

Gases: Their Properties and Behavior

CONTENTS

- 10.1 ▶ Gases and Gas Pressure
- 10.2 ▶ The Gas Laws
- 10.3 ▶ The Ideal Gas Law
- 10.4 ▶ Stoichiometric Relationships with Gases
- 10.5 ▶ Mixtures of Gases: Partial Pressure and Dalton's Law
- 10.6 ▶ The Kinetic-Molecular Theory of Gases
- 10.7 ▶ Gas Diffusion and Effusion: Graham's Law
- 10.8 ▶ The Behavior of Real Gases
- 10.9 ▶ The Earth's Atmosphere and Pollution
- 10.10 ▶ The Greenhouse Effect
- 10.11 ▶ Climate Change

STUDY GUIDE

The Earth's atmosphere is not only beautiful to behold but serves many critical functions. We need oxygen to survive and plants require carbon dioxide and nitrogen to grow. Even small changes in atmospheric composition from human activities can greatly impact the quality of the air we breathe and the delicate thermal balance that controls our climate.

? Which gases are greenhouse gases?

The answer to this question can be found in **INQUIRY** ▶▶ on page 392.

A quick look around tells you that matter takes many forms. Most of the things around you are *solids*, substances whose constituent atoms, molecules, or ions are held rigidly together in a definite way, giving the solid a definite volume and shape. Other substances are *liquids*, whose constituent atoms or molecules are held together less strongly, giving the liquid a definite volume but a changeable and indefinite shape. Still other substances are *gases*, whose constituent atoms or molecules have little attraction for one another and are therefore free to move about in whatever volume is available.

Although gases are few in number—only about a hundred substances are gases at room temperature and atmospheric pressure—experimental studies of their properties were enormously important in the historical development of atomic theories. We'll look briefly at this historical development in the present chapter, and we'll see how the behavior of gases can be described.

10.1 ► GASES AND GAS PRESSURE

We live surrounded by a blanket of air—the mixture of gases that make up the Earth's atmosphere. As shown in **TABLE 10.1**, nitrogen and oxygen account for more than 99% by volume of dry air. The remaining 1% is largely argon, with trace amounts of several other substances also present. Carbon dioxide, about which there is so much current concern because of its relationship to global warming, is present in air only to the extent of about 0.040%, or 400 parts per million (ppm). Although small, this value has risen in the past 160 years from an estimated 290 ppm in 1850, as the burning of fossil fuels and the deforestation of tropical rain forests have increased.

Air is typical of gases in many respects, and its behavior illustrates several important points about gases. For instance, gas mixtures are always *homogeneous*, meaning that they are uniform in composition. Unlike liquids, which often fail to mix with one another and which may separate into distinct layers—oil and water, for example—gases always mix completely. Furthermore, gases are *compressible*. When pressure is applied, the volume of a gas contracts proportionately. Solids and liquids, however, are nearly incompressible, and even the application of great pressure changes their volume only slightly.

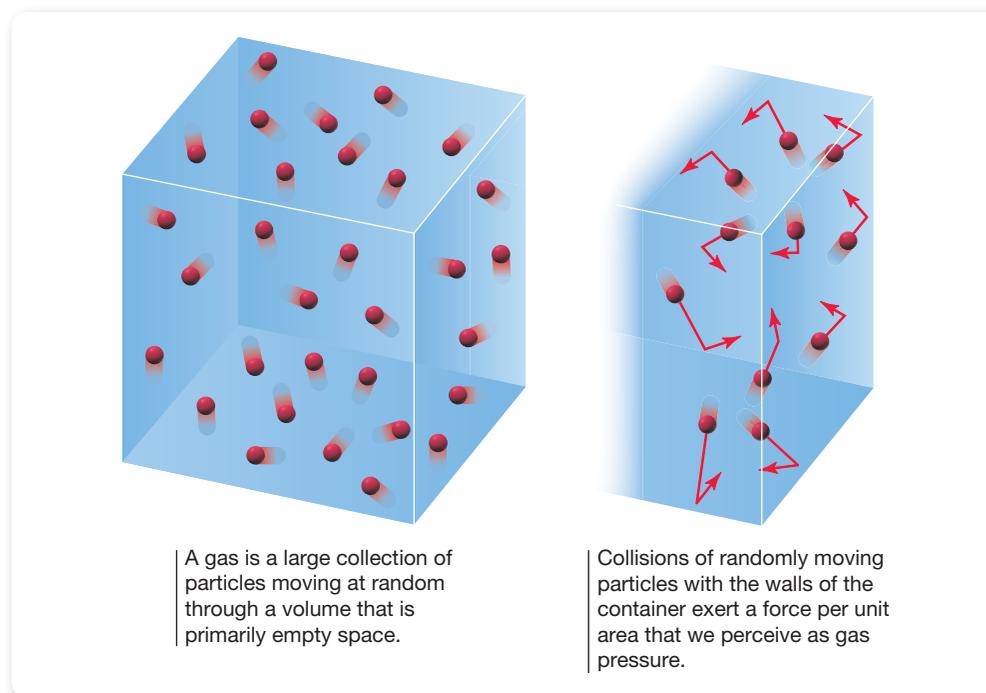
Homogeneous mixing and compressibility of gases both occur because the constituent particles—whether atoms or molecules—are far apart (**FIGURE 10.1**). Mixing occurs because individual gas particles have little interaction with their neighbors so the chemical identity of those neighbors is irrelevant. In solids and liquids, by contrast, the constituent particles are packed closely together, where they are affected by various attractive and repulsive forces that can inhibit their mixing. Compressibility is possible in gases because less than 0.1% of the volume of a typical gas is taken up by the particles themselves under normal circumstances; the remaining 99.9% is empty space. By contrast, approximately 70% of a solid's or liquid's volume is taken up by the particles.

One of the most obvious characteristics of gases is that they exert a measurable *pressure* on the walls of their container (Figure 10.1). We're all familiar with inflating a balloon or

TABLE 10.1 Composition of Dry Air at Sea Level

Constituent	% Volume	% Mass
N ₂	78.08	75.52
O ₂	20.95	23.14
Ar	0.93	1.29
CO ₂	0.040	0.060
Ne	1.82×10^{-3}	1.27×10^{-3}
He	5.24×10^{-4}	7.24×10^{-5}
CH ₄	1.7×10^{-4}	9.4×10^{-5}
Kr	1.14×10^{-4}	3.3×10^{-4}

► **FIGURE 10.1**
Molecular view of a gas.



pumping up a bicycle tire and feeling the hardness that results from the pressure inside. In scientific terms, **pressure** (P) is defined as a force (F) exerted per unit area (A). Force, in turn, is defined as mass (m) times acceleration (a), which, on Earth, is usually the acceleration due to gravity, $a = 9.81 \text{ m/s}^2$.

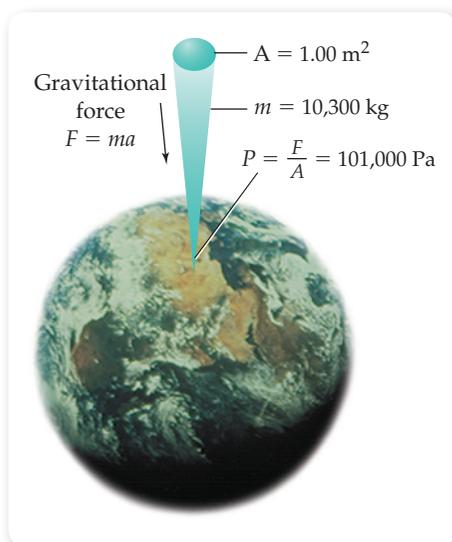
$$\text{Pressure } (P) = \frac{F}{A} = \frac{m \times a}{A}$$

The SI unit for force is the **newton** (N), where $1 \text{ N} = 1 (\text{kg} \cdot \text{m})/\text{s}^2$, and the SI unit for pressure is the **pascal** (Pa), where $1 \text{ Pa} = 1 \text{ N}/\text{m}^2 = 1 \text{ kg}/(\text{m} \cdot \text{s}^2)$. Expressed in more familiar units, a pascal is actually a very small amount—the pressure exerted by a mass of 10.2 mg resting on an area of 1.00 cm^2 .

$$P = \frac{m \times a}{A} = \frac{(10.2 \text{ mg}) \left(\frac{1 \text{ kg}}{10^6 \text{ mg}} \right) \left(9.81 \frac{\text{m}}{\text{s}^2} \right)}{(1.00 \text{ cm}^2) \left(\frac{1 \text{ m}}{10^2 \text{ cm}} \right)^2} = \frac{1.00 \times 10^{-4} \frac{\text{kg} \cdot \text{m}}{\text{s}^2}}{1.00 \times 10^{-4} \text{ m}^2}$$

$$= 1.00 \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = 1.00 \text{ Pa}$$

In rough terms, a penny sitting on the tip of your finger exerts a pressure of about 250 Pa. Just as the air in a tire and a penny on your finger exert pressure, the mass of air in the atmosphere pressing down on the Earth's surface exerts what we call *atmospheric pressure*. In fact, a 1 m^2 column of air extending from the Earth's surface through the upper atmosphere has a mass of about 10,300 kg, producing an atmospheric pressure of approximately 101,000 Pa, or 101 kPa (**FIGURE 10.2**).



▲ **FIGURE 10.2**
Atmospheric pressure. A column of air 1 m^2 in cross-sectional area extending from the Earth's surface through the upper atmosphere has a mass of about 10,300 kg, producing an atmospheric pressure of approximately 101,000 Pa.

$$P = \frac{m \times a}{A} = \frac{10,300 \text{ kg} \times 9.81 \frac{\text{m}}{\text{s}^2}}{1.00 \text{ m}^2} = 101,000 \text{ Pa} = 101 \text{ kPa}$$

Pressure in everyday objects such as tires and basketballs is measured in units of pounds per square inch (lb/in^2 or psi). Atmospheric pressure can be expressed in lb/in^2 by converting

the mass (10,300 kg) and the area (1 m²) of a column of the atmosphere from SI units to units of pounds and inches (Figure 10.2).

$$\frac{10,300 \text{ kg}}{1 \text{ m}^2} \times \frac{2.21 \text{ lb}}{1 \text{ kg}} \times \left(\frac{1 \text{ m}}{10^2 \text{ cm}}\right)^2 \times \left(\frac{2.54 \text{ cm}}{1 \text{ in.}}\right)^2 = 14.7 \frac{\text{lb}}{\text{in.}^2}$$

We don't feel the atmosphere pushing down on us because of an equivalent force within our body pushing outward. However, the force due to atmospheric pressure can be demonstrated by attaching a metal can to a vacuum pump. When the pump is turned on, the pressure inside the can decreases and atmospheric pressure is strong enough to crush the can (FIGURE 10.3)!

As is frequently the case with SI units, which must serve many disciplines, the pascal is an inconvenient size for most chemical measurements. Thus, the alternative pressure units *millimeter of mercury (mm Hg)*, *atmosphere (atm)*, and *bar* are more often used.

The **millimeter of mercury**, also called a *torr* after the seventeenth-century Italian scientist Evangelista Torricelli (1608–1647), is based on atmospheric pressure measurements using a mercury *barometer*. As shown in FIGURE 10.4, a barometer consists of a long, thin tube that is sealed at one end, filled with mercury, and then inverted into a dish of mercury. Some mercury runs from the tube into the dish until the downward pressure of mercury due to the pull of gravity inside the column is exactly balanced by the outside atmospheric pressure, which presses on the mercury in the dish and pushes it up the column. The height of the mercury column varies slightly from day to day depending on the altitude and weather conditions, but atmospheric pressure at sea level is defined as exactly 760 mm Hg.

Knowing the density of mercury ($1.35951 \times 10^4 \text{ kg/m}^3$ at 0 °C) and the acceleration due to gravity (9.80665 m/s^2), it's possible to calculate the pressure exerted by the column of mercury 760 mm (0.760 m) in height. Thus, 1 standard **atmosphere (atm)** of pressure (1 atm) is now defined as exactly 101,325 Pa:

$$P = (0.760 \text{ m}) \left(1.35951 \times 10^4 \frac{\text{kg}}{\text{m}^3}\right) \left(9.80665 \frac{\text{m}}{\text{s}^2}\right) = 101,325 \text{ Pa}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 101,325 \text{ Pa}$$

Although not strictly an SI unit, the **bar** is quickly gaining popularity as a unit of pressure because it is a convenient power of 10 of the SI unit pascal and because it differs from 1 atm by only about 1%:

$$1 \text{ bar} = 100,000 \text{ Pa} = 100 \text{ kPa} = 0.986923 \text{ atm}$$



◀ FIGURE 10.3

Effect of atmospheric pressure on an evacuated can. (a) A vacuum pump is connected to a can. (b) Once the vacuum is turned on pressure inside the can decreases and atmospheric pressure crushes the can.

► FIGURE 10.4

A mercury barometer. The barometer measures atmospheric pressure by determining the height of a mercury column supported in a sealed glass tube.

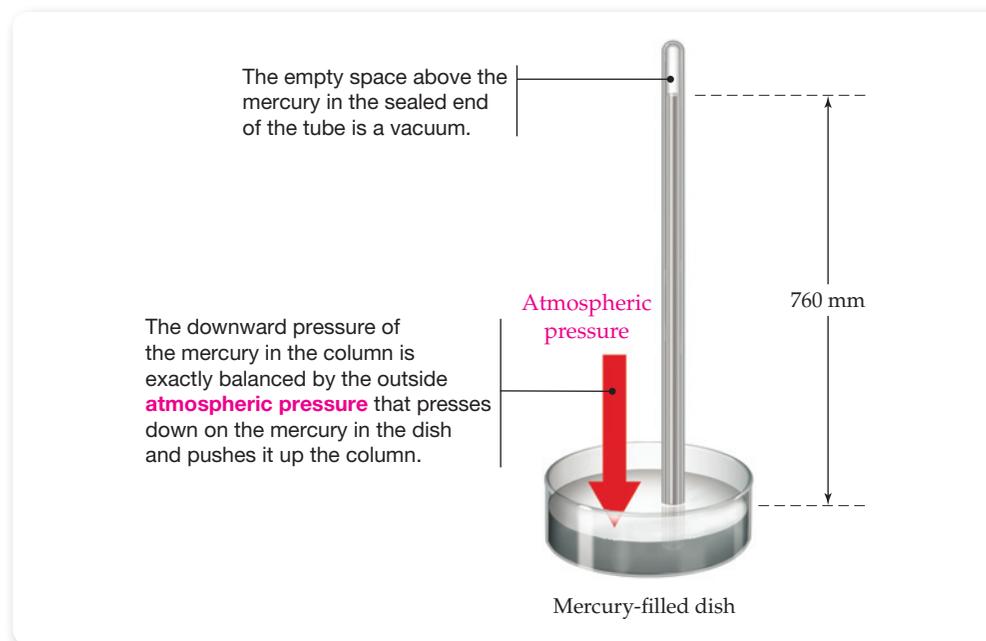


TABLE 10.2 Conversions between Common Units of Pressure

1 atm	
Pa (1 N/m ²)	*1.013 25 × 10 ⁵
kPa	*101.325
bar	*1.013 25
mm Hg	*760
lb/in. ² or psi	14.7

*The following conversions are exact and do not limit the number of significant figures in a calculation.

TABLE 10.2 summarizes different units of pressure and the conversion factor between atmospheres and the specified unit.

Gas pressure inside a container is often measured using an open-end **manometer**, a simple instrument similar in principle to the mercury barometer. As shown in **FIGURE 10.5**, an open-end manometer consists of a U-tube filled with mercury, with one end connected to a gas-filled container and the other end open to the atmosphere. The difference between the pressure of the gas in the container and the pressure of the atmosphere is equal to the difference between the heights of the mercury levels in the two arms of the U-tube. If the gas pressure

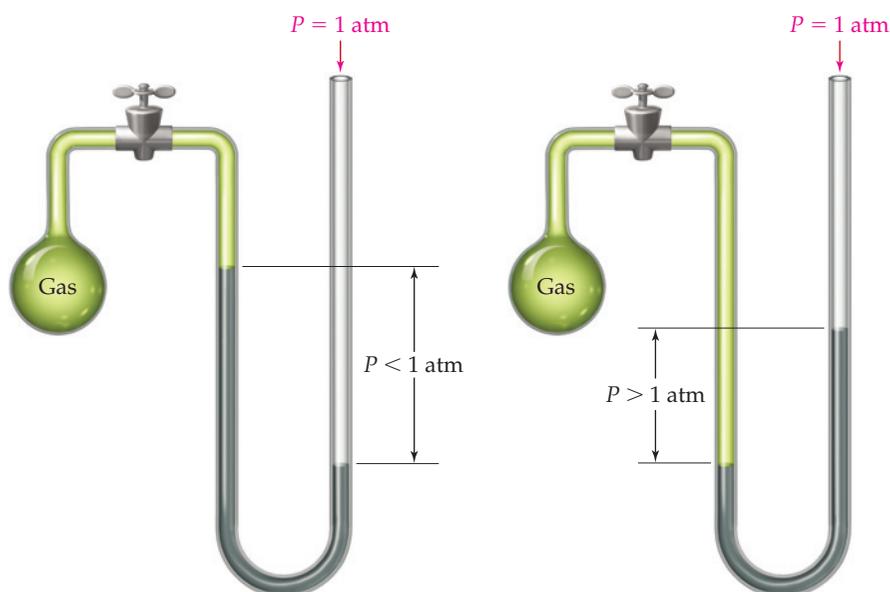
► FIGURE 10.5

Open-end manometers for measuring pressure in a gas-filled bulb.

Figure It Out

Describe the mercury level in the arm open to the bulb and the arm open to the atmosphere when the gas pressure equals 1 atm.

Answer: The mercury levels in both arms are identical.



(a) The mercury level is higher in the arm open to the bulb because the pressure in the bulb is lower than atmospheric.

(b) The mercury level is higher in the arm open to the atmosphere because the pressure in the bulb is higher than atmospheric.

inside the container is less than atmospheric, the mercury level is higher in the arm connected to the container (Figure 10.5a). If the gas pressure inside the container is greater than atmospheric, the mercury level is higher in the arm open to the atmosphere (Figure 10.5b).

WORKED EXAMPLE 10.1

Converting Between Different Units of Pressure

Typical atmospheric pressure on top of Mt. Everest, whose official altitude is 8848 m, is 265 mm Hg. Convert this value to pascals, atmospheres, and bars.

STRATEGY

Use the conversion factors 101,325 Pa/760 mm Hg, 1 atm/760 mm Hg, and 1 bar/10⁵ Pa to carry out the necessary calculations.

SOLUTION

$$(265 \text{ mm Hg}) \left(\frac{101,325 \text{ Pa}}{760 \text{ mm Hg}} \right) = 3.53 \times 10^4 \text{ Pa}$$

$$(265 \text{ mm Hg}) \left(\frac{1 \text{ atm}}{760 \text{ mm Hg}} \right) = 0.349 \text{ atm}$$

$$(3.53 \times 10^4 \text{ Pa}) \left(\frac{1 \text{ bar}}{10^5 \text{ Pa}} \right) = 0.353 \text{ bar}$$

CHECK

One atmosphere equals 760 mm Hg pressure. Since 265 mm Hg is about one-third of 760 mm Hg, the air pressure on Mt. Everest is about one-third of standard atmospheric pressure—approximately 30,000 Pa, 0.3 atm, or 0.3 bar.

▶ **PRACTICE 10.1** Barometric pressure changes are used by meteorologists to forecast short-term changes in the weather and are reported in units of inches of mercury. If the local barometric pressure is 28.48 inches of mercury, calculate the pressure in units of atm, bar, and Pa. (1 inch = 2.54 cm exactly)

▶ APPLY 10.2

- (a) If a barometer were filled with liquid water instead of mercury (Figure 10.4), what would be the height (m) of the column of water if the atmospheric pressure were 1 atm? In other words, express the pressure of 1 atm in units of meters of water instead of millimeters of mercury. (The density of mercury is 13.6 g/mL and the density of water is 1.00 g/mL.)
- (b) Why is Hg more commonly used in a barometer than water?

Conceptual WORKED EXAMPLE 10.2

Using an Open-End Manometer to Measure Gas Pressure

What is the pressure of the gas inside the apparatus shown in mm Hg if the outside pressure is 750 mm Hg?

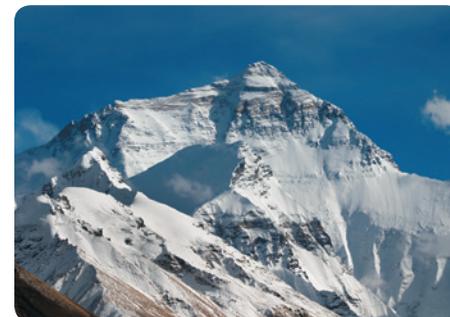
STRATEGY

The gas pressure in the bulb equals the difference between the outside pressure and the manometer reading. The pressure of the gas in the bulb is higher than atmospheric pressure because the liquid level is higher in the arm open to the atmosphere.

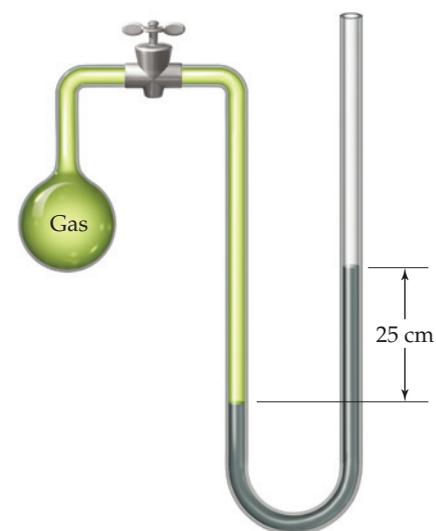
SOLUTION

$$P_{\text{gas}} = 750 \text{ mm Hg} + \left(25 \text{ cm Hg} \times \frac{10 \text{ mm}}{1 \text{ cm}} \right) = 1000 \text{ mm Hg} = 1.0 \times 10^3 \text{ mm Hg}$$

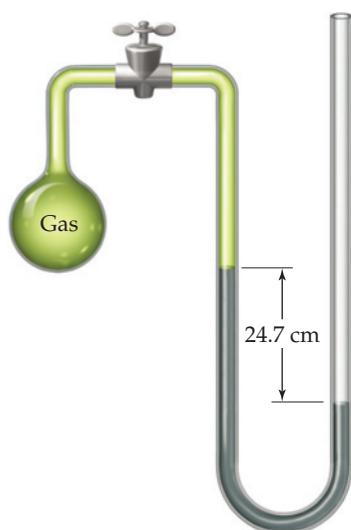
continued on next page



▲ Atmospheric pressure decreases as altitude increases. On the top of Mt. Everest, typical atmospheric pressure is 265 mm Hg.



▲ Open-end manometer for Worked Example 10.2.



▲ Open-end manometer for Problem 10.3.

Conceptual PRACTICE 10.3 What is the pressure of the gas inside the apparatus in mm Hg if the outside pressure is 0.975 atm?

Conceptual APPLY 10.4 Assume that you are using an open-end manometer filled with mineral oil rather than mercury. The level of mineral oil in the arm connected to the bulb is 237 mm higher than the level in the arm connected to the atmosphere and atmospheric pressure is 746 mm Hg.

- Draw a picture of the manometer similar to Figure 10.5.
- What is the gas pressure in the bulb in mm of Hg? (The density of mercury is 13.6 g/mL, and the density of mineral oil is 0.822 g/mL.)

10.2 ► THE GAS LAWS

Unlike solids and liquids, different gases show remarkably similar physical behavior regardless of their chemical makeup. Helium and fluorine, for example, are vastly different in their chemical properties yet are almost identical in much of their physical behavior. Numerous observations made in the late 1600s showed that the properties of any gas can be defined by four variables: pressure (P), temperature (T), volume (V), and amount, or number of moles (n). The specific relationships among these four variables are called the **gas laws**, and a gas whose behavior follows the laws exactly is called an **ideal gas**.

