure of compound A and the total pressure as gas B is pumped into a closed system containing A.
116. Mole fraction is one of the few quantities that is expressed as a fraction. Frequently, percent is used instead. Cite an

example earlier in this textbook where percent was used instead of a fraction. Write an equation that relates mole fraction and mole percent.

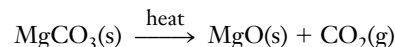
117. Explain why gases at high pressure or low temperature do not act as ideal gases.

### BUILDING YOUR KNOWLEDGE

118. A 5.00-L reaction vessel contains hydrogen at a partial pressure of 0.588 atm and oxygen gas at a partial pressure of 0.302 atm. Which element is the limiting reactant in the following reaction?

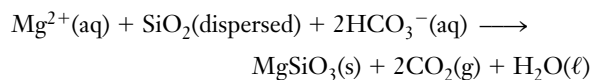


119. Suppose the gas mixture in Exercise 118 is ignited and the reaction produces the theoretical yield of the product. What would be the partial pressure of each substance present in the final mixture?
120. A 0.422-g sample of pentane,  $\text{C}_5\text{H}_{12}$ , is placed in a 4.00-L reaction vessel with excess  $\text{O}_2$ . The mixture is then ignited and the sample burns with complete combustion. What will be the partial pressures of  $\text{CO}_2$  and of  $\text{H}_2\text{O}(\text{g})$  in the reaction vessel if the final temperature is 300.°C?
121. When magnesium carbonate,  $\text{MgCO}_3$ , is heated to a high temperature, it decomposes.



A 20.29-gram sample of impure magnesium carbonate is completely decomposed at 1000.°C in a previously evacuated 2.00-L reaction vessel. After the reaction was complete, the solid residue (consisting only of  $\text{MgO}$  and the original impurities) had a mass of 15.90 grams. Assume that no other constituent of the sample produced a gas and that the volume of any solid was negligible compared with the gas volume. (a) How many grams of  $\text{CO}_2$  were produced? (b) What was the pressure of the  $\text{CO}_2$  produced? (c) What percent of the original sample was magnesium carbonate?

122. One natural source of atmospheric carbon dioxide is precipitation reactions such as the precipitation of silicates in the oceans.



How many grams of magnesium silicate would be precipitated during the formation of 100. L of carbon dioxide at 30.°C and 775 torr?

123. Table 12-2 states that dry air is 20.94% (by volume) oxygen. What is the partial pressure of oxygen under the conditions of STP? *Hint:* For gaseous samples the mole ratios are equal to the volume ratios.