Boyle's Law: The Relationship between Gas Volume and Pressure

Imagine that you have a sample of gas inside a cylinder with a movable piston at one end (FIGURE 10.6). What would happen if you were to increase the pressure on the gas by pushing down on the piston? Experience probably tells you that the volume of gas in the cylinder would decrease as you increase the pressure. According to **Boyle's law**, the volume of a fixed amount of gas at a constant temperature varies inversely with its pressure. If the gas pressure is doubled, the volume is halved; if the pressure is halved, the gas volume doubles.

Boyle's law $V \propto 1/P$ or $PV = k$ at constant n and T The volume of an ideal gas varies inversely with pressure. That is, P times V is constant when n and T are kept constant. (The symbol \propto means "is proportional to," and k denotes a constant.)

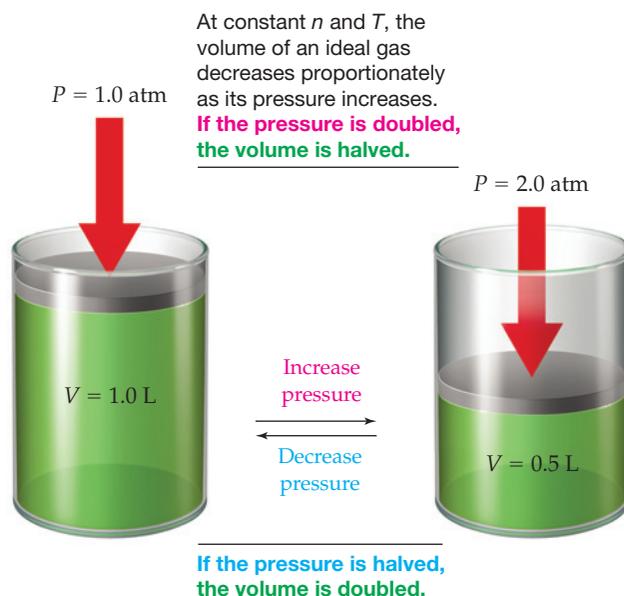
► FIGURE 10.6

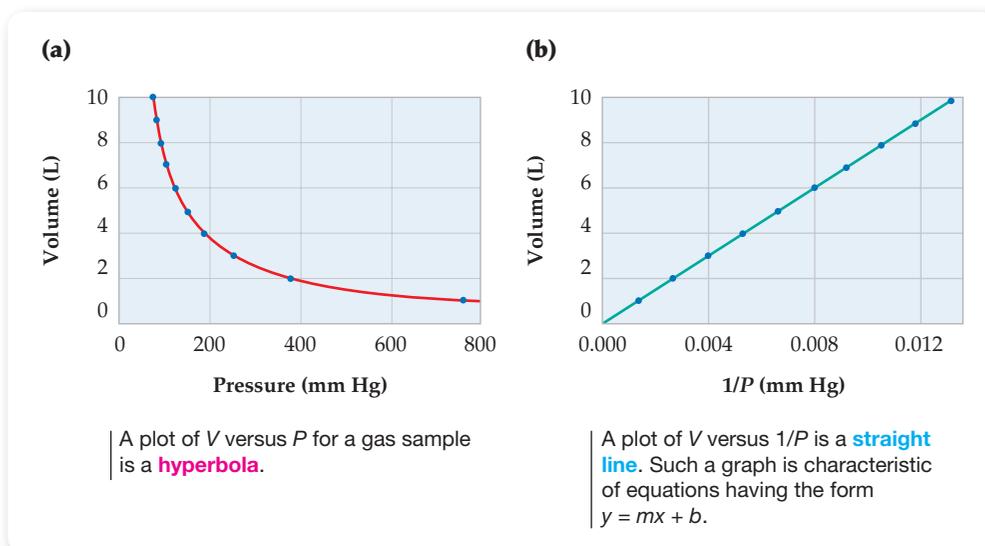
Boyle's law.

Figure It Out

If the pressure were tripled, what would happen to the volume?

Answer: The volume would be one-third of its original amount.





The validity of Boyle's law can be demonstrated by making a simple series of pressure–volume measurements on a gas sample (TABLE 10.3) and plotting them as in FIGURE 10.7. When V is plotted versus P , the result is a curve in the form of a hyperbola (Figure 10.7a). When V is plotted versus $1/P$, however, the result is a straight line (Figure 10.7b). Such graphical behavior is characteristic of mathematical equations of the form $y = mx + b$. In this case, $y = V$, $m =$ the slope of the line (the constant k in the present instance), $x = 1/P$, and $b =$ the y -intercept (a constant; 0 in the present instance). (See Appendix A.3 for a review of linear equations.)

$$V = k \left(\frac{1}{P} \right) + 0 \quad (\text{or } PV = k)$$

$$\begin{array}{ccccccc} \uparrow & \uparrow & \uparrow & & \uparrow & & \\ y & = & m & x & + & b & \end{array}$$

Charles's Law: The Relationship between Gas Volume and Temperature

Imagine again that you have a gas sample inside a cylinder with a movable piston at one end (FIGURE 10.8). What would happen if you were to raise the temperature of the sample while letting the piston move freely to keep the pressure constant? Experience tells you that the piston would move up because the volume of the gas in the cylinder would expand. According to **Charles's law**, the volume of a fixed amount of an ideal gas at a constant pressure varies directly with its absolute temperature. If the gas temperature in kelvins is doubled, the volume is doubled; if the gas temperature is halved, the volume is halved.

Charles's law $V \propto T$ or $V/T = k$ at constant n and P The volume of an ideal gas varies directly with absolute temperature. That is, V divided by T is constant when n and P are held constant.

The validity of Charles's law can be demonstrated by making a series of temperature–volume measurements on a gas sample, giving the results listed in TABLE 10.4. Like Boyle's law, Charles's law takes the mathematical form $y = mx + b$, where $y = V$, $m =$ the slope

◀ FIGURE 10.7
Boyle's law plot.

TABLE 10.3 Pressure–Volume Measurements on a Gas Sample at Constant n , T

Pressure (mm Hg)	Volume (L)
760	1
380	2
253	3
190	4
152	5
127	6
109	7
95	8
84	9
76	10

TABLE 10.4 Temperature–Volume Measurements on a Gas Sample at Constant n and P

Temperature (K)	Volume (L)
123	0.45
173	0.63
223	0.82
273	1.00
323	1.18
373	1.37

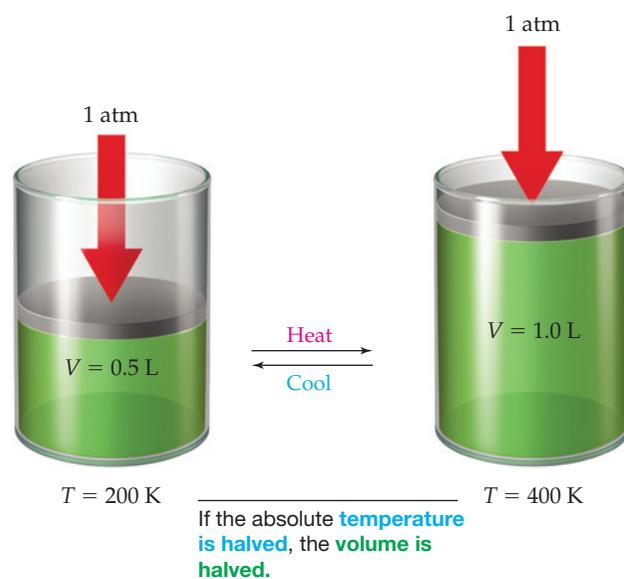
► FIGURE 10.8

Charles's law.

Figure It Out

If the absolute temperature were decreased by a factor of 3, what happens to the volume?

Answer: The volume is one-third of its initial amount.



At constant n and P , the volume of an ideal gas changes proportionately as its absolute temperature changes. If the absolute temperature doubles, the volume doubles.

of the line (the constant k in the present instance), $x = T$, and $b =$ the y -intercept (0 in the present instance). A plot of V versus T is therefore a straight line whose slope is the constant k (FIGURE 10.9).

$$V = kT + 0 \quad (\text{or } \frac{V}{T} = k)$$

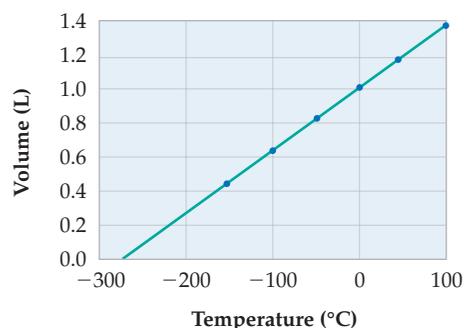
$$\begin{array}{ccccccc} \uparrow & \uparrow\uparrow & \uparrow & & & & \\ y & = & mx & + & b & & \end{array}$$

The plots of volume versus temperature in Figure 10.9 demonstrate an interesting point. When temperature is plotted on the Celsius scale, the straight line can be extrapolated to $V = 0$ at $T = -273.15$ (Figure 10.9a). But because matter can't have a negative volume, this extrapolation suggests that -273.15 must be the lowest possible temperature, or *absolute zero* on the Kelvin scale (Figure 10.9b). In fact, the approximate value of absolute zero was first determined using this simple method.

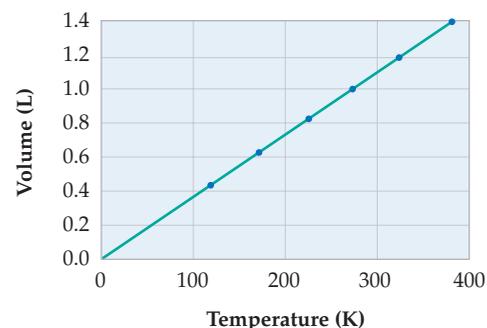
► FIGURE 10.9

Charles's law plot.

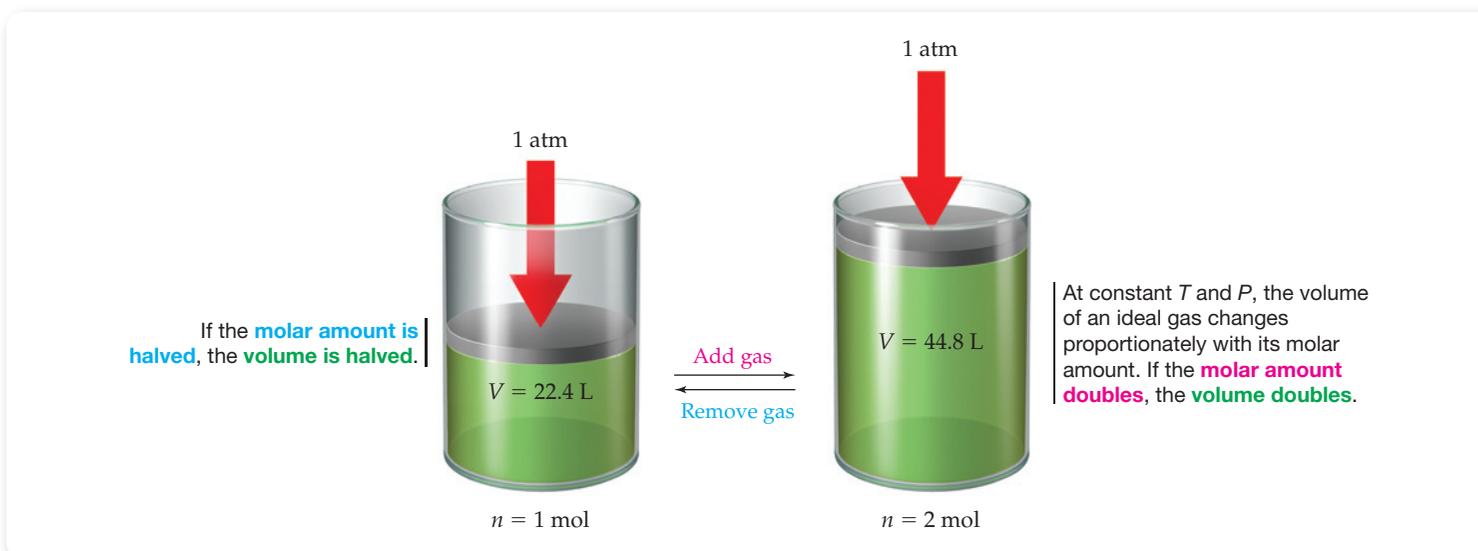
(a) Celsius scale plot



(b) Kelvin scale plot



A plot of V versus T for a gas sample is a straight line that can be extrapolated to absolute zero, $0 \text{ K} = -273.15 \text{ } ^\circ\text{C}$.



▲ **FIGURE 10.10**
Avogadro's law.

Avogadro's Law: The Relationship between Volume and Amount

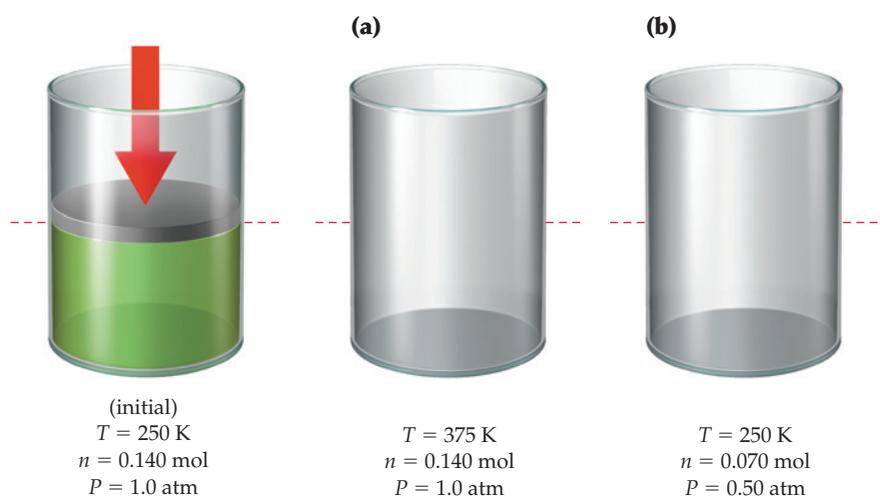
Imagine that you have two gas samples inside cylinders with movable pistons (**FIGURE 10.10**). One cylinder contains 1 mol of a gas and the other contains 2 mol of gas at the same temperature and pressure as the first. Common sense says that the gas in the second cylinder will have twice the volume of the gas in the first cylinder because there is twice as much of it. According to **Avogadro's law**, the volume of an ideal gas at a fixed pressure and temperature depends only on its molar amount. If the amount of the gas is doubled, the gas volume is doubled; if the amount is halved, the volume is halved.

Avogadro's law $V \propto n$ or $V/n = k$ at constant T and P The volume of an ideal gas varies directly with its molar amount. That is, V divided by n is constant when T and P are held constant.

Put another way, Avogadro's law also says that equal volumes of different gases at the same temperature and pressure contain the same molar amounts. A 1 L container of oxygen contains the same number of moles as a 1 L container of helium, fluorine, argon, or any other gas at the same T and P . Furthermore, 1 mol of an ideal gas occupies a volume, called the **standard molar volume**, of 22.414 L at 0°C and exactly 1 atm pressure. For comparison, the standard molar volume is nearly identical to the volume of three basketballs.

Conceptual WORKED EXAMPLE 10.3**Visual Representations of Gas Laws**

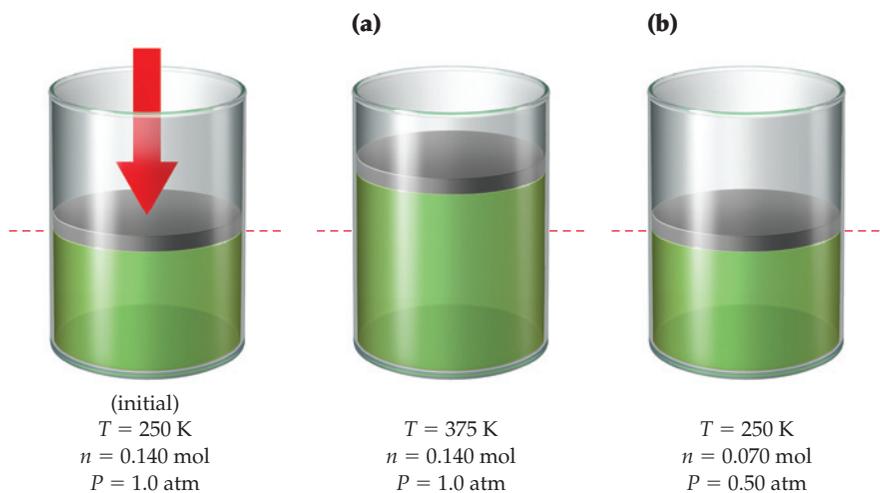
Show the approximate level of the movable piston in drawings (a) and (b) after the indicated changes have been made to the initial gas sample.

**STRATEGY**

Identify which of the variables P , n , and T have changed, and calculate the effect of each change on the volume according to the appropriate gas law.

SOLUTION

- (a) The temperature T has increased by a factor of $375/250 = 1.5$, while the molar amount n and the pressure P are unchanged. Charles's law states that $V \propto T$, therefore the volume will increase by a factor of 1.5.
- (b) The temperature T is unchanged, while both the molar amount n and the pressure P are halved. Avogadro's law states that $V \propto n$, therefore halving the molar amount will halve the volume. Similarly, since $V \propto 1/P$ (Boyle's law), halving the pressure will double the volume. The two changes cancel, so the volume is unchanged.



Conceptual PRACTICE 10.5 Show the approximate level of the movable piston in drawings (a) and (b) after the indicated changes have been made to the initial gas sample at a constant pressure of 1.0 atm.

1 atm

(initial)
 $T = 300\text{ K}$
 $n = 0.3\text{ mol}$

(a)
 $T = 400\text{ K}$
 $n = 0.225\text{ mol}$

(b)
 $T = 200\text{ K}$
 $n = 0.225\text{ mol}$

► **Conceptual APPLY 10.6** Show the approximate level of the movable piston in drawings (a) and (b) after the indicated changes have been made to the initial gas sample.

1 atm

(initial)
 $T = 300\text{ K}$
 $n = 1.0\text{ mol}$
 $P = 1.00\text{ atm}$

(a)
 $T = 600\text{ K}$
 $n = 2.0\text{ mol}$
 $P = 2.00\text{ atm}$

(b)
 $T = 400\text{ K}$
 $n = 1.5\text{ mol}$
 $P = 1.33\text{ atm}$

10.3 ► THE IDEAL GAS LAW

All three gas laws discussed in the previous section can be combined into a single statement called the **ideal gas law**, which describes how the volume of a gas is affected by changes in pressure, temperature, and amount. When the values of any three of the variables P , V , T , and n are known, the value of the fourth can be calculated using the ideal gas law. The proportionality constant R in the equation is called the **gas constant (R)** and has the same value for all gases.

Ideal gas law $V = \frac{nRT}{P}$ or $PV = nRT$

The ideal gas law can be rearranged in different ways to take the form of Boyle's law, Charles's law, or Avogadro's law.

$$\text{Boyle's law: } PV = nRT = k \quad (\text{When } n \text{ and } T \text{ are constant})$$

$$\text{Charles's law: } \frac{V}{T} = \frac{nR}{P} = k \quad (\text{When } n \text{ and } P \text{ are constant})$$

$$\text{Avogadro's law: } \frac{V}{n} = \frac{RT}{P} = k \quad (\text{When } T \text{ and } P \text{ are constant})$$

The value of the gas constant R can be calculated from knowledge of the standard molar volume of a gas. Since 1 mol of a gas occupies a volume of 22.414 L at 0 °C (273.15 K) and 1 atm pressure, the gas constant R is equal to 0.082 058 (L · atm)/(K · mol), or 8.3145 J/(K · mol) in SI units:

$$\begin{aligned} R &= \frac{P \cdot V}{n \cdot T} = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} = 0.082 \, 058 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \\ &= 8.3145 \text{ J}/(\text{K} \cdot \text{mol}) \quad (\text{When } P \text{ is in pascals and } V \text{ is in cubic meters}) \end{aligned}$$

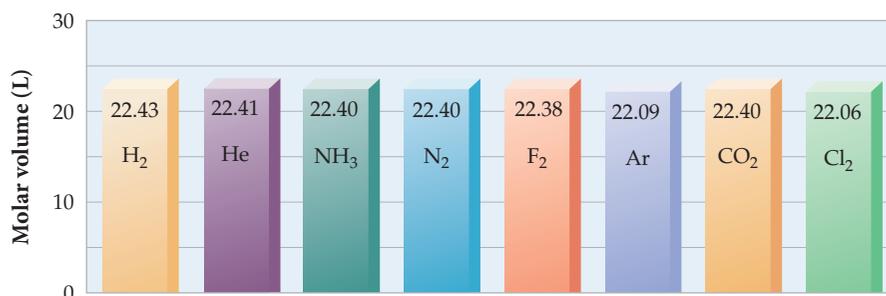
The specific conditions used in the calculation—0 °C (273.15 K) and 1 atm pressure—are said to represent **standard temperature and pressure**, abbreviated **STP**. These standard conditions are generally used when reporting measurements on gases. Note that the standard temperature for gas measurements (0 °C, or 273.15 K) is different from that usually assumed for thermodynamic measurements (25 °C, or 298.15 K; Section 9.5).

Standard temperature and pressure (STP) for gases $T = 0^\circ\text{C}$ $P = 1 \text{ atm}$

We should also point out that the standard pressure for gas measurements, still listed here and in most other books as 1 atm (101,325 Pa), has actually been redefined to be 1 bar, or 100,000 Pa. This new standard pressure is now 0.986 923 atm, making the newly defined standard molar volume 22.711 L rather than 22.414 L. Like most other books, we'll continue for the present using 1 atm as the standard pressure.

The name *ideal* gas law implies that there must be some gases whose behavior is *non-ideal*. In fact, there is no such thing as an ideal gas that obeys the equation perfectly under all circumstances. All real gases are nonideal to some extent and deviate slightly from the behavior predicted by the gas laws. As **TABLE 10.5** shows, for example, the actual molar volume of a real gas often differs slightly from the 22.414 L ideal value. Under most conditions, though, the deviations from ideal behavior are so slight as to make little difference. We'll discuss circumstances in Section 10.8 where the deviations are greater.

TABLE 10.5 Molar Volumes of Some Real Gases at 0 °C and 1 atm



WORKED EXAMPLE 10.4

Using the Ideal Gas Law to Solve for an Unknown Variable

How many moles of gas (air) are in the lungs of an average adult with a lung capacity of 3.8 L? Assume that the lungs are at 1.00 atm pressure and a normal body temperature of 37 °C.

IDENTIFY

Known	Unknown
Volume ($V = 3.8 \text{ L}$)	Moles of gas (n)
Pressure ($P = 1.00 \text{ atm}$)	
Temperature ($T = 37 \text{ }^\circ\text{C}$)	

STRATEGY

This problem asks for a value of n when V , P , and T are given. Rearrange the ideal gas law to the form $n = PV/RT$, convert the temperature from degrees Celsius to kelvin, and substitute the given values of P , V , and T into the equation.

SOLUTION

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(3.8 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(310 \text{ K})} = 0.15 \text{ mol}$$

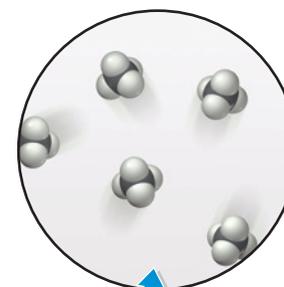
The lungs of an average adult hold 0.15 mol of air.

CHECK

A lung volume of 4 L is about one-sixth of 22.4 L, the standard molar volume of an ideal gas. Thus, the lungs have a capacity of about one-sixth mol, or 0.17 mol.

▶ **PRACTICE 10.7** How many moles of methane gas, CH_4 , are in a storage tank with a volume of $1.000 \times 10^5 \text{ L}$ at STP? How many grams?

▶ **APPLY 10.8** An aerosol spray can with a volume of 350 mL contains 3.2 g of propane gas (C_3H_8) as propellant. What is the pressure in atmospheres of gas in the can at 20 °C?



▲ How many moles of methane are in these tanks?

WORKED EXAMPLE 10.5

Using the Ideal Gas Law When Variables Change

In a typical automobile engine, the mixture of gasoline and air in a cylinder is compressed from 1.0 atm to 9.5 atm prior to ignition. If the uncompressed volume of the cylinder is 410 mL, what is the volume in milliliters when the mixture is fully compressed?

IDENTIFY

Known	Unknown
Initial pressure ($P_i = 1.0 \text{ atm}$)	Final volume (V_f)
Final pressure ($P_f = 9.5 \text{ atm}$)	
Initial volume ($V_i = 410 \text{ mL}$)	

STRATEGY

Rearrange the ideal gas law so that variables that have changing values are on one side of the equation and constants are on the other side of the equation.

SOLUTION

In the ideal gas law, pressure and volume change and therefore remain on the left side of the equation, while n , R , and T remain constant.

$$\underbrace{PV}_{\text{Variables that change}} = \underbrace{nRT}_{\text{Constants}} = k$$

continued on next page

Because pressure times volume is a constant (Boyle's law), the equation $P_i V_i = P_f V_f$ can be used to solve for the final volume:

$$V_f = \frac{P_i V_i}{P_f} = \frac{(1.0 \text{ atm})(410 \text{ mL})}{(9.5 \text{ atm})} = 43 \text{ mL}$$

CHECK

Because the pressure in the cylinder increases about 10-fold, the volume must decrease about 10-fold according to Boyle's law, from approximately 400 mL to 40 mL.

► **PRACTICE 10.9** What final temperature ($^{\circ}\text{C}$) is required for the pressure inside an automobile tire to increase from 2.15 atm at 0°C to 2.37 atm, assuming the volume remains constant?

► **APPLY 10.10** A weather balloon has a volume of 45.0 L when released under conditions of 745 mm Hg and 25.0°C . What is the volume of the balloon at an altitude of 10,000 m where the pressure is 178 mm Hg and the temperature is 225 K?



▲ Automobile air bags are inflated with N_2 gas produced by decomposition of sodium azide.

10.4 ► STOICHIOMETRIC RELATIONSHIPS WITH GASES

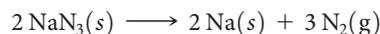
Many chemical reactions, including some of the most important processes in the chemical industry, involve gases. Approximately 130 million metric tons of ammonia, for instance, is manufactured each year worldwide by the reaction of hydrogen with nitrogen according to the equation $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \longrightarrow 2 \text{NH}_3(\text{g})$. Thus, it's necessary to be able to calculate amounts of gaseous reactants just as it's necessary to calculate amounts of solids, liquids, and solutions.

Most gas calculations are just applications of the ideal gas law in which three of the variables P , V , T , and n are known and the fourth variable must be calculated. The reaction used in the deployment of automobile air bags, for instance, is the high-temperature decomposition of sodium azide, NaN_3 , to produce N_2 gas. (The sodium is then removed by a subsequent reaction.) Worked Example 10.6 shows how to calculate the volume of a gaseous product given the amount reactant.

WORKED EXAMPLE 10.6

Calculating the Volume of Gas Produced in a Chemical Reaction

How many liters of N_2 gas at 1.15 atm and 30°C are produced by decomposition of 45.0 g of NaN_3 ?

**IDENTIFY**

Known	Unknown
Pressure ($P = 1.15 \text{ atm}$)	Volume of N_2 (V)
Temperature ($T = 30^{\circ}\text{C}$)	
Mass of NaN_3 (45.0 g)	

STRATEGY

Use stoichiometric relationships to find the number of moles of N_2 produced from 45.0 g of NaN_3 and then use the ideal gas law to find the volume of N_2 .

SOLUTION

To find n , the number of moles of N_2 gas produced, we first need to find how many moles of NaN_3 are in 45.0 g:

$$\begin{aligned} \text{Molar mass of } \text{NaN}_3 &= 65.0 \text{ g/mol} \\ \text{Moles of } \text{NaN}_3 &= (45.0 \text{ g } \text{NaN}_3) \left(\frac{1 \text{ mol } \text{NaN}_3}{65.0 \text{ g } \text{NaN}_3} \right) = 0.692 \text{ mol } \text{NaN}_3 \end{aligned}$$

Next, find how many moles of N_2 are produced in the decomposition reaction. According to the balanced equation, 2 mol of NaN_3 yields 3 mol of N_2 , so 0.692 mol of NaN_3 yields 1.04 mol of N_2 :

$$\text{Moles of } N_2 = (0.692 \text{ mol } NaN_3) \left(\frac{3 \text{ mol } N_2}{2 \text{ mol } NaN_3} \right) = 1.04 \text{ mol } N_2$$

Finally, use the ideal gas law to calculate the volume of N_2 . Remember to use the Kelvin temperature (303 K) rather than the Celsius temperature (30 °C) in the calculation.

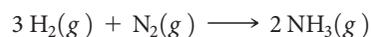
$$V = \frac{nRT}{P} = \frac{(1.04 \text{ mol } N_2) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (303 \text{ K})}{1.15 \text{ atm}} = 22.5 \text{ L}$$

- ▶ **PRACTICE 10.11** Carbonate-bearing rocks like limestone ($CaCO_3$) react with dilute acids such as HCl to produce carbon dioxide, according to the equation



How many grams of CO_2 are formed by complete reaction of 33.7 g of limestone? What is the volume in liters of this CO_2 at STP?

- ▶ **APPLY 10.12** Approximately 83% of all ammonia produced is used as fertilizer for crops. Ammonia is synthesized from hydrogen and nitrogen gas according to the equation

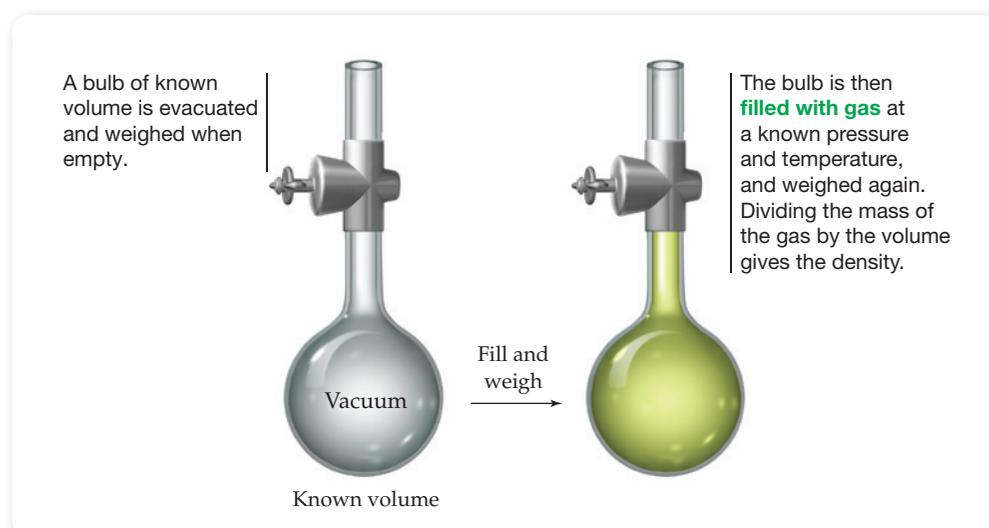


What volume of hydrogen and nitrogen gas is needed to synthesize 500.0 L of ammonia at STP?



▲ Carbonate-bearing rocks like limestone ($CaCO_3$) react with dilute acids such as HCl to produce bubbles of carbon dioxide.

Other applications of the ideal gas law make it possible to calculate such properties as density and molar mass. Densities are calculated by weighing a known volume of a gas at a known temperature and pressure, as shown in **FIGURE 10.11**. Gas density changes dramatically with temperature and pressure so values for these variables must be specified. Gas density values are commonly reported at STP for consistency. The ideal gas law can be used to convert a density measured at any temperature and pressure to its value at STP. For example, if a sample of ammonia gas weighs 0.672 g and occupies a 1.000 L bulb at 25 °C and 733.4 mm Hg pressure, the density at STP can be calculated as follows. The density of any substance is mass divided by volume. For the ammonia sample, the mass is 0.672 g but the volume of the gas is given under nonstandard conditions and must first be converted to STP. Because the amount



◀ **FIGURE 10.11** Determining the density of an unknown gas.

of sample n is constant, we can set the quantity PV/RT measured under nonstandard conditions equal to PV/RT at STP and then solve for V at STP.

$$n = \left(\frac{PV}{RT}\right)_{\text{measured}} = \left(\frac{PV}{RT}\right)_{\text{STP}} \quad \text{or} \quad V_{\text{STP}} = \left(\frac{PV}{RT}\right)_{\text{measured}} \left(\frac{RT}{P}\right)_{\text{STP}}$$

$$V_{\text{STP}} = \left(\frac{733.4 \text{ mm Hg} \times 1.000 \text{ L}}{298 \text{ K}}\right) \left(\frac{273 \text{ K}}{760 \text{ mm Hg}}\right) = 0.884 \text{ L}$$

The amount of gas in the 1.000 L bulb under the measured nonstandard conditions would have a volume of only 0.884 L at STP. Dividing the given mass by this volume gives the density of ammonia at STP:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{0.672 \text{ g}}{0.884 \text{ L}} = 0.760 \text{ g/L}$$

An equation relating gas density to molar mass can be found by rearranging the ideal gas law. Since density equals mass divided by volume, a term for mass must be added to the ideal gas law. Multiplying both sides of the equation by molar mass (M) incorporates mass into the equation because moles multiplied by molar mass equals mass as shown.

$$PV(M) = \underbrace{n(M)RT}_{\text{mass } (m)}$$

The equation can be rearranged to solve for density, which is defined as mass divided by volume:

$$PV(M) = mRT$$

$$\frac{PV(M)}{V} = \frac{mRT}{V} \quad \text{dividing both sides of the equation by } (V) \text{ yields:}$$

$$PM = \left(\frac{m}{V}\right)RT$$

$$\frac{PM}{RT} = \left(\frac{m}{V}\right) \quad \text{dividing both sides of the equation by } (RT) \text{ yields:}$$

$$\text{Gas density } d = \frac{m}{V} = \frac{PM}{RT}$$

If the density of an unknown gas is measured under conditions of known pressure and temperature, the molar mass of the gas can be calculated. Worked Example 10.7 shows how to identify an unknown gas from a density measurement.

WORKED EXAMPLE 10.7

Identifying an Unknown by Using Gas Density to Find Molar Mass

An unknown gas found bubbling up in a swamp is collected, placed in a glass bulb, and found to have a density of 0.714 g/L at STP. What is the molar mass of the gas? What is a possible identity of the gas?

IDENTIFY

Known	Unknown
Density ($d = 0.714 \text{ g/L}$)	Molar Mass (M)
Temperature ($T = 0^\circ\text{C}$)	
Pressure ($P = 1 \text{ atm}$)	

STRATEGY

Since d , T , and P are known, the equation for gas density can be rearranged to solve for molar mass. Once molar mass is known the identity of the gas can be suggested.

SOLUTION

Remember to use the Kelvin temperature (273 K) rather than the Celsius temperature (0°C) in the gas density equation.

$$d = \frac{P(M)}{RT} \quad \text{or} \quad M = \frac{dRT}{P}$$

$$M = \frac{(0.714 \text{ g/L}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (273 \text{ K})}{(1 \text{ atm})} = 16.0 \text{ g/mol}$$

Thus, the molar mass of the unknown gas (actually methane, CH_4) is 16.0 g/mol.

► **PRACTICE 10.13** A foul-smelling gas produced by the reaction of HCl with Na_2S was collected, and a 1.00 L sample was found to have a mass of 1.52 g at STP. What is the molar mass of the gas? What is its likely formula and name?

► **APPLY 10.14** The image shows carbon dioxide gas generated by adding dry ice, $\text{CO}_2(\text{s})$, to water. The carbon dioxide flows downward because it is denser than air.



- (a) What is the density in g/L of carbon dioxide at 1 atm and 25°C ?
 (b) Why is carbon dioxide denser than air?

10.5 ► MIXTURES OF GASES: PARTIAL PRESSURE AND DALTON'S LAW

Just as the gas laws apply to all pure gases, regardless of chemical identity, they also apply to *mixtures* of gases, such as air. The pressure, volume, temperature, and amount of a gas mixture are all related by the ideal gas law.

What is responsible for the pressure in a gas mixture? Because the pressure of a pure gas at constant temperature and volume is proportional to its amount ($P = nRT/V$), the pressure contribution from each individual gas in a mixture is also proportional to its amount in the mixture. In other words, the total pressure exerted by a mixture of gases in a container at constant V and T is equal to the sum of the pressures of each individual gas in the container, a statement known as **Dalton's law of partial pressures**.

Dalton's law of partial pressures $P_{\text{total}} = P_1 + P_2 + P_3 + \dots$ at constant V and T , where P_1, P_2, \dots refer to the pressures each individual gas would have if it were alone.

The individual pressure contributions of the various gases in the mixture, P_1, P_2 , and so forth, are called partial pressures and refer to the pressure each individual gas would exert if it were alone in the container. That is,

$$P_1 = n_1 \left(\frac{RT}{V} \right) \quad P_2 = n_2 \left(\frac{RT}{V} \right) \quad P_3 = n_3 \left(\frac{RT}{V} \right) \quad \dots \quad \text{and so forth}$$

But because all the gases in the mixture have the same temperature and volume, we can re-write Dalton's law to indicate that the total pressure depends only on the total molar amount of gas present and not on the chemical identities of the individual gases:

$$P_{\text{total}} = (n_1 + n_2 + n_3 + \dots) \left(\frac{RT}{V} \right)$$

The concentration of any individual component in a gas mixture is usually expressed as a **mole fraction** (X), which is defined simply as the number of moles of the component divided by the total number of moles in the mixture:

$$\text{Mole fraction } (X) = \frac{\text{Moles of component}}{\text{Total moles in mixture}}$$

The mole fraction of component 1, for example, is

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots} = \frac{n_1}{n_{\text{total}}}$$

But because $n = PV/RT$, we can also write

$$X_1 = \frac{P_1 \left(\frac{V}{RT} \right)}{P_{\text{total}} \left(\frac{V}{RT} \right)} = \frac{P_1}{P_{\text{total}}}$$

which can be rearranged to solve for P_1 .

The partial pressure of component 1 in a gas mixture is:

$$\text{Partial pressure } P_1 = X_1 \cdot P_{\text{total}}$$

This equation says that the partial pressure exerted by each component in a gas mixture is equal to the mole fraction of that component times the total pressure. In air, for example, the mole fractions of N_2 , O_2 , Ar, and CO_2 are 0.7808, 0.2095, 0.0093, and 0.00039, respectively (Table 10.1), and the total pressure of the air is the sum of the individual partial pressures:

$$P_{\text{air}} = P_{\text{N}_2} + P_{\text{O}_2} + P_{\text{Ar}} + P_{\text{CO}_2} + \dots$$

Thus, at a total air pressure of 1 atm (760 mm Hg), the partial pressures of the individual components are

$$\begin{aligned} P_{\text{N}_2} &= 0.7808 \times 1.00 \text{ atm} &= 0.7808 \text{ atm} \\ P_{\text{O}_2} &= 0.2095 \times 1.00 \text{ atm} &= 0.2095 \text{ atm} \\ P_{\text{Ar}} &= 0.0093 \times 1.00 \text{ atm} &= 0.0093 \text{ atm} \\ P_{\text{CO}_2} &= 0.0004 \times 1.00 \text{ atm} &= 0.0004 \text{ atm} \\ P_{\text{air}} &= P_{\text{N}_2} + P_{\text{O}_2} + P_{\text{Ar}} + P_{\text{CO}_2} &= 1.0000 \text{ atm} \end{aligned}$$

There are numerous practical applications of Dalton's law, ranging from the use of anesthetic agents in hospital operating rooms, where partial pressures of both oxygen and anesthetic in the patient's lungs must be constantly monitored, to the composition of diving gases used for underwater exploration. Worked Example 10.8 gives an illustration.

WORKED EXAMPLE 10.8

Calculating Partial Pressure

A 1.50 L steel container at 90 °C contains 5.50 g of H₂, 7.31 g of N₂, and 2.42 g of NH₃. What is the partial pressure of each gas and the total pressure in the container?

IDENTIFY

Known	Unknown
Mass of each gas	Partial pressure (P_{H_2} , P_{N_2} , P_{NH_3})
Volume ($V = 1.50 \text{ L}$)	Total pressure (P_{tot})
Temperature ($T = 90 \text{ }^\circ\text{C}$)	

STRATEGY

Convert the mass of each gas into moles using molar mass. Find the partial pressure of each gas using the general formula $P_1 = n_1(RT/V)$. Find the total pressure of the gas mixture by summing the partial pressure of each gas.

SOLUTION

Moles of each gas:

$$5.50 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0 \text{ g H}_2} = 2.75 \text{ mol H}_2 \quad 7.31 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} = 0.261 \text{ mol N}_2$$

$$2.42 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} = 0.142 \text{ mol NH}_3$$

Partial pressure of each gas:

$$P_{\text{H}_2} = \frac{(2.75 \text{ mol H}_2) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (363 \text{ K})}{1.50 \text{ L}} = 54.6 \text{ atm}$$

$$P_{\text{N}_2} = \frac{(0.261 \text{ mol N}_2) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (363 \text{ K})}{1.50 \text{ L}} = 5.18 \text{ atm}$$

$$P_{\text{NH}_3} = \frac{(0.142 \text{ mol NH}_3) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (363 \text{ K})}{1.50 \text{ L}} = 2.81 \text{ atm}$$

The total pressure is the sum of the partial pressure of each gas:

$$P_{\text{tot}} = P_{\text{H}_2} + P_{\text{N}_2} + P_{\text{NH}_3} = 54.6 \text{ atm} + 5.18 \text{ atm} + 2.81 \text{ atm} = 62.6 \text{ atm}$$

PRACTICE 10.15 Nitrox is a gas mixture used by scuba divers to prevent nitrogen narcosis, a loss of mental and physical function, caused by increased levels of dissolved nitrogen in the blood. The mole fraction of O₂ is 0.36, and the mole fraction of N₂ is 0.64 in a 10.0 L tank with a pressure of 50 atm at 25 °C.

- Calculate the partial pressure of O₂ and N₂.
- Calculate the number of moles of O₂ and N₂.

APPLY 10.16 At an underwater depth of 250 ft, the pressure is 8.38 atm. What should the mole fraction of oxygen in the diving gas be for the partial pressure of oxygen in the gas to be 0.21 atm, the same as in air at 1.0 atm?



▲ The partial pressure of oxygen in the scuba tanks must be the same underwater as in air at atmospheric pressure.

10.6 ► THE KINETIC–MOLECULAR THEORY OF GASES

Thus far, we've concentrated on just describing the behavior of gases rather than on understanding the reasons for that behavior. Actually, the reasons are straightforward and were explained more than a century ago using a model called the **kinetic–molecular theory**. The kinetic–molecular theory is based on the following assumptions:

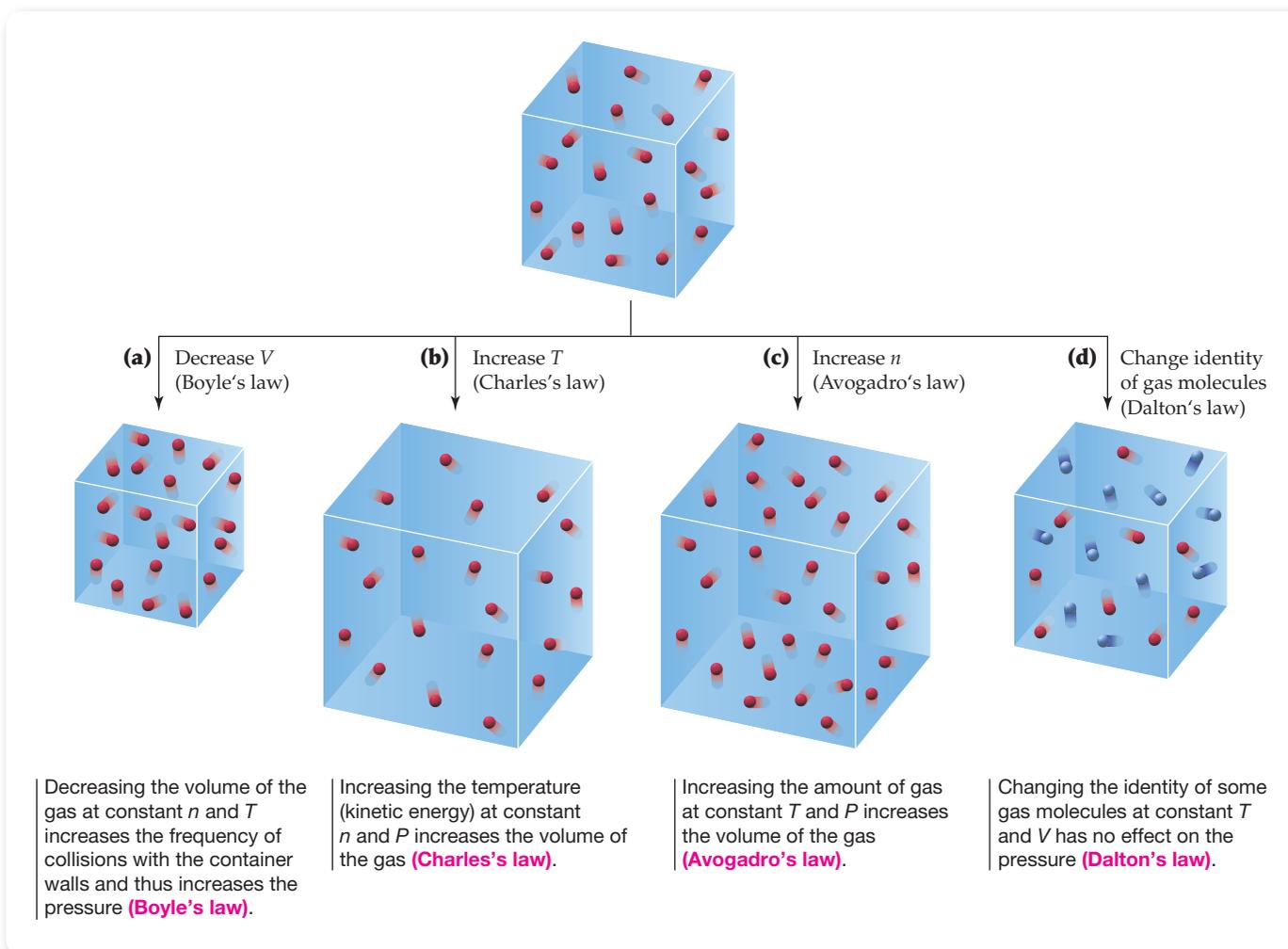
1. A gas consists of tiny particles, either atoms or molecules, moving about at random.
2. The volume of the particles themselves is negligible compared with the total volume of the gas. Most of the volume of a gas is empty space.
3. The gas particles act independently of one another; there are no attractive or repulsive forces between particles.
4. Collisions of the gas particles, either with other particles or with the walls of a container, are elastic. That is, they bounce off the walls at the same speed and therefore the same energy they hit with, so that the total kinetic energy of the gas particles is constant at constant T .
5. The average kinetic energy of the gas particles is proportional to the Kelvin temperature of the sample.

Beginning with these assumptions, it's possible not only to understand the behavior of gases but also to derive quantitatively the ideal gas law (though we'll not do so here). For example, look at how the individual gas laws follow from the five postulates of kinetic–molecular theory:

- **Boyle's law ($P \propto 1/V$):** Gas pressure is a measure of the number and forcefulness of collisions between gas particles and the walls of their container. The smaller the volume at constant n and T , the smaller the distance between the particles and the greater the frequency of collisions. Thus, pressure increases as volume decreases (**FIGURE 10.12a**).
- **Charles's law ($V \propto T$):** Temperature is a measure of the average kinetic energy of the gas particles. The higher the temperature at constant n and P , the faster the gas particles move. A greater volume is required to avoid increasing the number of collisions with the walls of the container in order to maintain constant pressure. Thus, volume increases as temperature increases (**FIGURE 10.12b**).
- **Avogadro's law ($V \propto n$):** The more particles there are in a gas sample, the more volume the particles need at constant P and T to avoid increasing the number collisions with the walls of the container in order to maintain constant pressure. Thus, volume increases as amount increases (**FIGURE 10.12c**).
- **Dalton's law ($P_{total} = P_1 + P_2 + \dots$):** Because gas particles are far apart and act independently of one another, the chemical identity of the particles is irrelevant. Total pressure of a fixed volume of gas depends only on the temperature T and the total number of moles of gas n . The pressure exerted by a specific kind of particle thus depends on the mole fraction of that kind of particle in the mixture, not on the identity of the particle (**FIGURE 10.12d**).

One of the more important conclusions from kinetic–molecular theory comes from assumption 5—the relationship between temperature and E_K , the kinetic energy of molecular motion. Although we won't do so in this book, it can be shown that the total kinetic energy of a mole of gas particles equals $3RT/2$ and that the average kinetic energy per particle is thus $3RT/2N_A$, where N_A is Avogadro's number. Knowing this relationship makes it possible to calculate the average speed u of a gas particle at a given temperature. To take a helium atom at room temperature (298 K), for instance, we can write

$$E_K = \frac{3RT}{2N_A} = \frac{1}{2}mu^2$$

▲ **FIGURE 10.12**

A kinetic-molecular view of the gas laws.

which can be rearranged to give

Average speed of a gas particle (u).

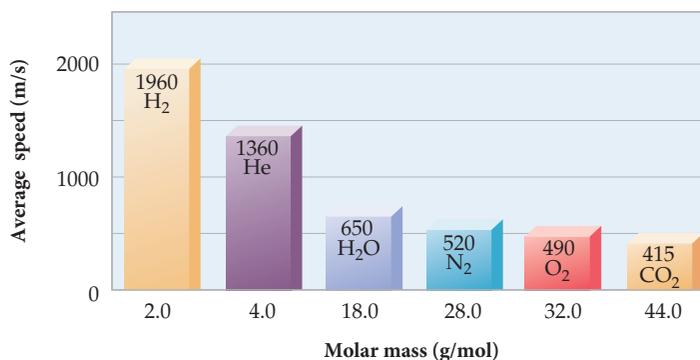
$$u^2 = \frac{3RT}{mN_A}$$

$$\text{or } u = \sqrt{\frac{3RT}{mN_A}} = \sqrt{\frac{3RT}{M}} \quad \text{where } M \text{ is the molar mass}$$

Substituting appropriate values for R [$8.314 \text{ J}/(\text{K} \cdot \text{mol})$] and for M , the molar mass of helium ($4.00 \times 10^{-3} \text{ kg/mol}$), we have

$$u = \sqrt{\frac{(3) \left(8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) (298 \text{ K})}{4.00 \times 10^{-3} \frac{\text{kg}}{\text{mol}}}} = \sqrt{1.86 \times 10^6 \frac{\text{J}}{\text{kg}}}$$

$$= \sqrt{1.86 \times 10^6 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \text{ kg}}} = 1.36 \times 10^3 \text{ m/s}$$

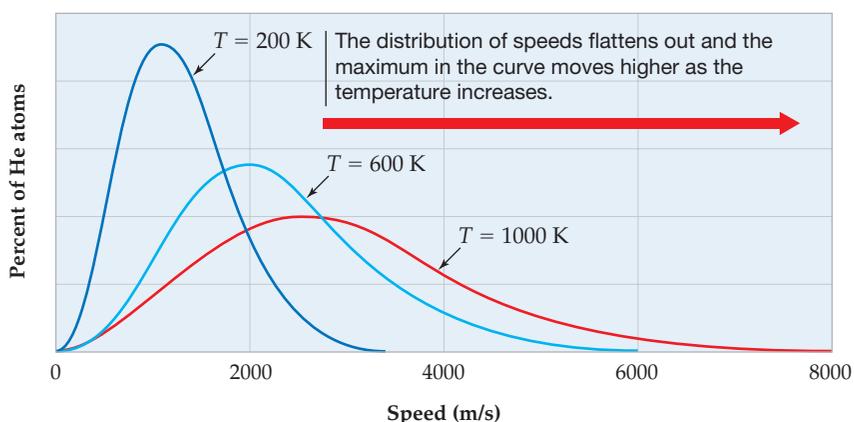
TABLE 10.6 Average Speeds (m/s) of Some Gas Molecules at 25 °C**FIGURE 10.13**

The distribution of speeds for helium atoms at different temperatures.

Figure It Out

What happens to the average speed of gas particles as temperature increases? What happens to the shape of the curve for the distribution of speeds of gas particles as the temperature increases?

Answer: The average speed of gas particles increases as temperature increases. The shape of the curve becomes more broad meaning there is a wider range of speeds at higher temperature.



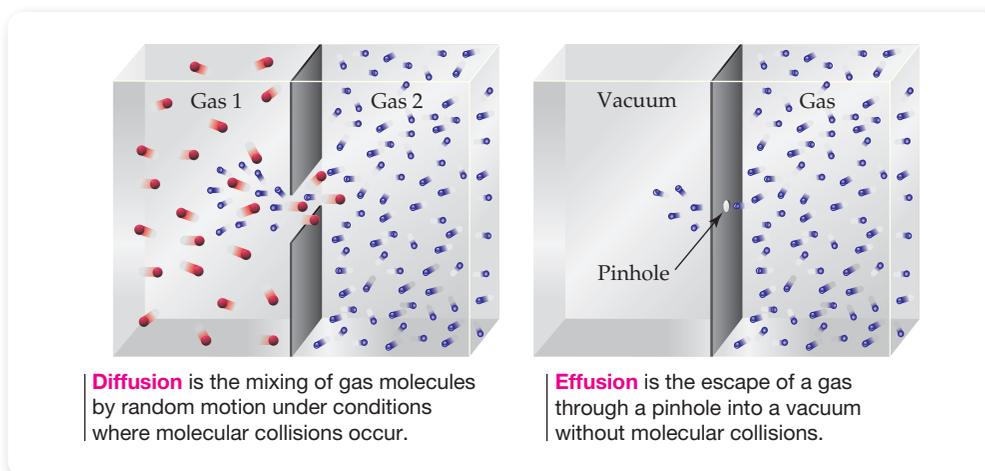
Thus, the average speed of a helium atom at room temperature is more than 1.3 km/s, or about 3000 mi/h! Average speeds of some other molecules at 25 °C are given in **TABLE 10.6**. The heavier the molecule, the slower the average speed.

Just because the average speed of helium atoms at 298 K is 1.36 km/s doesn't mean that all helium atoms are moving at that speed or that a given atom will travel from Maine to California in one hour. As shown in **FIGURE 10.13**, there is a broad distribution of speeds among particles in a gas, a distribution that flattens out and moves higher as the temperature increases. This means that there is a greater range in molecular speed at higher temperatures. Furthermore, an individual gas particle is likely to travel only a very short distance before it collides with another particle and bounces off in a different direction. Thus, the actual path followed by a gas particle is a random zigzag.

For helium at room temperature and 1 atm pressure, the average distance between collisions, called the *mean free path*, is only about 2×10^{-7} m, or 1000 atomic diameters, and there are approximately 10^{10} collisions per second. For a larger O₂ molecule, the mean free path is about 6×10^{-8} m.

10.7 ► GAS DIFFUSION AND EFFUSION: GRAHAM'S LAW

The constant motion and high speeds of gas particles have some important practical consequences. One such consequence is that gases mix rapidly when they come in contact. Take the stopper off a bottle of perfume, for instance, and the odor will spread rapidly through a room as perfume molecules mix with the molecules in the air. This mixing of different molecules by random molecular motion with frequent collisions is called **diffusion**. A similar process in which gas molecules escape without collisions through a tiny hole into a vacuum is called **effusion** (**FIGURE 10.14**).



◀ **FIGURE 10.14**
Diffusion and effusion of gases.

According to **Graham's law**, formulated in the mid-1800s by the Scottish chemist Thomas Graham (1805–1869), the rate of effusion of a gas is inversely proportional to the square root of its mass. In other words, the lighter the molecule, the more rapidly it effuses.

Graham's law Rate of effusion $\propto \frac{1}{\sqrt{m}}$

The rate of effusion of a gas is inversely proportional to the square root of its mass, m .

In comparing two gases at the same temperature and pressure, we can set up an equation showing that the ratio of the effusion rates of the two gases is inversely proportional to the ratio of the square roots of their masses:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}} = \sqrt{\frac{m_2}{m_1}}$$

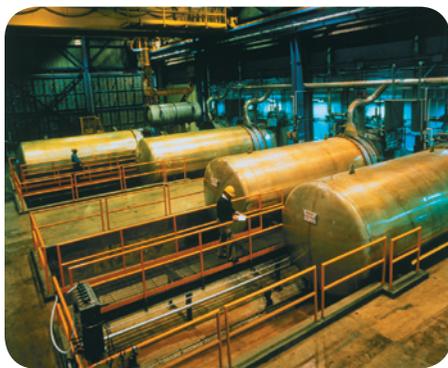
The inverse relationship between the rate of effusion and the square root of the mass follows directly from the connection between temperature and kinetic energy described in the previous section. Because temperature is a measure of average kinetic energy and is independent of the gas's chemical identity, different gases at the same temperature have the same average kinetic energy:

$$\begin{aligned} \text{Since } \frac{1}{2}mu^2 &= \frac{3RT}{2N_A} \text{ for any gas} \\ \text{then } \left(\frac{1}{2}mu^2\right)_{\text{gas 1}} &= \left(\frac{1}{2}mu^2\right)_{\text{gas 2}} \text{ at the same } T \end{aligned}$$

Canceling the factor of 1/2 from both sides and rearranging, we find that the average speeds of the molecules in two gases vary as the inverse ratio of the square roots of their masses:

$$\begin{aligned} \text{Since } \left(\frac{1}{2}mu^2\right)_{\text{gas 1}} &= \left(\frac{1}{2}mu^2\right)_{\text{gas 2}} \\ \text{then } (mu^2)_{\text{gas 1}} &= (mu^2)_{\text{gas 2}} \text{ and } \frac{(u_{\text{gas 1}})^2}{(u_{\text{gas 2}})^2} = \frac{m_2}{m_1} \\ \text{so } \frac{u_{\text{gas 1}}}{u_{\text{gas 2}}} &= \frac{\sqrt{m_2}}{\sqrt{m_1}} = \sqrt{\frac{m_2}{m_1}} \end{aligned}$$

If, as seems reasonable, the rate of effusion of a gas is proportional to the average speed of the gas molecules, then Graham's law results.



▲ Much of the uranium-235 used as a fuel in nuclear reactors is obtained by gas diffusion of UF_6 in cylinders like these.

Diffusion is more complex than effusion because of the molecular collisions that occur, but Graham's law usually works as a good approximation. One of the most important practical consequences is that mixtures of gases can be separated into their pure components by taking advantage of the different rates of diffusion of the components. For example, naturally occurring uranium is a mixture of isotopes, primarily ^{235}U (0.72%) and ^{238}U (99.28%). In uranium enrichment plants that purify the fissionable uranium-235 used for fuel in nuclear reactors, elemental uranium is converted into volatile uranium hexafluoride (bp 56°C), and the UF_6 gas is allowed to diffuse from one chamber to another through a permeable membrane. The $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ molecules diffuse through the membrane at slightly different rates according to the square root of the ratio of their masses:

$$\begin{aligned} \text{For } ^{235}\text{UF}_6, m &= 349.03 \\ \text{For } ^{238}\text{UF}_6, m &= 352.04 \\ \text{so } \frac{\text{Rate of } ^{235}\text{UF}_6 \text{ diffusion}}{\text{Rate of } ^{238}\text{UF}_6 \text{ diffusion}} &= \sqrt{\frac{352.04}{349.03}} = 1.0043 \end{aligned}$$

The UF_6 gas that passes through the membrane is thus very slightly enriched in the lighter, faster-moving isotope. After repeating the process many thousands of times, a separation of isotopes can be achieved. Approximately 30% of the Western world's nuclear fuel supply—some 5000 tons per year—is produced by this gas diffusion method, although the percentage is dropping because better methods are now available.

WORKED EXAMPLE 10.9

Using Graham's Law to Calculate Diffusion Rates

Assume that you have a sample of hydrogen gas containing H_2 , HD, and D_2 that you want to separate into pure components. What are the relative rates of diffusion of the three molecules according to Graham's law? ($\text{H} = {}^1\text{H}$) and ($\text{D} = {}^2\text{H}$).

STRATEGY

First, find the masses of the three molecules: for H_2 , $m = 2.016$; for HD, $m = 3.022$; for D_2 , $m = 4.028$. Then apply Graham's law to different pairs of gas molecules.

SOLUTION

The relative rate of diffusion of each gas relative to the heaviest gas, D_2 , can be calculated as shown.

Comparing HD with D_2 , we have

$$\frac{\text{Rate of HD diffusion}}{\text{Rate of } \text{D}_2 \text{ diffusion}} = \sqrt{\frac{\text{mass of } \text{D}_2}{\text{mass of HD}}} = \sqrt{\frac{4.028}{3.022}} = 1.155$$

Comparing H_2 with D_2 , we have

$$\frac{\text{Rate of } \text{H}_2 \text{ diffusion}}{\text{Rate of } \text{D}_2 \text{ diffusion}} = \sqrt{\frac{\text{mass of } \text{D}_2}{\text{mass of } \text{H}_2}} = \sqrt{\frac{4.028}{2.016}} = 1.414$$

Thus, the relative rates of diffusion are H_2 (1.414) > HD (1.155) > D_2 (1.000).

CHECK

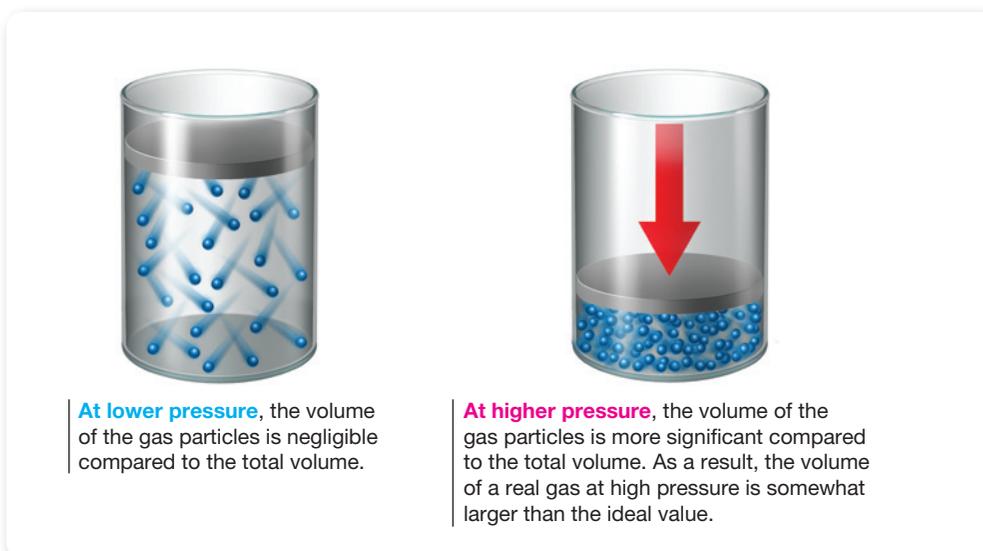
The answer makes sense because the lower the mass of the gas, the higher the relative diffusion rate.

▶ **PRACTICE 10.17** Which gas in each of the following pairs diffuses more rapidly, and what are the relative rates of diffusion?

(a) Kr and O_2

(b) N_2 and acetylene (C_2H_2)

▶ **APPLY 10.18** An unknown gas is found to diffuse through a porous membrane 1.414 times faster than SO_2 . What is the molecular weight of the gas? What is the likely identity of the gas?

◀ **FIGURE 10.15**

The volume of a real gas.

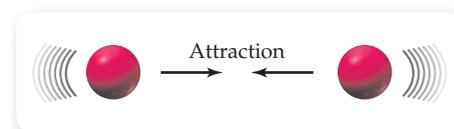
10.8 ► THE BEHAVIOR OF REAL GASES

Here we expand on a point made earlier: The behavior of a real gas is often slightly different from that of an ideal gas. For instance, kinetic-molecular theory assumes that the volume of the gas particles themselves is negligible compared with the total gas volume. The assumption is valid at STP, where the volume taken up by molecules of a typical gas is less than 0.1% of the total volume, but the assumption is not valid at 500 atm and 0 °C, where the volume of the molecules is about 20% of the total volume (**FIGURE 10.15**). As a result, the volume of a real gas at high pressure is larger than predicted by the ideal gas law.

A second issue arising with real gases is the assumption that there are no attractive forces between particles. At lower pressures, this assumption is reasonable because the gas particles are so far apart. At higher pressures, however, the particles are much closer together and the attractive forces between them become more important. In general, intermolecular attractions become significant at a distance of about 10 molecular diameters and increase rapidly as the distance diminishes (**FIGURE 10.16**). The result is to draw the molecules of real gases together slightly, decreasing the volume at a given pressure (or decreasing the pressure for a given volume).

Note that the effect of molecular volume—to increase V —is opposite that of intermolecular attractions—to decrease V . The two factors therefore tend to cancel at intermediate pressures, but the effect of molecular volume dominates above about 350 atm.

Both deviations in the behavior of real gases can be dealt with mathematically by a modification of the ideal gas law called the **van der Waals equation**, which uses two correction factors, called a and b . The increase in V , caused by the volume of the individual gas particles, is corrected by subtracting the amount nb from the observed volume, where n is the number of moles of gas. The decrease in V at constant P (or, equivalently, the decrease in P at constant V), caused by the effect of attractive forces between gas particles, is corrected by adding an amount an^2/V^2 to the pressure.

▲ **FIGURE 10.16**

Molecules attract one another at distances up to about 10 molecular diameters. The result is a decrease in the actual volume of most real gases when compared with ideal gases at pressures up to 300 atm.

van der Waals equation

Correction for
intermolecular attractions

Correction for
molecular volume

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

$$\text{or } P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

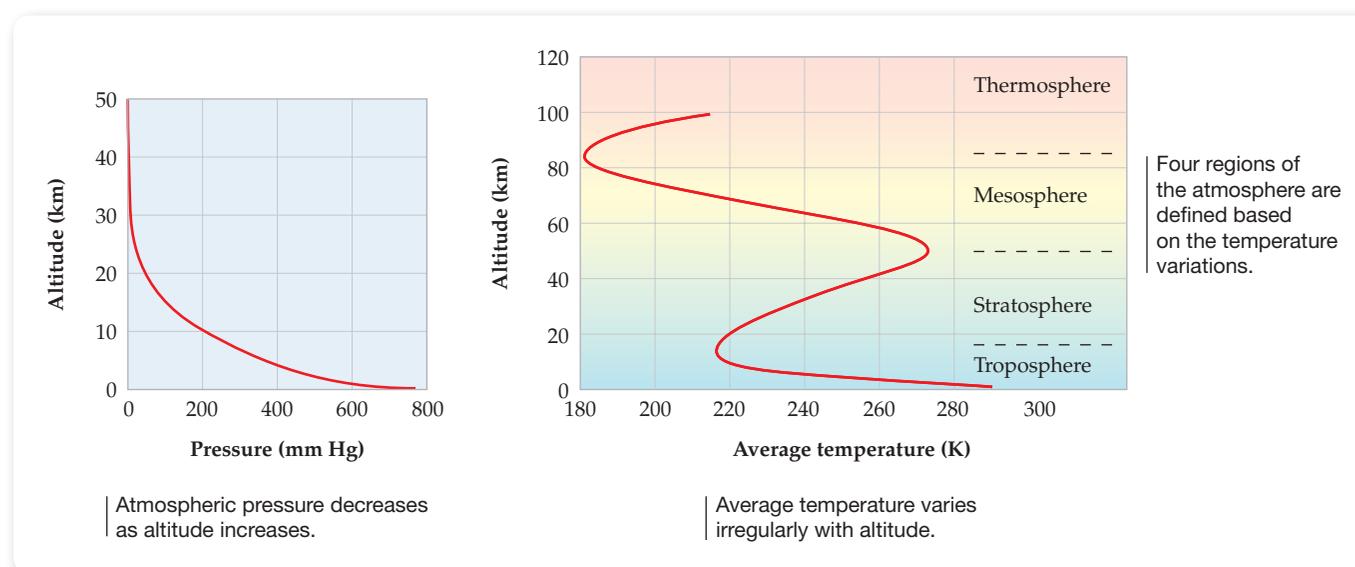
10.9 ► THE EARTH'S ATMOSPHERE AND AIR POLLUTION

The mantle of gases surrounding the Earth is far from the uniform mixture you might expect. Although atmospheric pressure decreases in a regular way at higher altitudes, the profile of temperature versus altitude is much more complex (FIGURE 10.17). Four regions of the atmosphere have been defined based on this temperature curve. The temperature in the *troposphere*, the region nearest the Earth's surface, decreases regularly up to about 12 km altitude, where it reaches a minimum value, and then increases in the *stratosphere*, up to about 50 km. Above the stratosphere, in the *mesosphere* (50–85 km), the temperature again decreases but then again increases in the *thermosphere* (above 85 km). To give you a feeling for these altitudes, passenger jets normally fly near the top of the troposphere at altitudes of 10 to 12 km, and the world altitude record for jet aircraft is 37.65 km—roughly in the middle of the stratosphere.

The most well-known environmental problems relating to the atmosphere are air pollution, acid rain, climate change, and ozone depletion. In this chapter we'll explore the chemistry of air pollution and climate change. Ozone depletion will be considered in Chapter 13, which covers principles of chemical kinetics that are central to the issue. Acid rain will be addressed in the chapter on acids and bases (Chapter 15).

Not surprisingly, it's the layer nearest the Earth's surface—the troposphere—that is the most easily disturbed by human activities. Air pollution has appeared in the last two centuries as an unwanted by-product of industrialized societies. Its causes are relatively straightforward; its control is difficult. Pollutants can be grouped into two main categories. **Primary pollutants** are those that enter the environment directly from a source such as vehicle or industrial emissions. **Secondary pollutants** are formed by the chemical reaction of a primary pollutant and are not directly emitted from a source.

The United States Environmental Protection Agency has set air quality standards for six principal pollutants called “criteria” pollutants. The standards for the criteria pollutants, shown in TABLE 10.7, are maximum concentrations that are safe for public health and the environment based upon current knowledge of their effects. Both toxicity and exposure time are considered in setting the standards. More toxic pollutants have standards set at lower concentrations although higher concentrations of toxic substances are acceptable for limited



▲ FIGURE 10.17 Variations of atmospheric pressure and average temperature with altitude.

amounts of time. For example, a concentration of 9 ppm of carbon monoxide is safe over a period of 8 hours, while exposure to 35 ppm is safe for only 1 hour. As new research emerges about health effects, the standards are modified. In 2008, the 8-hour standard for ozone was lowered from 80 to 75 ppb and further lowering of the standard to 65 ppb is currently under discussion.

The units of measure for the standards (parts per million and parts per billion by volume) are similar to the unit of percent volume of atmospheric components given in Table 10.1 at the start of the chapter. These quantities are all found by multiplying the mole fraction of a gas (X) by a given factor: 100 for percentage, 10^6 for ppm, and 10^9 for ppb. The mole fraction can be used to calculate volume percent because Avogadro's law states that ($V \propto n$). These quantities can be calculated for a given gas (a) as follows:

$$\text{Percent by volume} = (X_a) \times 100$$

$$\text{Parts per million (ppm) by volume} = (X_a) \times 10^6$$

$$\text{Parts per billion (ppb) by volume} = (X_a) \times 10^9$$

The concentration units of ppm and ppb represent extremely low levels. One way to grasp the magnitude of these units is to relate them to the timescale. One ppm corresponds to the first second in a total of 10^6 seconds or 11.6 days. If a pollutant has a concentration of 1 ppm, this represents one molecule of pollutant for every 10^6 (one million) air molecules. One ppb represents an even smaller concentration and corresponds to the first second in total of 10^9 seconds or 31.7 years. The 8-hour standard for ozone of 75 ppb therefore represents 75 ozone molecules in a total of 10^9 (one billion) air molecules. Worked Example 10.10 demonstrates how to calculate different concentration units for pollutants.

WORKED EXAMPLE 10.10

Calculating Concentration Units for Pollutants

A home carbon monoxide (CO) meter gives a reading of 155 ppm.

- Express the concentration of CO as a percentage.
- Find the number of CO molecules inhaled in one breath if an average breath of air contains 3.3×10^{-2} total moles of gas.

IDENTIFY

Known	Unknown
Concentration of CO (155 ppm)	Concentration in units of percent
Moles of gas (3.3×10^{-2})	Number of CO molecules

STRATEGY

- Use the formula for calculating ppm to find the mole fraction of CO. Once the mole fraction is found it can be substituted into the formula for percent volume.
- To find the number of moles of CO, multiply the mole fraction by the total number of moles of air. Convert moles of CO to molecules using Avogadro's number.

SOLUTION

$$(a) \quad 155 \text{ ppm} = (X_{CO}) \times 10^6 \quad X_{CO} = \frac{155}{1 \times 10^6} = 1.55 \times 10^{-4}$$

$$\text{Percent by volume} = (X_{CO}) \times 100 = (1.55 \times 10^{-4}) \times 100 = 0.0155\%$$

$$(b) \quad 3.32 \times 10^{-2} \text{ mol air} \times \frac{(1.55 \times 10^{-4} \text{ mol CO})}{1 \text{ mol air}} \times \frac{(6.02 \times 10^{23} \text{ molecules CO})}{1 \text{ mol CO}}$$

$$= 3.00 \times 10^{18} \text{ molecules CO}$$

continued on next page

TABLE 10.7 National Ambient Air Quality Standard for Criteria Pollutants, 2014.

Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air ($\mu\text{g}/\text{m}^3$)

Pollutant	Standard
Carbon monoxide (CO)	
1-hour	35 ppm
8-hour	9 ppm
Lead (Pb)	
3-month average	0.15 $\mu\text{g}/\text{m}^3$
Nitrogen dioxide (NO₂)	
1-hour	100 ppb
Annual	53 ppb
Ozone (O₃)	
8-hour	75 ppb
Sulfur dioxide (SO₂)	
1-hour	75 ppb
Particle pollution	
Particle diameter less than 2.5 μm (PM _{2.5})	
Annual	12 $\mu\text{g}/\text{m}^3$
24-hour	35 $\mu\text{g}/\text{m}^3$
Particle diameter between 2.5 and 10 μm (PM ₁₀)	
24-hour	150 $\mu\text{g}/\text{m}^3$

CHECK

The low value for volume percent is reasonable because units of ppm are very small. The multiplication factor between percentage (10^2) and ppm (10^6) differ by a factor of 10^4 . Therefore, a simple way to convert between ppm and percent is to move the decimal four places to the left to arrive at 0.0155%. The number of molecules of CO is very large even though the concentration is small. If one breath contains $\sim 10^{-2}$ moles of air total, this corresponds to $\sim 10^{21}$ molecules. There are a large number of total molecules in each breath so we would also expect a rather large number of CO molecules.

► **PRACTICE 10.19** The local news in an urban area reports an ozone concentration of 110 ppb on a hot summer day. What is the concentration of ozone in units of ppm and volume percent? How many ozone molecules are inhaled in one breath that contains 3.3×10^{-2} moles of air?

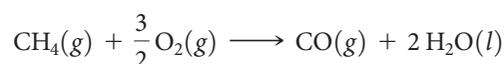
► **APPLY 10.20** A hot summer day in Denver has an ozone concentration of 95 ppb. Calculate the partial pressure of ozone if the total pressure in the “mile high city” is 0.79 atm.

Primary Pollutants

Carbon Monoxide Carbon monoxide (CO) is a colorless, odorless gas emitted from combustion processes. So far in this book, we have written the products of hydrocarbon combustion reactions as CO_2 and H_2O . The balanced combustion reaction for natural gas (CH_4) is:



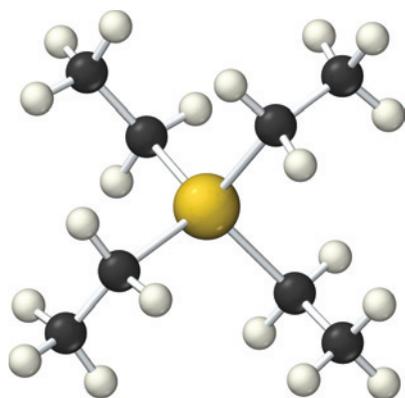
In reality, combustion reactions produce a mixture of CO_2 and CO and the proportion of CO increases under conditions of limited oxygen. The balanced combustion reaction of natural gas when CO is the product is:



Notice that the coefficient for O_2 ($3/2$) in the reaction forming CO is smaller than the coefficient for O_2 (2) when CO_2 is product. In the United States, particularly in urban areas, the majority of CO emissions to ambient air come from the combustion of gasoline in vehicles. If an engine is running efficiently, the amount of CO emitted is less. Many states require vehicle emissions tests that directly measure CO in the tailpipe exhaust and if the vehicle fails to meet the standard (1.20% in several states) then the engine must be serviced so that it complies.

Carbon monoxide is a poisonous gas because it enters the bloodstream through the lungs and forms *carboxyhemoglobin*, a compound that inhibits the blood's capacity to carry oxygen to organs and tissues. CO levels above the 8-hour standard of 9 ppm and 1-hour standard of 35 ppm can cause headaches, confusion, and even death. It is extremely important to have a CO monitor in your home because a malfunctioning furnace can emit fatal levels of CO.

Lead Lead (Pb) is a metal found naturally in the environment and in man-made products. Historically, the major source of lead emissions was leaded gasoline in fuel for vehicles. Tetraethyl lead, $(\text{CH}_3\text{CH}_2)_4\text{Pb}$, was an additive to gasoline that allowed engine compression to be increased, improving vehicle performance and fuel economy. Even small amounts of lead are extremely toxic and once taken into the body accumulates in the bones. Depending on the level of exposure, lead can adversely affect kidney function, neurological development, and the immune, reproductive, and cardiovascular systems. Infants and young children are especially sensitive to even very low levels of lead. Blood concentrations as low as $10 \mu\text{g}/\text{dL}$



▲ Tetraethyl lead $(\text{CH}_3\text{CH}_2)_4\text{Pb}$ was added to gasoline to improve engine performance but was phased out of use in the 1970s due to the toxic effects of lead.

cause learning deficits and reduced IQ levels, impaired hearing, and stunted growth in children.

Lead additives to fuel were phased out in the United States starting in the early 1970s; as a result, lead emissions from the transportation sector have decreased dramatically. By 1990 many other countries had banned lead additives or significantly reduced the lead concentration in leaded gasoline (from about 1 g/L to 0.1 g/L). However, leaded gasoline is still used in many parts of Africa, Asia, and South America. In the United States today, major sources of lead emissions to the air are ore and metal processing and some grades of aviation gasoline.

Particulate Pollution Particulate matter (PM) is composed of extremely small solid particles and liquid droplets that can be made up of a number of different components including salts of sulfates and nitrates, organic molecules, soot, metal, and dust. The particles that are of concern for human health are too small to see and have diameters less than 10 μm . For reference a human hair has a diameter of about 70 μm . The PM_{10} classification corresponds to “inhalable coarse particles” (such as those found near roadways and industry), which have diameters between 2.5 and 10 μm . $\text{PM}_{2.5}$ are particles less than 2.5 μm in diameter and are referred to as “fine particles” (such as those found in smoke and haze).

Both classifications of particles are small enough to pass through the throat and nose and enter the lungs. Health effects include premature death in people with heart or lung disease, irregular heartbeat, aggravated asthma, and decreased lung function. While sensitive groups, such as asthmatics or the elderly, are most affected, healthy individuals may experience temporary symptoms such as irritation of the airways, coughing, or difficulty breathing. Particulate pollution also affects the environment by decreasing visibility (haze) in many parts of the United States, including treasured national parks. Particulates can also be transported over long distances and can damage forests, crops, and aquatic ecosystems by increasing acidity and depleting nutrients.

Sulfur Dioxide Sulfur dioxide (SO_2) is a highly reactive gas that is a major contributor to particulate pollution and **acid rain**. The largest sources of SO_2 emissions are from the combustion of fossil fuels at power plants and other industrial facilities. While coal consists mostly of carbon and hydrogen, it contains between 0.5% and 4% sulfur, which is incorporated either into its organic components or as inorganic mineral impurities such as pyrite (FeS_2). When coal is burned, sulfur is converted in gaseous SO_2 , which is emitted directly to the atmosphere unless it is removed by a process called **scrubbing**. A smaller source of SO_2 emissions is smelting which extracts metals from their ores.

SO_2 is very irritating to tissues and damaging to vegetation. Exposure to $\text{SO}_2(\text{g})$ has adverse respiratory effects including constriction of the airways that results in coughing, wheezing, and shortness of breath. Scientific studies show a connection between short-term exposure and increased visits to emergency departments for respiratory illnesses.

Secondary Pollutants

Nitrogen Dioxide, Ozone, and Photochemical Smog Photochemical smog is a hazy, brownish layer lying over many cities. Nitrogen dioxide (NO_2) and ozone (O_3) are secondary pollutants in photochemical smog that are harmful to human health, vegetation, and materials such as rubber. Ground-level ozone is a powerful oxidant that irritates and inflames airways causing coughing, a burning sensation, wheezing, and shortness of breath. It greatly exacerbates the effects of asthma and other lung diseases. It is a serious concern even for healthy individuals who exercise or work outdoors because it can permanently scar lung tissue.

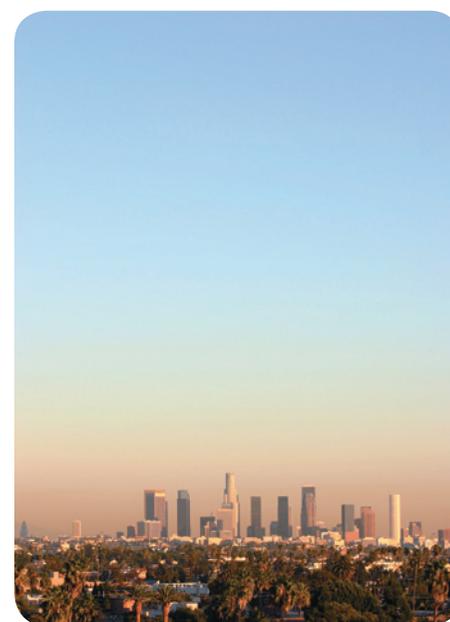
Photochemical smog is a worldwide problem and in the United States both urban and rural areas often issue “ozone alerts” or “ozone action days,” especially during hot, summer months when ozone reaches unhealthy levels.



▲ The difference between a clear and a hazy day from pollution, as seen from Dickey Ridge, Shenandoah National Park. New regulations have decreased the level of haze and improved visibility in some national parks.

LOOKING AHEAD...

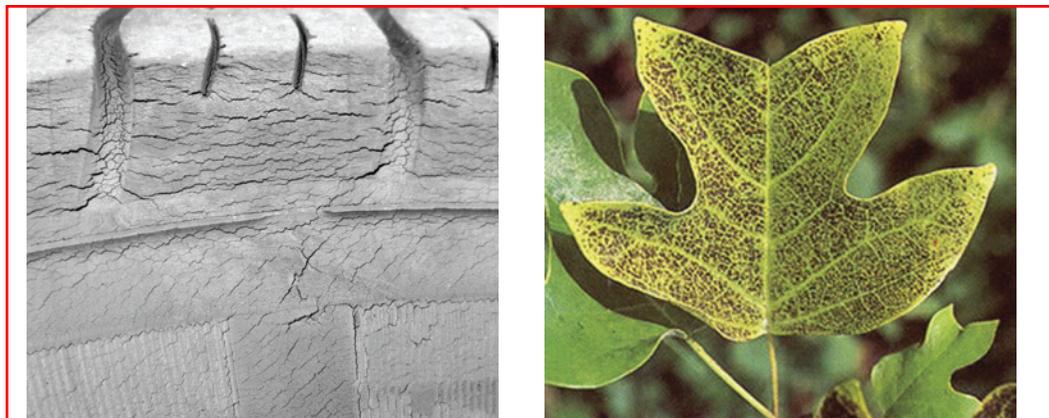
The causes of **acid rain** and the **scrubbing** process used to remove sulfur from coal will be described in the *Inquiry* in Chapter 15.



▲ The photochemical smog over many cities is the end result of pollution from vehicles and industry.

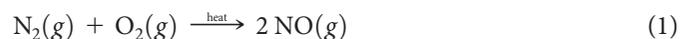
(a) Ozone degrades rubber.

(b) Brown spots indicate ozone damage on this tulip poplar leaf.



▲ Effects of ozone on materials and vegetation.

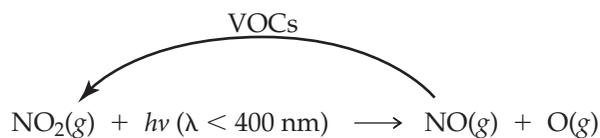
Let's look at the mechanism for ozone formation to understand why photochemical smog typically occurs in areas with lots of sunshine or in warm summer months. The process begins with the emission of a primary pollutant, nitric oxide (NO), from combustion reactions. At the high temperature in a car's engine, nitrogen and oxygen react to form a small amount of NO.

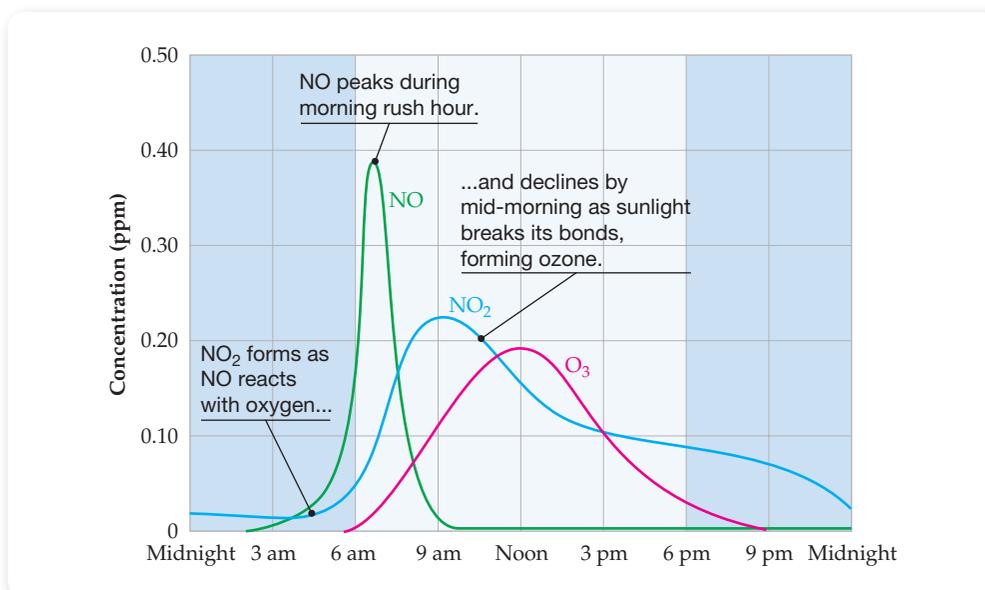


The NO is further oxidized by reaction with oxygen to yield nitrogen dioxide, NO_2 , which splits into NO plus free oxygen atoms (O) in the presence of sunlight (symbolized by $h\nu$). Highly reactive oxygen atoms then combine with oxygen molecules to make ozone (O_3).



These two reactions alone would not necessarily produce unhealthy levels of ozone because the amount of ozone depends on the initial amount of NO_2 . An additional reaction that regenerates NO_2 , however, can initiate a cyclic process in which one molecule of NO_2 forms many molecules of ozone. Volatile organic compounds (VOCs) participate in reactions that regenerate NO_2 from NO. *Volatile* means that the substance readily evaporates from the liquid to the gaseous phase. VOCs are emitted as unburned hydrocarbons in fuel exhaust, industrial processes, and even by some natural sources such as trees. You have directly observed the emission of VOCs when you fuel your car with gasoline and smell the fumes in the air. Thus, reaction 2 above can be modified to show that oxygen-containing VOCs initiate a complex series of reactions to turn NO back into NO_2 which can produce more ozone. The cycle continues as long as there is nitric oxide from combustion, sunlight, and VOCs.





◀ **FIGURE 10.18**
Time profile for pollutants in a photochemical smog event.

The mechanism for ozone formation explains the time profile of pollutants in an urban photochemical smog event (**FIGURE 10.18**). Measurements of NO are typically high in the morning as a consequence of emissions from the morning commute. By midmorning NO has been oxidized to produce appreciable amounts of NO₂. By noon NO₂ begins to decline as sunlight breaks the nitrogen–oxygen bond, forming O atoms which react with O₂ to form O₃. O₃ reaches a peak concentration in the afternoon during periods of intense sunlight.

As scientists discover the chemistry behind pollution, solutions can be developed to reduce the problems. The good news is that air quality in the United States has improved over the last quarter century. **TABLE 10.8** shows that the national average of nearly every pollutant has decreased and certain pollutants, such as Pb and CO have declined dramatically. New technology, such as catalytic converters in cars (described in Section 13.13), sulfur scrubbing from power plant emissions, and oxygenated fuels, along with state and government regulations have made the air much safer to breathe today than in the 1970s and 1980s. But many air quality issues remain to be addressed. Ozone and particulate matter frequently contribute to unhealthy levels of air quality in many regions of the United States. While national averages for SO₂, Pb, and CO have decreased significantly, high levels persist in industrial areas, particularly in the Midwest and East where electricity is primarily generated from coal. Internationally, severe air quality problems exist in major urban areas such as Beijing, China; Mexico City, Mexico; and Paris, France.

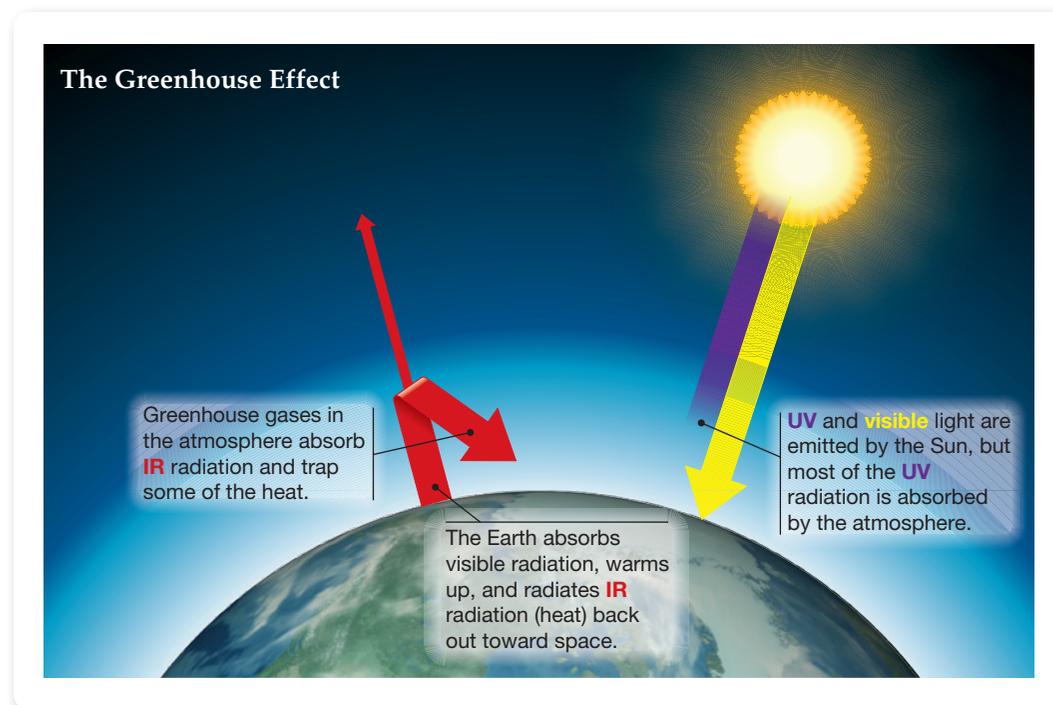
TABLE 10.8 Trends in United States Air Quality Based on Measurements from Hundreds of Sites

Pollutant	Percent Change (1980–2012)
Carbon monoxide (CO)	–83%
Lead (Pb)	–91%
Nitrogen dioxide (NO ₂)	–60%
Ozone (O ₃)	–25%
Sulfur dioxide (SO ₂)	–78%
Particulate Pollution	
PM _{2.5}	–33% (2000–2012)
PM ₁₀	–39% (1990–2012)

10.10 ► THE GREENHOUSE EFFECT

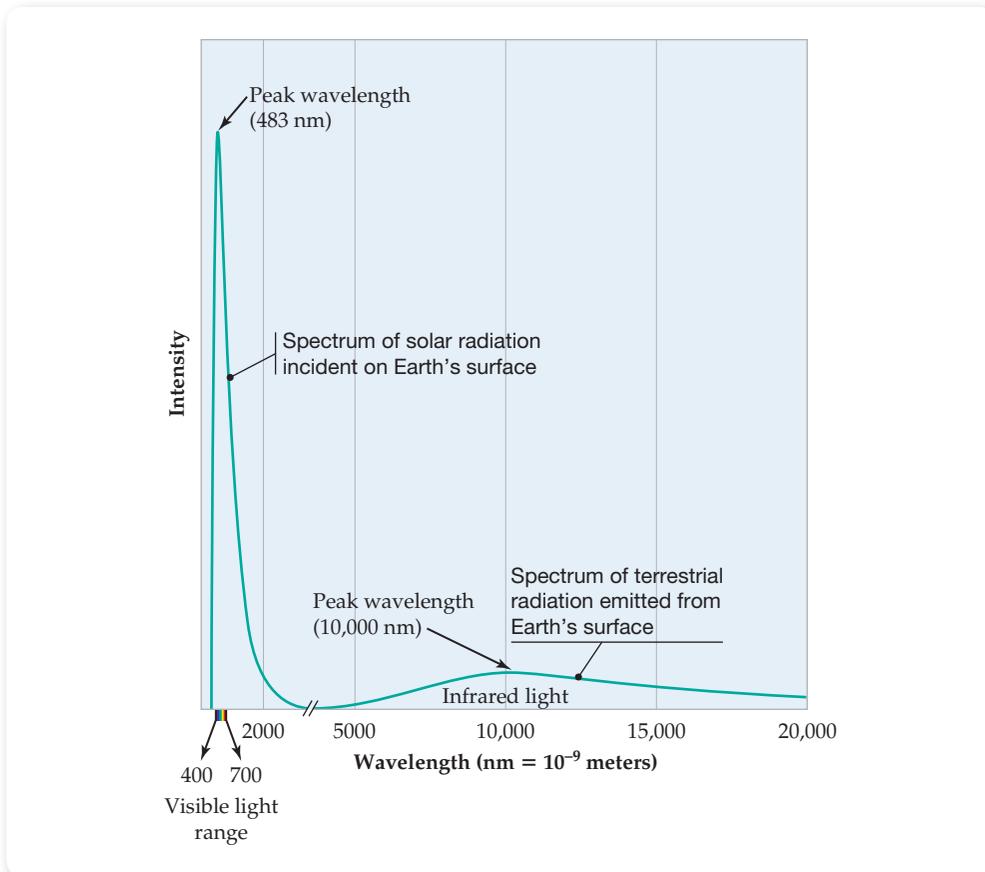
The **greenhouse effect** refers to the absorption of infrared (IR) radiation, also known as heat radiation, by gases in the atmosphere which causes an increase in planetary temperature. **Greenhouse gases** are gases that absorb infrared (IR) radiation. The greenhouse effect is a naturally occurring phenomenon that is critical in regulating climate. The average temperature of our planet would be only about 0 °F if the amount of solar radiation reaching the Earth was the only factor controlling climate. Most water would be frozen and the planet would not be suitable for maintaining life! The presence of greenhouse gases such as water, carbon dioxide, and methane increases the Earth's average global temperature to nearly 60 °F.

► **FIGURE 10.19**
The greenhouse effect.



The principle of the greenhouse effect is illustrated in **FIGURE 10.19**. The Sun, Earth's primary energy source, emits radiation most strongly in the ultraviolet (UV) and visible regions of the electromagnetic spectrum (purple and yellow arrow). Most high-energy, biologically damaging UV radiation (purple arrow) is absorbed by ozone and oxygen in the stratosphere and therefore does not reach ground level. Consequently, most of the radiation reaching Earth is visible light (yellow arrow), which is absorbed by the Earth's surface (vegetation, rocks, water, concrete), causing it to heat up. The warm surface then re-emits heat or IR radiation toward space (red arrow). You can sense the radiation of IR from Earth in the heat you feel well after dark from a black asphalt road that warmed up during the day. The IR radiation emitted from the Earth either escapes into space or is absorbed by greenhouse gases. The greenhouse gases, in turn, reradiate infrared energy and some of it returns to Earth resulting in an increase in the temperature of the planet. The greenhouse effect is so named because the glass windows in a greenhouse act in a similar manner to the Earth's atmosphere. Visible light transmitted through the glass and absorbed by surfaces causes the inside to warm. Infrared radiation emitted by warm interior surfaces is absorbed by the glass, preventing some of the heat from escaping. Soon the greenhouse interior is much warmer than the temperature outside.

FIGURE 10.20 illustrates differences in the nature of the electromagnetic radiation emitted by the Sun and Earth. Incoming solar radiation has a maximum intensity at 483 nm which is in the visible region of the electromagnetic spectrum (blue light), while the Earth's emission has a maximum intensity near 10,000 nm in the IR. Why do the Earth and Sun emit different wavelengths of light? The answer is that the sun is a lot hotter than the Earth. Both the Sun and Earth emit light as a *black-body*, meaning that a continuous spectrum is emitted from a hot object with wavelength dependent on temperature. A familiar example of black-body radiation is the reddish-orange glow of a hot electric burner. The peak wavelength of 483 nm in the sun's emission spectrum corresponds to a very hot temperature, 6000 K, while the peak wavelength in the Earth's emission spectrum near 10,000 nm corresponds to a temperature of 288 K (15 °C or 59 °F).



◀ **FIGURE 10.20** Spectrum of solar radiation incident on the Earth's surface and spectrum of radiation emitted from Earth.



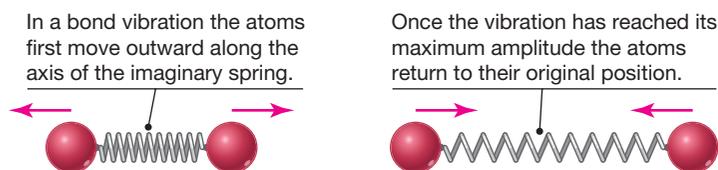
▲ A hot electric burner emits black body radiation.

INQUIRY ►►► WHICH GASES ARE GREENHOUSE GASES?

Why are some atmospheric gases classified as greenhouse gases and others are not? The two most concentrated gases in the atmosphere N_2 (~80% by volume) and O_2 (~20% by volume) do not absorb infrared radiation and therefore are not classified as greenhouse gases. In contrast, CO_2 with an atmospheric concentration of only 0.04% by volume is a greenhouse gas that plays an important role in the regulation of climate. In order to explain why CO_2 is a greenhouse gas and N_2 and O_2 are not, we must understand what occurs on a molecular level when a photon of IR radiation is absorbed.

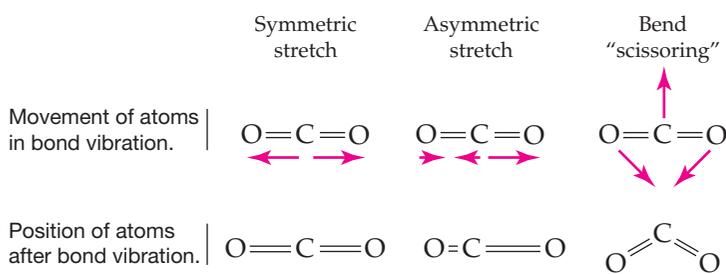
Let's begin by revisiting the interaction of visible light with atoms. Recall from Section 5.3 that electrons falling from higher-energy to lower-energy orbitals emit a discrete series of colored lines called atomic line spectra. Conversely, when these same wavelengths of light are *absorbed* by an atom, electrons move from a lower-energy to higher-energy orbitals. The same absorption process occurs in molecules, but in this case electrons change positions not between atomic orbitals, but between molecular orbitals (Section 8.7).

Absorbed IR radiation, in the greenhouse effect, is not sufficiently energetic to cause electrons to jump to a higher energy orbital but does increase bond vibrations in molecules. To visualize a bond vibration, imagine two balls representing atoms on either end of a spring (FIGURE 10.21). The spring can stretch and retract. The absorption of IR radiation causes a molecule to reach an excited vibrational state in which stretching moves atoms further apart.



▲ **FIGURE 10.21**
Visualization of a bond vibration in a diatomic molecule.

Let's examine some bond vibrations that occur in the greenhouse gas CO_2 . CO_2 has two double bonds around the central carbon atom resulting in linear geometry. However, these bonds are not stationary and vibrate in three different ways, as shown below.



In the symmetric stretch, both $C=O$ bonds lengthen and in the asymmetric stretch both oxygen atoms move in the same direction

resulting in one longer and one shorter $C=O$ bond. The bending vibration changes the linear geometry of CO_2 to a bent geometry. Once the atoms reach their new positions the motion is reversed and the atoms oscillate around their original position. Every CO_2 molecule is constantly undergoing these vibrational motions.

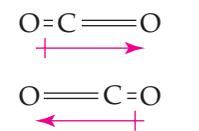
A molecule will absorb a photon of IR radiation if two conditions are met:

1. **The energy difference between the lower vibrational state and the excited vibrational state exactly matches the energy of the IR photon.** Recall that energy levels in atoms and molecules are quantized (Section 5.4). The photon can only be absorbed if its energy is exactly matched to the energy difference between states.
2. **The vibration results in a change in dipole moment** (Section 8.5)

Let's evaluate each vibration in CO_2 to determine if this requirement is met.

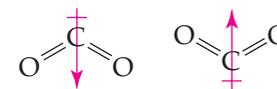
Symmetric stretch: Each $C=O$ bond has a bond dipole because oxygen is more electronegative than carbon, but the dipoles exactly cancel each other out and CO_2 does not have a net dipole moment. When both $C=O$ bonds elongate during the symmetric stretch, the bond dipoles still exactly cancel and there is no change in dipole moment. Thus the symmetric stretch vibration does not absorb IR radiation.

Asymmetric stretch: In the asymmetric stretch, both oxygen atoms carry a partial negative charge and they move in the same direction during the vibration. This results in shifting in negative charge to one side of the CO_2 molecule creating a net dipole moment. Therefore, the asymmetric stretch absorbs IR radiation.



The asymmetric stretch produces an alternating dipole moment.

Bending (scissoring) vibration: The bending vibration changes CO_2 from a linear geometry with no dipole moment to a bent geometry with a dipole moment. Both bond dipoles point toward the partial negative charges on the oxygen atoms, giving the end of CO_2 with two oxygen atoms a partial negative charge and the end with the carbon atom a partial positive charge. Thus the bending vibration creates a change in dipole moment and absorbs IR radiation.



The bending vibration produces an alternating dipole moment.

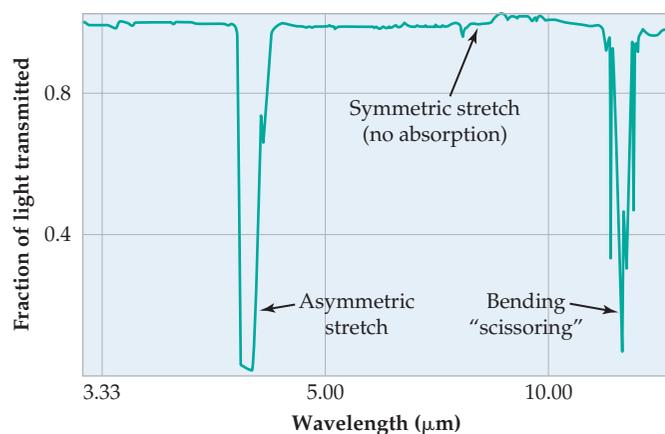
REMEMBER...

The measure of net molecular polarity is a quantity called the **dipole moment**, μ (Greek mu), which is defined as the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges: $\mu = Q \times r$ (Section 8.5).

FIGURE 10.22 shows the infrared absorption spectrum for CO_2 . The vertical axis is the fraction of light transmitted by the sample, and the negative peaks indicate absorption of IR radiation. Notice that both the asymmetric stretch and the bending vibration have absorption peaks. The wavelength (frequency) for the symmetric stretch is indicated, but no absorption peak is present because this vibration does not cause a net change in dipole moment.

Molecules that absorb IR radiation are greenhouse gases, and water is one of the most important examples. The observation that clear nights are often cooler than cloudy ones is a familiar example of the greenhouse effect; water vapor in clouds strongly absorbs IR. Although water vapor is the largest contributor to the natural greenhouse effect, the amount in the atmosphere is mainly controlled by air temperature and not by emissions from human activities. The greenhouse gas emissions from human activities that are of greatest concern are carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and halogen-containing gases. Carbon dioxide is added to the atmosphere primarily from burning fossil fuels, but industrial processes and decaying organic matter also contribute significant amounts. Methane is emitted from fossil fuel mining and use, landfills, agricultural practices, livestock cultivation, and termites. Natural microbial activity in soil and oceans and the use of fertilizer in agricultural practices are sources of nitrous oxide. Halogenated gases, such as hydrofluorocarbons (CHClF_2) or sulfur hexafluoride (SF_6), are synthetic greenhouse gases emitted from a variety of industrial applications such as refrigeration and air conditioning.

Global-warming potential (GWP) is a relative measure of how much heat a greenhouse gas traps in the atmosphere on a per mass basis and carbon dioxide is set to a reference value of 1. A GWP is calculated over a specific time interval, commonly 20, 100, or 500 years, and is influenced by how strongly a gas absorbs IR and how long it remains in the atmosphere. **TABLE 10.9** gives GWP values for the major greenhouse gases associated with human activities. Table 10.9 also includes radiative forcing values which describe the



▲ **FIGURE 10.22**
Infrared absorption spectrum of carbon dioxide.

TABLE 10.9 Global-Warming Potentials and Radiative Forcing of Greenhouse Gases

Greenhouse Gas	Global Warming Potential (100-year value)	Atmospheric Concentration	Radiative Forcing (W/m^2)
CO_2	1	400 ppm	1.82
CH_4	21	1.8 ppm	0.48
N_2O	310	325 ppb	0.17
CFC-12	4600	0.52 ppb	0.17
SF_6	22,800	0.007 ppb	0.004
Halogenated gases (total)			0.360

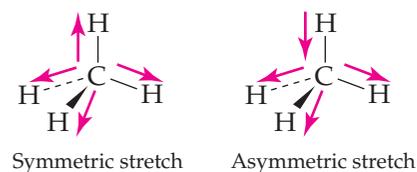
(Intergovernmental Panel on Climate Change—Climate Change 2013: The Physical Science Basis)

relative contribution of each gas to the greenhouse effect. Higher positive values for radiative forcing indicate larger warming effects. Radiative forcing is defined as the net change in the energy balance of the Earth and is expressed in units of watts per square meter (W/m^2). Although CO_2 has the lowest GWP of the greenhouse gases listed in Table 10.9, it makes the greatest contribution to the greenhouse effect because it has a higher concentration than the other gases.

PROBLEM 10.21 Explain why nitrogen and oxygen are not greenhouse gases.

PROBLEM 10.22 The water molecule has similar bond vibrations to carbon dioxide. Decide whether the symmetric, asymmetric, and bending vibrations in water will result in the absorption of IR radiation.

PROBLEM 10.23 Bond vibrations for the symmetric and asymmetric stretch in methane are illustrated below. Decide whether each vibration will result in the absorption of IR radiation. Arrows indicate the movement of atoms during the vibration.



PROBLEM 10.24 How many times larger is carbon dioxide's contribution to the greenhouse effect than methane? (Use radiative forcing values in Table 10.9 to compare the two gases.)

PROBLEM 10.25 N_2O has a GWP value of 310 and CO_2 has a GWP value 1, but CO_2 makes a greater contribution to the greenhouse effect. Explain.

PROBLEM 10.26 Although human activities do not have significant influence on the concentration of water vapor in the atmosphere, the surface warming caused by other greenhouse gases could increase rates of evaporation. If more water vapor entered the atmosphere, what would be the effect on climate based on the greenhouse effect?

10.11 ► CLIMATE CHANGE

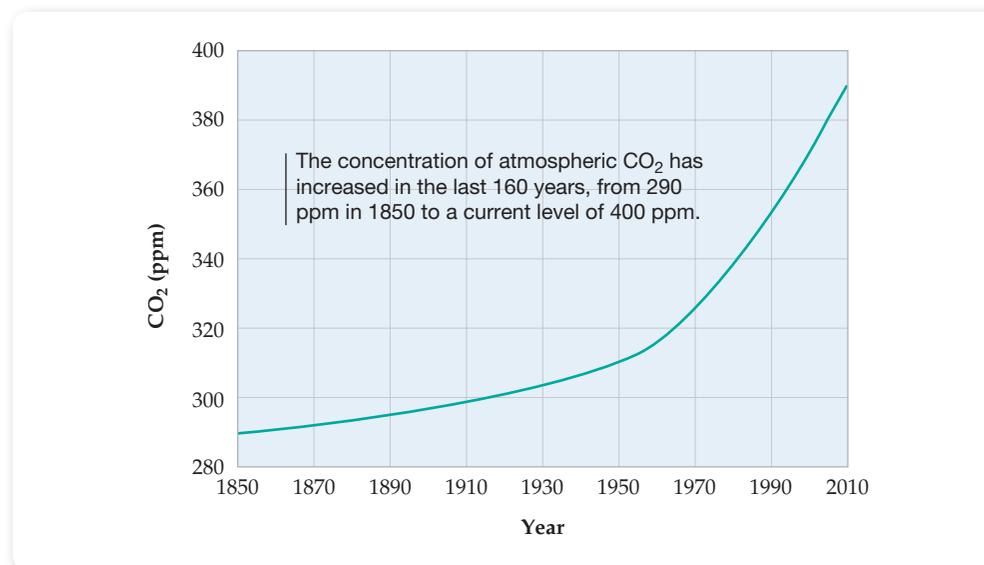
Global warming refers to the idea that increasing concentrations of greenhouse gases will upset the delicate thermal balance of incoming and outgoing radiation on Earth. Rising levels of greenhouse gases will absorb more IR radiation and cause an enhanced warming effect. The term global warming has been replaced with **climate change** because there will not be a uniform rise in temperature at all locations. Instead, different areas will warm by varying degrees and other areas may even experience cooling. Climate science is complex because it is a global issue and greenhouse gas concentration is only one of many factors that influence climate. Cloud cover, particulate matter, solar energy, and changing surface reflectivity due to melting polar ice caps or deforestation are just a few variables that influence global and regional temperature. In this section, we will describe how concentrations of greenhouse gases have changed over time and their impact on climate both today and in the future.

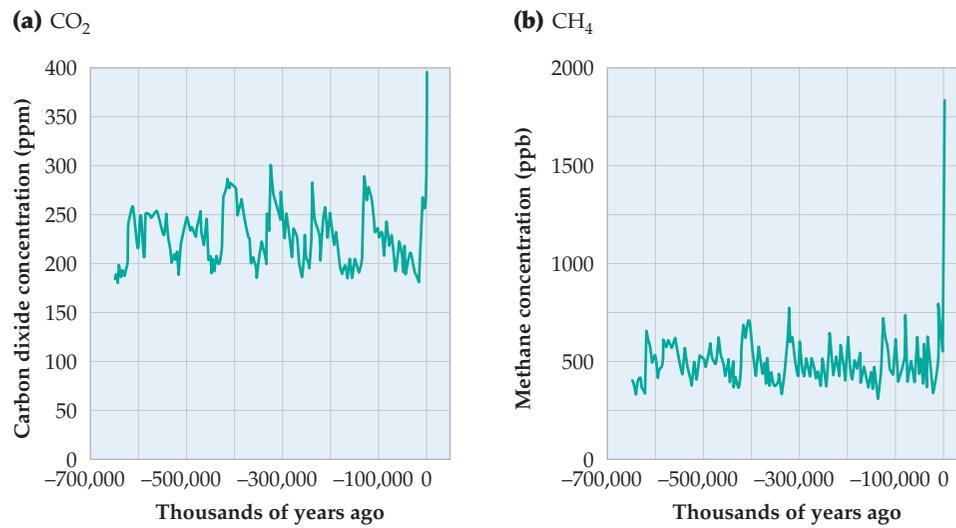
Since the Industrial Revolution began in the late 1700s, people have added a significant amount of greenhouse gases to the atmosphere by burning fossil fuels for energy, cutting down forests, and producing industrial goods such as cement or metals. Although natural mechanisms remove greenhouse gases from the atmosphere, concentrations are rising because the rate of addition exceeds the rate of loss. For example, careful measurements show that concentrations of atmospheric carbon dioxide have been rising in the last 160 years from an estimated 290 parts per million (ppm) in 1850 to 400 ppm in 2014 (**FIGURE 10.23**).

It is also useful to examine greenhouse gas levels on a longer timescale to compare our current situation to other time periods. Samples from polar ice caps are used to create historical records because the depth of the ice core sample can be correlated with time. Greenhouse gases trapped in air bubbles in the ice can be analyzed when the ice is melted. Measurements show that current global atmospheric concentrations of CO_2 and CH_4 are unprecedented compared with their levels in the past 650,000 years (**FIGURE 10.24**). Concentrations of these greenhouse gases have fluctuated over time, but dramatic increases are evident in the last century. Note that CO_2 levels never exceeded 300 ppm in the long-term historical record, but burning of fossil fuels has caused the level to rise to 400 ppm. Methane concentrations did not exceed 0.8 ppm (800 ppb) in the historical record, but have recently risen to 1.8 ppm (1,800 ppb). Similarly, N_2O levels have not exceeded 280 ppb over the past 100,000 years but have increased to a concentration of 325 ppb. Most of the halogenated gases are man-made, and their atmospheric concentration began rising as they were used in industrial processes over the last few decades.

Ever since Earth formed, its climate has undergone dramatic shifts, from “ice ages” with high glacial coverage to relatively warm periods. Factors such as surface reflectivity, airborne dust, variations in the Earth’s orbit, and solar intensity combined with greenhouse gas levels contributed to these periodic fluctuations in climate. Ice core samples can also be used to measure a long-term historical record of past climate. Analysis of the ratio of hydrogen isotopes ($^2\text{H}:^1\text{H}$) in H_2O in ice core samples helps scientists estimate long-term shifts in average global temperature. **FIGURE 10.25** shows the correlation between past carbon dioxide (CO_2)

► **FIGURE 10.23**
Annual concentration of atmospheric CO_2 since 1850.





Source: U.S. Environmental Protection Agency, Climate Change, Greenhouse Gases.

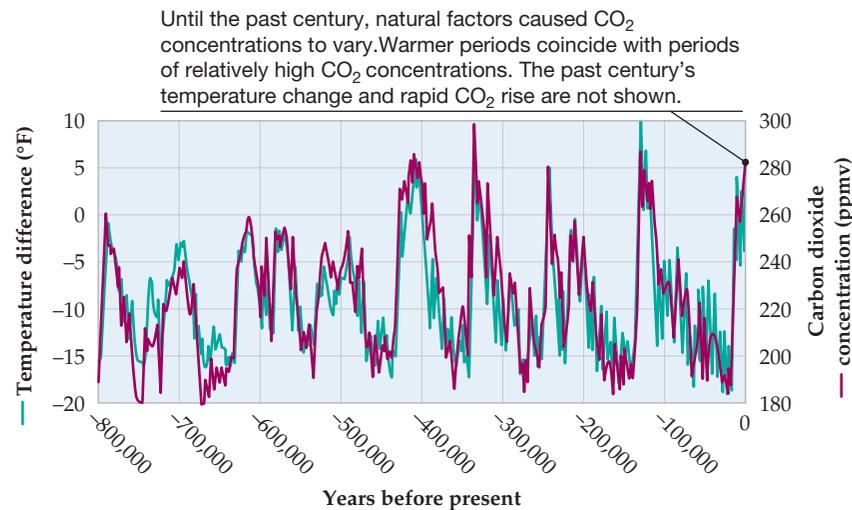
◀ **FIGURE 10.24**

Long-term historical record of greenhouse gases obtained from ice core and atmospheric measurements.

Figure It Out

How do current levels of CO₂ and CH₄ in the atmosphere compare to levels over the past 650,000 years?

Answer: The historical record shows that both CO₂ and CH₄ levels have risen dramatically in the past few centuries, and the current level is significantly higher than any time in the past 650,000 years.



Source: National Research Council. Advancing the Science of Climate Change. The National Academies Press, 2010.

◀ **FIGURE 10.25**

Correlation of CO₂ levels and past global temperatures measured in ice cores.

Figure It Out

Does this figure show that an increase in CO₂ concentration causes an increase in temperature?

Answer: No, it does not prove that the temperature changed in direct response to changes in CO₂ levels. It is possible that the opposite occurred: a temperature change could have caused changes in CO₂ levels. The factors are related in a complex way, but the data clearly shows that higher temperatures correspond with higher CO₂ levels.

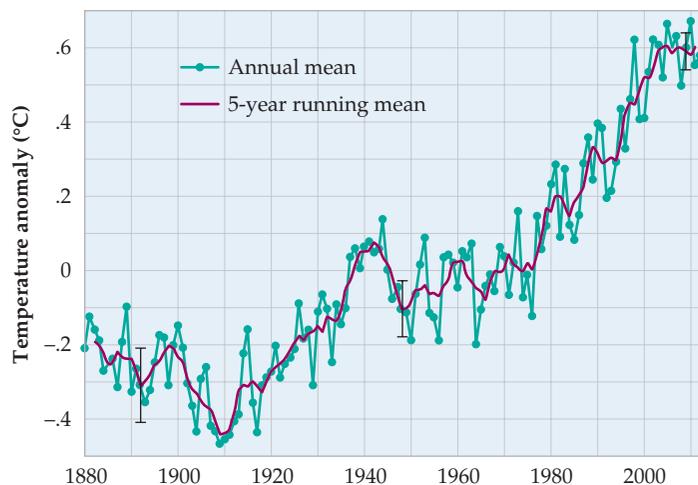
concentrations (top) and Antarctic temperature (bottom) over the past 800,000 years. Warmer periods coincide with higher CO₂ concentrations.

Most atmospheric scientists believe the climate has changed rapidly in recent years due to human-induced changes to the atmosphere. **FIGURE 10.26** illustrates the change in global surface temperature (°C) from 1880 to present relative to the average temperature during the time period 1951–1980. Roughly two-thirds of the warming occurred since 1975. While the temperature increase may seem small (approximately 1 °C from 1990 to present), it is important to realize that warming is occurring at a much more rapid pace than past climate shifts, which occurred over thousands of years. Climate models predict that average global temperatures may increase by 3.5–4 °C (~6–7 °F) by 2100, depending on levels of future greenhouse gas emissions and that warming will continue at an accelerated pace.

Scientists track the effects of climate change using indicators that show trends in environmental conditions, such as the extent of sea ice, changes in sea level, changes in biodiversity, and ocean acidity. The Arctic is warming at a rate much faster than the rest of the Earth and sea ice is melting at an astonishing rate. The area of Arctic sea ice in September 2012 was 1.3 million square miles (an area five times the size of Texas) less than the historical 1979–2000 average (**FIGURE 10.27**). Climate is an important influence on ecosystems and the rate of temperature change may simply be too fast for many species to adapt in order to survive. Species that are especially climate sensitive such as those dependent on sea ice (polar bears and seals) or those adapted to mountain or cold water environments (pikas and salmon) may

► FIGURE 10.26

Change in global surface temperature (°C) relative to 1951–1980 average temperatures. The dotted green line is the annual mean and the solid red line is the 5-year mean.



Source: National Aeronautics and Space Administration, GISS Surface Temperature Analysis.



▲ Climate change may be the leading factor decreasing the populations of the American pika.

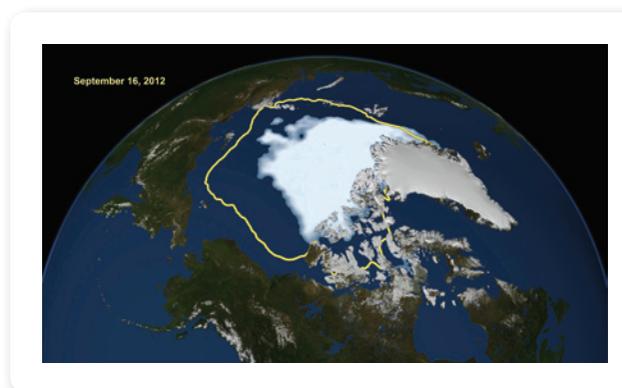
suffer significant declines in population or in extreme cases extinction. A study by the Intergovernmental Panel on Climate Change estimates that 20–30% of plant and animal species evaluated are at risk of extinction if temperature reaches levels projected to occur by the end of the century. In the past century, sea level has risen by nearly 10 inches due to the melting of ice on land and the thermal expansion of water as its temperature increases. Changing sea levels can affect human activities in coastal areas. For example, rising sea levels lead to increased coastal flooding and erosion and greater damage from storms. Sea level rise can alter ecosystems, transforming marshes and other freshwater systems into salt water. Coral reefs, home to much biodiversity in the oceans, are dying at a rapid rate due to higher temperatures and acidity from increased levels of dissolved carbon dioxide.

A great majority of climate scientists (over 97% in a recent survey) agree that warming trends over the past century are very likely due to human activities, and most of the leading scientific organizations worldwide, such as the Intergovernmental Panel on Climate Change, The National Academy of Sciences, and the American Chemical Society, have issued public statements endorsing this position. Consequences of ongoing climate change have been scientifically documented, and humans must consider the increasing risk of extreme weather events (heat waves, droughts, and floods), loss of coastline, and changing weather patterns that impact agriculture and our food supply.

We must decide how to respond to this long-term environmental issue. Solutions can be complex, costly, and difficult to implement, but several options are being researched and tested. These include alternative energy sources (such as solar, wind, and nuclear), carbon sequestration—the trapping and storing of carbon dioxide—and conservation measures (increasing efficiency or decreasing use). Many scientists and policy makers believe that it is more economical to develop a sustainable energy system rather than dealing with the costs associated with the negative consequences of climate change.

► FIGURE 10.27

Sea ice extent in the Arctic. September 2012 had the lowest sea ice extent on record, 49% below the 1979–2000 average for that month shown by the yellow line.



STUDY GUIDE

Section	Concept Summary	Learning Objectives	Test Your Understanding
10.1 ▶ Gases and Gas Pressure	A gas is a collection of atoms or molecules moving independently through a volume that is largely empty space. Collisions of randomly moving particles with the walls of their container exert a force per unit area that we perceive as pressure (P). The SI unit for pressure is the pascal (Pa) , but the atmosphere (atm) , the millimeter of mercury , and the bar are more commonly used.	10.1 Convert between different units of pressure. 10.2 Describe how a barometer and manometer measure pressure.	Worked Example 10.1; Problems 10.38, 10.42, 10.43 Worked Example 10.2; Problems 10.27, 10.28, 10.29, 10.44–10.46
10.2 ▶ The Gas Laws	The physical condition of any gas is defined by four variables: pressure (P), temperature (T), volume (V), and molar amount (n). The specific relationships among these variables are called the gas laws : Boyle's law, Charles's law, and Avogadro's law.	10.3 Use the individual gas laws to calculate pressure, volume, molar amount, or temperature for a gas sample when conditions change.	Worked Example 10.3; Problems 10.31, 10.36, 10.50
10.3 ▶ The Ideal Gas Law	The three individual gas laws can be combined into a single ideal gas law , $PV = nRT$. If any three of the four variables P , V , T , and n are known, the fourth can be calculated. The constant R in the equation is called the gas constant (R) and has the same value for all gases. At standard temperature and pressure (STP) ; 1 atm and 0°C , the standard molar volume of an ideal gas is 22.414 L.	10.4 Use the ideal gas law to calculate pressure, volume, molar amount, or temperature for a gas sample.	Worked Examples 10.4, 10.5; Problems 10.52–10.61
10.4 ▶ Stoichiometric Relationships with Gases	The ideal gas law can be used to calculate the number of moles in a gas sample. The number of moles in gaseous reactant or product can be related to other substances in a chemical reaction using stoichiometry. Gas density can be used to identify unknown gases and depends on pressure, molar mass, and temperature.	10.5 Calculate volumes of gases in chemical reactions. 10.6 Calculate the density or molar mass of a gas using the formula for gas density.	Worked Example 10.6; Problems 10.72–10.77, 10.156 Worked Example 10.7; Problems 10.68–10.71
10.5 ▶ Mixtures of Gases: Partial Pressure and Dalton's Law	The gas laws apply to mixtures of gases as well as to pure gases. According to Dalton's law of partial pressures , the total pressure exerted by a mixture of gases in a container is equal to the sum of the pressures each individual gas would exert alone.	10.7 Calculate the partial pressure, mole fraction, or amount of each gas in a mixture.	Worked Example 10.8; Problems 10.34, 10.80–10.88, 10.147, 10.148, 10.151, 10.159
10.6 ▶ The Kinetic-Molecular Theory of Gases	The behavior of gases can be accounted for using a model called the kinetic-molecular theory , a group of five postulates: <ol style="list-style-type: none">1. A gas consists of tiny particles moving at random.2. The volume of the gas particles is negligible compared with the total volume.3. There are no forces between particles, either attractive or repulsive.4. Collisions of gas particles are elastic.5. The average kinetic energy of gas particles is proportional to their absolute temperature.	10.8 Use the assumptions of kinetic-molecular theory to predict gas behavior. 10.9 Calculate the average molecular speed of a gas particle at a given temperature.	Problems 10.30, 10.32, 10.90, 10.146 Problems 10.94–10.99

Section	Concept Summary	Learning Objectives	Test Your Understanding
10.7 ▶ Gas Diffusion and Effusion: Graham's Law	The connection between temperature and kinetic energy obtained from the kinetic-molecular theory makes it possible to calculate the average speed of a gas particle at any temperature. An important practical consequence of this relationship is Graham's law , which states that the rate of a gas's effusion , or spontaneous passage through a pinhole in a membrane, depends inversely on the square root of the gas's mass.	10.10 Visualize the processes of effusion and diffusion. 10.11 Use Graham's Law to estimate relative rates of diffusion for two gases.	Problems 10.35, 10.37 Worked Example 10.9; Problems 10.100–10.103, 10.143
10.8 ▶ The Behavior of Real Gases	Real gases differ in their behavior from that predicted by the ideal gas law, particularly at high pressure, where gas particles are forced close together and intermolecular attractions become significant. The deviations from ideal behavior can be dealt with mathematically by the van der Waals equation .	10.12 Understand the conditions when gases deviate the most from ideal behavior. 10.13 Use the van der Waals equation to calculate the properties of real gases.	Problems 10.106, 10.107 Problems 10.108, 10.109
10.9 ▶ The Earth's Atmosphere and Pollution	The Earth's atmosphere is divided into layers based upon changes in temperature. Air pollution occurs in the lowest layer of the atmosphere called the troposphere. Pollutants that are emitted directly from sources are called primary pollutants and include lead, particulate matter, nitric oxide, sulfur dioxide, and carbon monoxide. Secondary pollutants are formed from reactions of primary pollutants and include ozone and nitrogen dioxide.	10.14 Convert between different units used to express the concentration of pollutants. 10.15 Use the gas laws, Dalton's Law, and stoichiometry to calculate amounts of pollutant gases in the atmosphere. 10.16 Identify the components and causes of photochemical smog.	Worked Example 10.10; Problems 10.113, 10.116–10.118 Problems 10.111, 10.120, 10.121 Problems 10.123–10.129
10.10 and 10.11 ▶ The Greenhouse Effect and Climate Change	The greenhouse effect is the trapping of heat emitted from the Earth by gases that absorb infrared radiation (greenhouse gases). Climate change is occurring as a result of rising levels of greenhouse gases from human activities. Measurements and models show that certain regions such as the Arctic and land masses will warm more than other regions, such as the ocean.	10.17 Explain the principle of the greenhouse effect. 10.18 Describe the trends in greenhouse gas concentrations over time and measured and predicted effects of climate change.	Problems 10.130–10.132 Problems 10.134–10.137

KEY TERMS

atmosphere (atm) 361
Avogadro's law 367
bar 361
Boyle's law 364
Charles's law 365
climate change 391
Dalton's law of partial pressures 375

diffusion 380
effusion 380
gas constant (R) 369
gas laws 364
global warming 391
Graham's law 381
greenhouse effect 390
greenhouse gas 390

ideal gas 364
ideal gas law 369
kinetic-molecular theory 378
manometer 362
millimeter of mercury (mm Hg) 361
mole fraction (X) 376
newton (N) 360

pascal (Pa) 360
primary pollutant 384
pressure (P) 360
secondary pollutant 384
standard molar volume 367
standard temperature and pressure (STP) 370
van der Waals equation 383

KEY EQUATIONS

- **Boyle's law (Section 10.2)**

$$V \propto 1/P \quad \text{or} \quad PV = k \text{ at constant } n \text{ and } T$$

- **Charles's law (Section 10.2)**

$$V \propto T \quad \text{or} \quad V/T = k \text{ at constant } n \text{ and } P$$

- **Avogadro's law (Section 10.2)**

$$V \propto n \quad \text{or} \quad V/n = k \text{ at constant } T \text{ and } P$$

- **Ideal gas law (Section 10.3)**

$$V = \frac{nRT}{P} \quad \text{or} \quad PV = nRT$$

- **Standard temperature and pressure (STP) for gases (Section 10.3)**

$$T = 0^\circ\text{C} \quad P = 1 \text{ atm}$$

- **Gas density (Section 10.4)**

$$d = \frac{m}{V} = \frac{PM}{RT}$$

- **Dalton's law of partial pressures (Section 10.5)**

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$$

where P_1, P_2, \dots are the pressures each individual gas would have if it were alone.

- **Mole fraction (Section 10.6)**

$$(X) = \frac{\text{Moles of component}}{\text{Total moles in mixture}}$$

- **Partial pressure (Section 10.6)**

$$P_1 = X_1 \cdot P_{\text{total}}$$

- **Average speed of gas particle at temperature T (Section 10.6)**

$$u = \sqrt{\frac{3RT}{mN_A}} = \sqrt{\frac{3RT}{M}} \quad \text{where } M \text{ is the molar mass.}$$

- **Graham's law (Section 10.7)**

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{m}}$$

- **van der Waals equation (Section 10.8)**

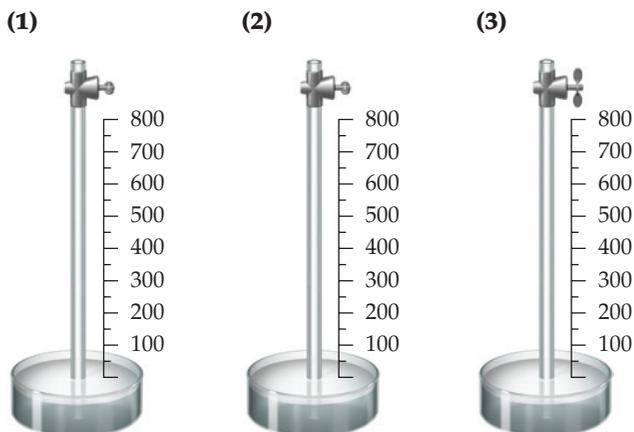
$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \text{or} \quad P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

where a and b are correction factors to the ideal gas law.

CONCEPTUAL PROBLEMS

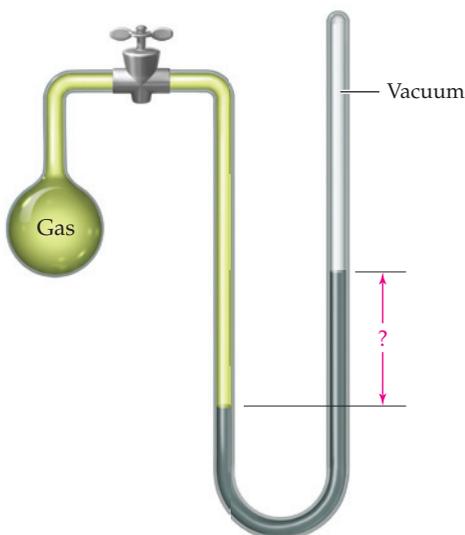
Problems 10.1–10.26 appear within the chapter.

10.27 A glass tube has one end in a dish of mercury and the other end closed by a stopcock. The distance from the surface of the mercury to the bottom of the stopcock is 850 mm. The apparatus is at 25 °C, and the mercury level in the tube is the same as that in the dish.

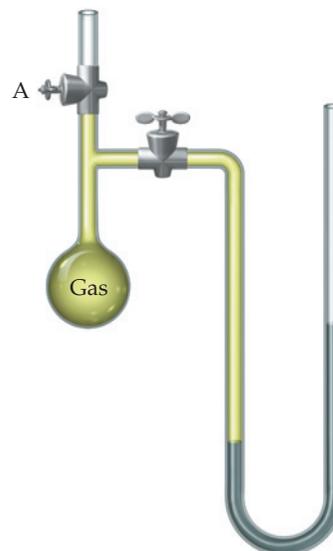


- (a) Show on drawing (1) what the approximate level of mercury in the tube will be when the temperature of the entire apparatus is lowered from +25 °C to –25 °C.
- (b) Show on drawing (2) what the approximate level of mercury in the tube will be when a vacuum pump is connected to the top of the tube, the stopcock is opened, the tube is evacuated, the stopcock is closed, and the pump is removed.
- (c) Show on drawing (3) what the approximate level of mercury in the tube will be when the stopcock in drawing (2) is opened.

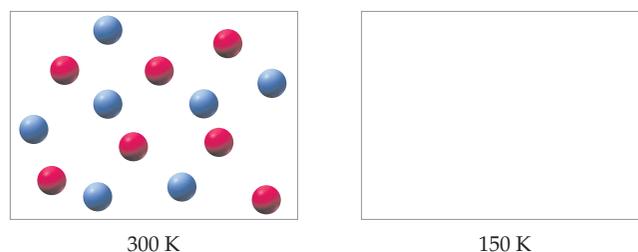
10.28 The apparatus shown is called a *closed-end* manometer because the arm not connected to the gas sample is closed to the atmosphere and is under vacuum. Explain how you can read the gas pressure in the bulb.



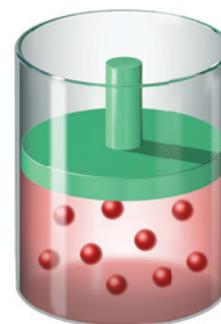
10.29 Redraw the following open-end manometer to show what it would look like when stopcock A is opened.



10.30 A 1:1 mixture of helium (red) and argon (blue) at 300 K is portrayed below on the left. Draw the same mixture when the temperature is lowered to 150 K.



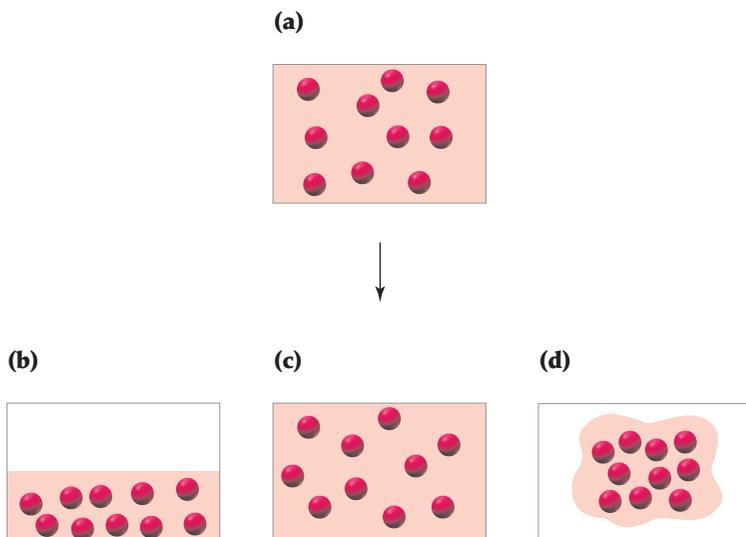
10.31 Assume that you have a sample of gas in a cylinder with a movable piston, as shown in the following drawing:



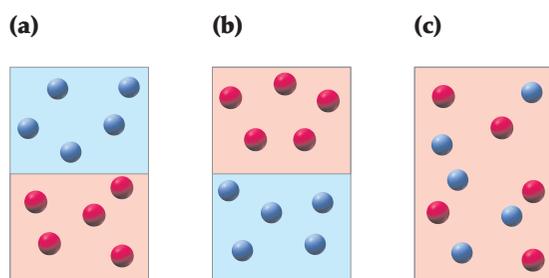
Redraw the apparatus to show what the sample will look like after (a) the temperature is increased from 300 K to 450 K at constant pressure, (b) the pressure is increased from 1 atm to 2 atm at constant temperature, and (c) the temperature is decreased from 300 K to 200 K and the pressure is decreased from 3 atm to 2 atm.

10.32 Assume that you have a sample of gas at 350 K in a sealed container, as represented in (a). Which of the drawings (b)–(d)

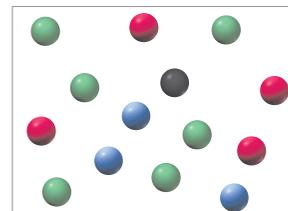
represents the gas after the temperature is lowered from 350 K to 150 K? The boiling point of the gas is 90 K.



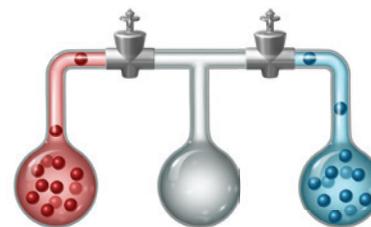
10.33 Assume that you have a mixture of He (atomic weight = 4) and Xe (atomic weight = 131) at 300 K. Which of the drawings best represents the mixture (blue = He; red = Xe)?



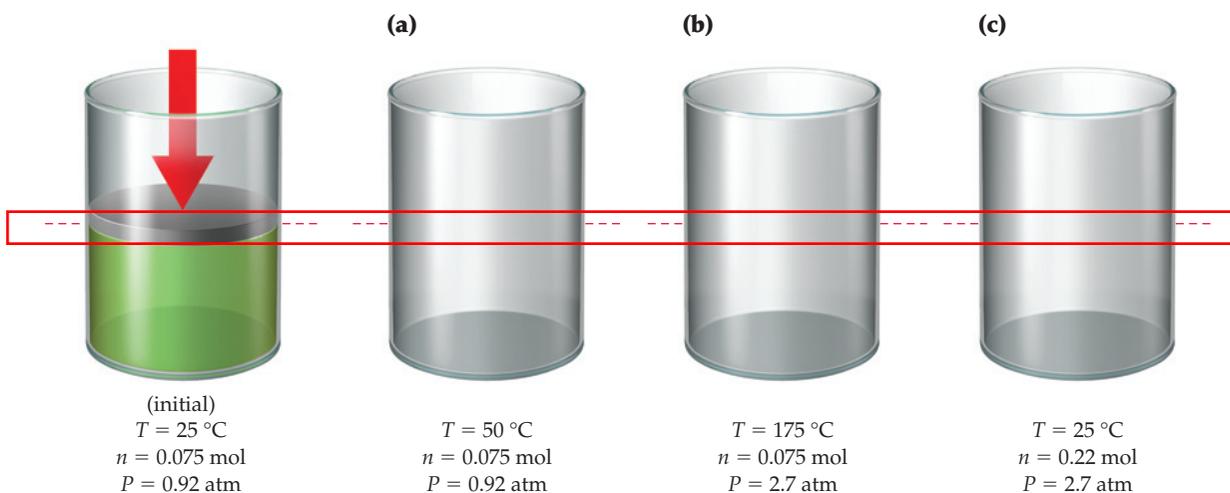
10.34 The following drawing represents a container holding a mixture of four gases, red, blue, green, and black. If the total pressure inside the container is 420 mm Hg, what is the partial pressure of each individual component?



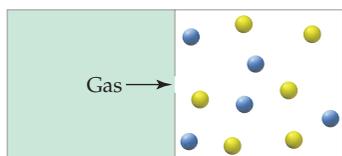
10.35 Three bulbs, two of which contain different gases and one of which is empty, are connected as shown in the following drawing. Redraw the apparatus to represent the gases after the stopcocks are opened and the system is allowed to come to equilibrium.



10.36 Show the approximate level of the movable piston in drawings (a), (b), and (c) after the indicated changes have been made to the gas.



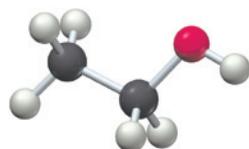
- 10.37 Effusion of a 1:1 mixture of two gases through a small pinhole produces the results shown below.
- Which gas molecules—yellow or blue—have a higher average speed?
 - If the yellow molecules have a molecular weight of 25, what is the molecular weight of the blue molecules?



SECTION PROBLEMS

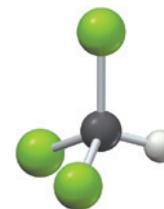
Gases and Gas Pressure (Section 10.1)

- 10.38 Yet another common measure of pressure is the unit pounds per square inch (psi). How many pounds per square inch correspond to 1.00 atm? To 1.00 mm Hg?
- 10.39 If the density of water is 1.00 g/mL and the density of mercury is 13.6 g/mL, how high a column of water in meters can be supported by standard atmospheric pressure? By 1 bar?
- 10.40 What is temperature a measure of?
- 10.41 Why are gases so much more compressible than solids or liquids?
- 10.42 Atmospheric pressure at the top of Pikes Peak in Colorado is approximately 480 mm Hg. Convert this value to atmospheres and to pascals.
- 10.43 Carry out the following conversions:
- 352 torr to kPa
 - 0.255 atm to mm Hg
 - 0.0382 mm Hg to Pa
- 10.44 What is the pressure in millimeters of mercury inside a container of gas connected to a mercury-filled open-end manometer of the sort shown in Figure 10.5 when the level in the arm connected to the container is 17.6 cm lower than the level in the arm open to the atmosphere and the atmospheric pressure reading outside the apparatus is 754.3 mm Hg?
- 10.45 What is the pressure in atmospheres inside a container of gas connected to a mercury-filled open-end manometer when the level in the arm connected to the container is 28.3 cm higher than the level in the arm open to the atmosphere and the atmospheric pressure reading outside the apparatus is 1.021 atm?
- 10.46 Assume that you have an open-end manometer filled with ethyl alcohol (density = 0.7893 g/mL at 20 °C) rather than mercury (density = 13.546 g/mL at 20 °C). What is the pressure in pascals if the level in the arm open to the atmosphere is 55.1 cm higher than the level in the arm connected to the gas sample and the atmospheric pressure reading is 752.3 mm Hg?



Ethyl alcohol

- 10.47 Assume that you have an open-end manometer filled with chloroform (density = 1.4832 g/mL at 20 °C) rather than mercury (density = 13.546 g/mL at 20 °C). What is the difference in height between the liquid in the two arms if the pressure in the arm connected to the gas sample is 0.788 atm and the atmospheric pressure reading is 0.849 atm? In which arm is the chloroform level higher?



Chloroform

- 10.48 Calculate the average molecular weight of air from the data given in Table 10.1.
- 10.49 What is the average molecular weight of a diving-gas mixture that contains 2.0% by volume O₂ and 98.0% by volume He?

The Gas Laws (Sections 10.2 and 10.3)

- 10.50 Assume that you have a cylinder with a movable piston. What would happen to the gas pressure inside the cylinder if you were to do the following?
- Triple the Kelvin temperature while holding the volume constant
 - Reduce the amount of gas by one-third while holding the temperature and volume constant
 - Decrease the volume by 45% at constant T
 - Halve the Kelvin temperature and triple the volume
- 10.51 Assume that you have a cylinder with a movable piston. What would happen to the gas volume of the cylinder if you were to do the following?
- Halve the Kelvin temperature while holding the pressure constant
 - Increase the amount of gas by one-fourth while holding the temperature and pressure constant
 - Decrease the pressure by 75% at constant T
 - Double the Kelvin temperature and double the pressure
- 10.52 Which sample contains more molecules: 1.00 L of O₂ at STP, 1.00 L of air at STP, or 1.00 L of H₂ at STP?
- 10.53 Which sample contains more molecules: 2.50 L of air at 50 °C and 750 mm Hg pressure or 2.16 L of CO₂ at -10 °C and 765 mm Hg pressure?
- 10.54 Oxygen gas is commonly sold in 49.0 L steel containers at a pressure of 150 atm. What volume in liters would the gas occupy at a pressure of 1.02 atm if its temperature remained unchanged? If its temperature was raised from 20 °C to 35 °C at constant $P = 150$ atm?
- 10.55 A compressed air tank carried by scuba divers has a volume of 8.0 L and a pressure of 140 atm at 20 °C. What is the volume of air in the tank in liters at STP?
- 10.56 If 15.0 g of CO₂ gas has a volume of 0.30 L at 300 K, what is its pressure in millimeters of mercury?
- 10.57 If 2.00 g of N₂ gas has a volume of 0.40 L and a pressure of 6.0 atm, what is its Kelvin temperature?

- 10.58** The matter in interstellar space consists almost entirely of hydrogen atoms at a temperature of 100 K and a density of approximately 1 atom/cm³. What is the gas pressure in millimeters of mercury?
- 10.59** Methane gas, CH₄, is sold in a 43.8 L cylinder containing 5.54 kg. What is the pressure inside the cylinder in kilopascals at 20 °C?
- 10.60** Many laboratory gases are sold in steel cylinders with a volume of 43.8 L. What mass in grams of argon is inside a cylinder whose pressure is 17,180 kPa at 20 °C?
- 10.61** A small cylinder of helium gas used for filling balloons has a volume of 2.30 L and a pressure of 13,800 kPa at 25 °C. How many balloons can you fill if each one has a volume of 1.5 L and a pressure of 1.25 atm at 25 °C?

Gas Stoichiometry (Section 10.4)

- 10.62** Which sample contains more molecules, 15.0 L of steam (gaseous H₂O) at 123.0 °C and 0.93 atm pressure or a 10.5 g ice cube at -5.0 °C?
- 10.63** Which sample contains more molecules, 3.14 L of Ar at 85.0 °C and 1111 mm Hg pressure or 11.07 g of Cl₂?
- 10.64** Imagine that you have two identical flasks, one containing hydrogen at STP and the other containing oxygen at STP. How can you tell which is which without opening them?
- 10.65** Imagine that you have two identical flasks, one containing chlorine gas and the other containing argon at the same temperature and pressure. How can you tell which is which without opening them?
- 10.66** What is the total mass in grams of oxygen in a room measuring 4.0 m by 5.0 m by 2.5 m? Assume that the gas is at STP and that air contains 20.95% oxygen by volume.
- 10.67** The average oxygen content of arterial blood is approximately 0.25 g of O₂ per liter. Assuming a body temperature of 37 °C, how many moles of oxygen are transported by each liter of arterial blood? How many milliliters?
- 10.68** One mole of an ideal gas has a volume of 22.414 L at STP. Assuming ideal behavior, what are the densities of the following gases in g/L at STP?
 (a) CH₄ (b) CO₂ (c) O₂
- 10.69** What is the density in g/L of a gas mixture that contains 27.0% F₂ and 73.0% He by volume at 714 mm Hg and 27.5 °C?
- 10.70** An unknown gas is placed in a 1.500 L bulb at a pressure of 356 mm Hg and a temperature of 22.5 °C, and is found to weigh 0.9847 g. What is the molecular weight of the gas?
- 10.71** What are the molecular weights of the gases with the following densities:
 (a) 1.342 g/L at STP
 (b) 1.053 g/L at 25 °C and 752 mm Hg
- 10.72** Pure oxygen gas was first prepared by heating mercury(II) oxide, HgO:

$$2 \text{HgO}(s) \longrightarrow 2 \text{Hg}(l) + \text{O}_2(g)$$
 What volume in liters of oxygen at STP is released by heating 10.57 g of HgO?
- 10.73** How many grams of HgO would you need to heat if you wanted to prepare 0.0155 mol of O₂ according to the equation in Problem 10.72?
- 10.74** Hydrogen gas can be prepared by reaction of zinc metal with aqueous HCl:

$$\text{Zn}(s) + 2 \text{HCl}(aq) \longrightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$$
- (a) How many liters of H₂ would be formed at 742 mm Hg and 15 °C if 25.5 g of zinc was allowed to react?
 (b) How many grams of zinc would you start with if you wanted to prepare 5.00 L of H₂ at 350 mm Hg and 30.0 °C?
- 10.75** Ammonium nitrate can decompose explosively when heated according to the equation

$$2 \text{NH}_4\text{NO}_3(s) \longrightarrow 2 \text{N}_2(g) + 4 \text{H}_2\text{O}(g) + \text{O}_2(g)$$
 How many liters of gas would be formed at 450 °C and 1.00 atm pressure by explosion of 450 g of NH₄NO₃?
- 10.76** The reaction of sodium peroxide (Na₂O₂) with CO₂ is used in space vehicles to remove CO₂ from the air and generate O₂ for breathing:

$$2 \text{Na}_2\text{O}_2(s) + 2 \text{CO}_2(g) \longrightarrow 2 \text{Na}_2\text{CO}_3(s) + \text{O}_2(g)$$
 (a) Assuming that air is breathed at an average rate of 4.50 L/min (25 °C; 735 mm Hg) and that the concentration of CO₂ in expelled air is 3.4% by volume, how many grams of CO₂ are produced in 24 h?
 (b) How many days would a 3.65 kg supply of Na₂O₂ last?
- 10.77** Titanium(III) chloride, a substance used in catalysts for preparing polyethylene, is made by high-temperature reaction of TiCl₄ vapor with H₂:

$$2 \text{TiCl}_4(g) + \text{H}_2(g) \longrightarrow 2 \text{TiCl}_3(s) + 2 \text{HCl}(g)$$
 (a) How many grams of TiCl₄ are needed for complete reaction with 155 L of H₂ at 435 °C and 795 mm Hg pressure?
 (b) How many liters of HCl gas at STP will result from the reaction described in part (a)?
- 10.78** A typical high-pressure tire on a bicycle might have a volume of 365 mL and a pressure of 7.80 atm at 25 °C. Suppose the rider filled the tire with helium to minimize weight. What is the mass of the helium in the tire?
- 10.79** Propane gas (C₃H₈) is often used as a fuel in rural areas. How many liters of CO₂ are formed at STP by the complete combustion of the propane in a container with a volume of 15.0 L and a pressure of 4.5 atm at 25 °C? The unbalanced equation is

$$\text{C}_3\text{H}_8(g) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$$

Dalton's Law and Mole Fraction (Section 10.5)

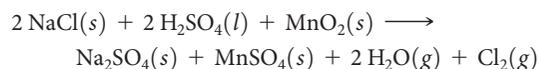
- 10.80** Use the information in Table 10.1 to calculate the partial pressure in atmospheres of each gas in dry air at STP.
- 10.81** Natural gas is a mixture of many substances, primarily CH₄, C₂H₆, C₃H₈, and C₄H₁₀. Assuming that the total pressure of the gases is 1.48 atm and that their mole ratio is 94:4.0:1.5:0.50, calculate the partial pressure in atmospheres of each gas.
- 10.82** A special gas mixture used in bacterial growth chambers contains 1.00% by weight CO₂ and 99.0% O₂. What is the partial pressure in atmospheres of each gas at a total pressure of 0.977 atm?
- 10.83** A gas mixture for use in some lasers contains 5.00% by weight HCl, 1.00% H₂, and 94% Ne. The mixture is sold in cylinders that have a volume of 49.0 L and a pressure of 13,800 kPa at 210 °C. What is the partial pressure in kilopascals of each gas in the mixture?
- 10.84** What is the mole fraction of each gas in the mixture described in Problem 10.83?
- 10.85** A mixture of Ar and N₂ gases has a density of 1.413 g/L at STP. What is the mole fraction of each gas?
- 10.86** A mixture of 14.2 g of H₂ and 36.7 g of Ar is placed in a 100.0 L container at 290 K.
 (a) What is the partial pressure of H₂ in atmospheres?
 (b) What is the partial pressure of Ar in atmospheres?

- 10.87** A 20.0 L flask contains 0.776 g of He and 3.61 g of CO₂ at 300 K.
 (a) What is the partial pressure of He in mm Hg?
 (b) What is the partial pressure of CO₂ in mm Hg?
- 10.88** A sample of magnesium metal reacts with aqueous HCl to yield H₂ gas:



The gas that forms is found to have a volume of 3.557 L at 25 °C and a pressure of 747 mm Hg. Assuming that the gas is saturated with water vapor at a partial pressure of 23.8 mm Hg, what is the partial pressure in millimeters of mercury of the H₂? How many grams of magnesium metal were used in the reaction?

- 10.89** Chlorine gas was first prepared in 1774 by the oxidation of NaCl with MnO₂:



Assume that the gas produced is saturated with water vapor at a partial pressure of 28.7 mm Hg and that it has a volume of 0.597 L at 27 °C and 755 mm Hg pressure.

- (a) What is the mole fraction of Cl₂ in the gas?
 (b) How many grams of NaCl were used in the experiment, assuming complete reaction?

Kinetic-Molecular Theory and Graham's Law (Sections 10.6 and 10.7)

- 10.90** What are the basic assumptions of the kinetic-molecular theory?
10.91 What is the difference between effusion and diffusion?
10.92 What is the difference between heat and temperature?
10.93 Why does a helium-filled balloon lose pressure faster than an air-filled balloon?
10.94 The average temperature at an altitude of 20 km is 220 K. What is the average speed in m/s of an N₂ molecule at this altitude?
10.95 Calculate the average speed of a nitrogen molecule in m/s on a hot day in summer ($T = 37^\circ\text{C}$) and on a cold day in winter ($T = -25^\circ\text{C}$).
10.96 At what temperature (°C) will xenon atoms have the same average speed that Br₂ molecules have at 20 °C?
10.97 At what temperature does the average speed of an oxygen molecule equal that of an airplane moving at 580 mph?
10.98 Which has a higher average speed, H₂ at 150 K or He at 375 °C?
10.99 Which has a higher average speed, a Ferrari at 145 mph or a gaseous UF₆ molecule at 145 °C?
10.100 An unknown gas is found to diffuse through a porous membrane 2.92 times more slowly than H₂. What is the molecular weight of the gas?
10.101 What is the molecular weight of a gas that diffuses through a porous membrane 1.86 times faster than Xe? What might the gas be?
10.102 Rank the following gases in order of their speed of diffusion through a membrane, and calculate the ratio of their diffusion rates: HCl, F₂, Ar.
10.103 Which will diffuse through a membrane more rapidly, CO or N₂? Assume that the samples contain only the most abundant isotopes of each element, ¹²C, ¹⁶O, and ¹⁴N.
10.104 A big-league fastball travels at about 45 m/s. At what temperature (°C) do helium atoms have this same average speed?
- 10.105** Traffic on the German autobahns reaches speeds of up to 230 km/h. At what temperature (°C) do oxygen molecules have this same average speed?

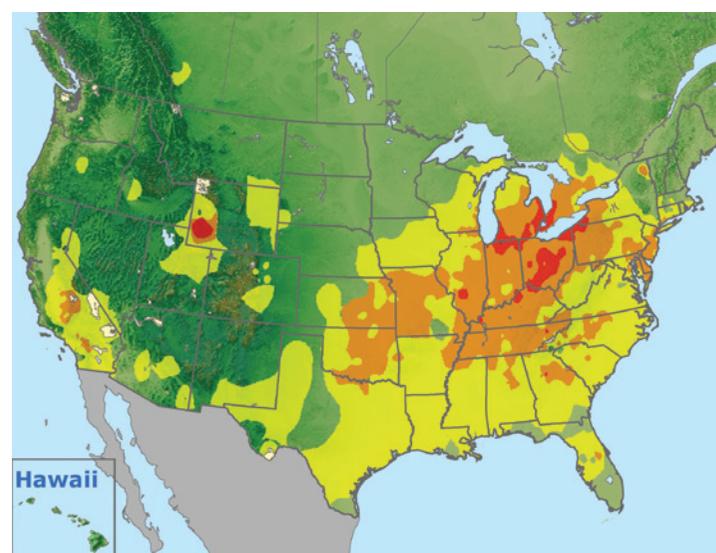
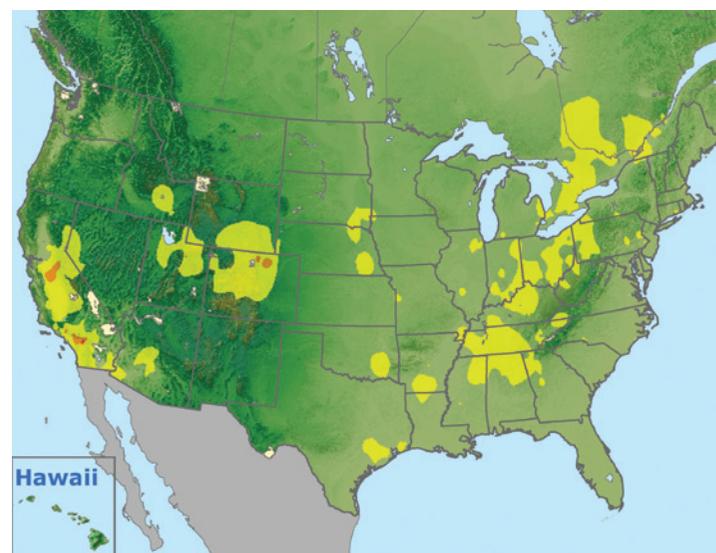
Real Gases (Section 10.8)

- 9.106** (a) The volume of the gas particles themselves most affect the overall volume of the gas sample at _____ (high or low) pressure.
 (b) The volume of each particle causes the true volume of the gas sample to be _____ (larger or smaller) than the volume calculated by the ideal gas law.
- 9.107** (a) The attractive forces between particles most affect the overall volume of the gas sample at _____ (high or low) pressure.
 (b) The attractive forces between particles causes the true volume of the gas sample to be _____ (larger or smaller) than the volume calculated by the ideal gas law.
- 10.108** Assume that you have 0.500 mol of N₂ in a volume of 0.600 L at 300 K. Calculate the pressure in atmospheres using both the ideal gas law and the van der Waals equation. For N₂, $a = 1.35(\text{L}^2 \cdot \text{atm})/\text{mol}^2$ and $b = 0.0387 \text{ L/mol}$.
- 10.109** Assume that you have 15.00 mol of N₂ in a volume of 0.600 L at 300 K. Calculate the pressure in atmospheres using both the ideal gas law and the van der Waals equation. For N₂, $a = 1.35(\text{L}^2 \cdot \text{atm})/\text{mol}^2$ and $b = 0.0387 \text{ L/mol}$.

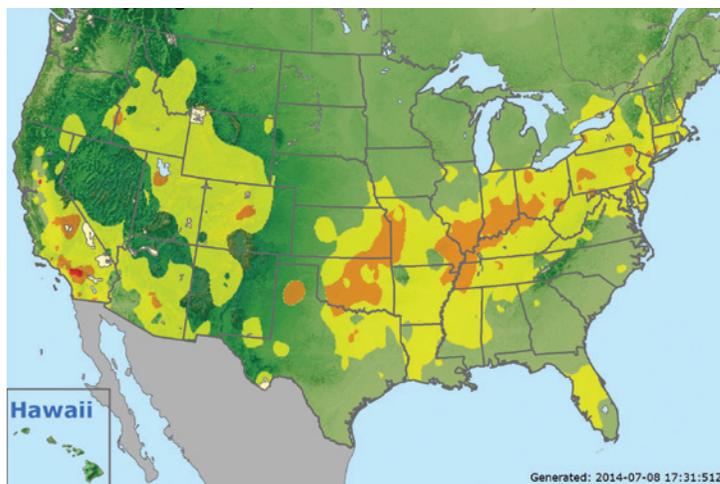
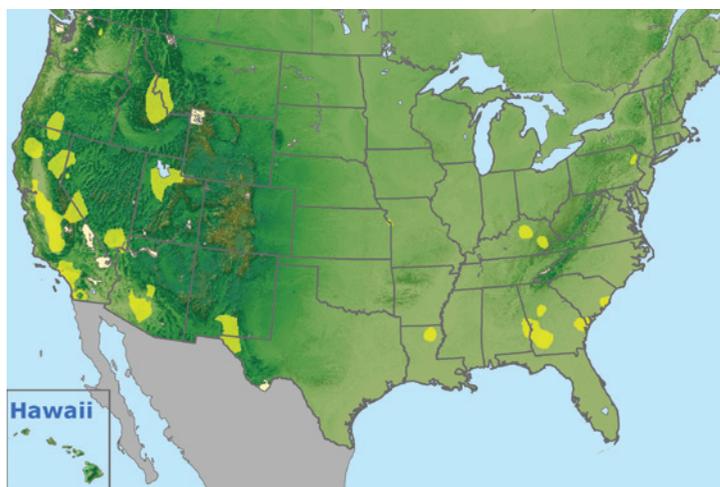
The Earth's Atmosphere and Pollution (Section 10.9)

- 10.110** Name the regions of the atmosphere. What property is used to distinguish between different regions of the atmosphere?
10.111 The Earth's atmosphere has a mass of approximately 5.15×10^{15} kg. If the average molar mass of air is 28.8 g/mol, how many moles of gas make up the atmosphere? What is the volume of the atmosphere in liters under conditions of STP? (Note: The average molar mass of air is the weighted average of the molar mass of nitrogen and oxygen. $0.20(32.0 \text{ g/mol}) + 0.80(28.0 \text{ g/mol}) = 28.8 \text{ g/mol}$.)
10.112 The troposphere contains about three quarters of the mass of the entire atmosphere. The troposphere is only 12 km thick while the whole atmosphere is about 120 km thick. Explain why the troposphere contains such a large fraction of the total mass.
10.113 The percent by volume of oxygen (20.95%) is constant throughout the troposphere.
 (a) Express this percentage as a mole fraction.
 (b) Give the partial pressure of oxygen at sea level where the total atmospheric pressure = 1.0 atm.
 (c) Give the partial pressure oxygen at 11 km, the altitude where airplanes fly, if the total atmospheric pressure is 0.20 atm.
10.114 Based on the national ambient air quality standards provided in Table 10.7, which size particle pollution is more toxic for humans (PM_{2.5} or PM₁₀)? Explain.
10.115 Based on the national ambient air quality standards provided in Table 10.7, which pollutant is more toxic for humans (SO₂ or CO)? Explain.
10.116 Table 10.1 gives the percentage of CO₂ in the atmosphere as 0.040%. What is the concentration of CO₂ in units of ppm?

- 10.117** The concentration of nitrous oxide (N_2O) in dry air at sea level is $5 \times 10^{-5}\%$. What is the concentration of N_2O in units of ppm and ppb?
- 10.118** The concentration of SO_2 in the air was measured to be $0.26 \mu\text{g}/\text{L}$ at a pressure of 1 atm and temperature of 25°C . Does this concentration exceed the 1-hour standard of 75 ppb?
- 10.119** A person inhales an average of 15,000 L per day. If the nitrogen dioxide concentration in air is 100 ppb, what mass of nitrogen dioxide is inhaled over the course of one day? (Assume the pressure is 1 atm and the temperature is 25°C .)
- 10.120** One of the largest sources of SO_2 to the atmosphere is coal-fired power plants. Calculate the volume of SO_2 in L produced by burning 1 kg of coal that contains 2% sulfur. Assume all the sulfur is converted to SO_2 .
- 10.121** Smelting of ores to produce pure metals is an atmospheric source of sulfur dioxide.
- (a) Galena, the most common mineral of lead is primarily lead(II) sulfide (PbS). The first step in the production of pure iron is to oxidize lead sulfide into lead(II) sulfite (PbSO_3). Lead(II) sulfite is then thermally decomposed into lead(II) oxide and sulfur dioxide gas. Balance the following equation.
- $$\text{PbSO}_3(s) \xrightarrow{\text{heat}} \text{PbO}(s) + \text{SO}_2(g)$$
- (b) How many liters of SO_2 are produced at 1 atm and 300°C , if 250 g of PbSO_3 is decomposed?
- 10.122** Which of the EPA criteria air pollutants are emitted
- (a) directly from cars?
- (b) directly from a coal-fired power plant?
- 10.123** What is a primary pollutant? Which of the criteria air pollutants are primary pollutants?
- 10.124** What is a secondary pollutant? Which of the criteria air pollutants are primary pollutants?
- 10.125** During ozone alerts, citizens are often asked to refrain from driving and from fueling their vehicles. Which primary pollutants that lead to ozone production are decreased by each eliminating each activity?
- 10.126** Photons with wavelengths less than 400 nm will break the nitrogen–oxygen bond in NO_2 in the series of reaction to form ozone. Calculate the bond energy in units of kJ/mol.
- 10.127** Key pollutants in a photochemical smog event are O_3 , NO_2 , and NO . Order the pollutants by the time of day that they reach their peak concentration. Explain their order of appearance.
- 10.128** The United States Environmental Protection Agency AirNow program reports an Air Quality Index (AQI) to protect human health. Colors are used to represent different levels of air quality (green = good, yellow = moderate, orange = unhealthy for sensitive groups, and red = unhealthy). The two maps shown below show air quality on June 17 and June 28, 2012. Propose an explanation for the drastically different levels of air quality in the Midwest and East.

Daily Peak AQI (Combined $\text{PM}_{2.5}$ and O_3)

- 10.129** The United States Environmental Protection Agency AirNow program reports an Air Quality Index (AQI) to protect human health. Colors are used to represent different levels of air quality (green = good, yellow = moderate, orange = unhealthy for sensitive groups, and red = unhealthy). One map is from August 8, and the other is from December 5 in the year 2012. Which map corresponds to each day? Explain.

Daily Peak AQI (Combined PM_{2.5} and O₃) August 8, 2012Daily Peak AQI (Combined PM_{2.5} and O₃) December 5, 2012

The Greenhouse Effect and Climate Change (Sections 10.10 and 10.11)

- 10.130** Fill in the blanks with the appropriate region of electromagnetic radiation. (UV, Visible, Infrared)
- The sun most strongly emits in the _____ and _____ regions of electromagnetic radiation.
 - The atmosphere filters out biologically damaging _____ radiation from incoming solar radiation and prevents it from reaching Earth.
 - The Earth most strongly emits _____ radiation.
 - Greenhouse gases absorb _____ radiation.
- 10.131**
- The wavelength of maximum emission of solar radiation is 483 nm. Calculate the energy of one mole of photons with a wavelength of 483 nm.
 - The wavelength of maximum emission of the Earth's radiation is 10,000 nm. Calculate the energy of one mole of photons with a wavelength of 10,000 nm.
 - Which emits higher energy radiation, the Earth or the Sun?
- 10.132** Why do the Earth and Sun have different emission spectra?
- 10.133** Ozone (O₃) is a harmful pollutant in the troposphere. Draw the electron-dot structure for ozone (O₃) and evaluate the symmetric and asymmetric stretch to determine whether ozone is also a greenhouse gas.
- 10.134** What major greenhouse gases are associated with human activities?
- 10.135** What is the trend in atmospheric CO₂ and CH₄ concentrations over the past 150 years? Over several hundred thousand years?
- 10.136** Has the Earth's surface experienced warming as a result of increasing levels of greenhouse gases? If so, by how much?
- 10.137** Name several indicators that scientists use to evaluate the effects of climate change.

CHAPTER PROBLEMS

- 10.138** Match each of the gases to the correct atmospheric problem: air quality, climate change, or both.
- | | |
|---------------------|---------------------|
| (a) O ₃ | (b) SO ₂ |
| (c) CO ₂ | (d) CH ₄ |
| (e) NO ₂ | |
- 10.139** Chlorine occurs as a mixture of two isotopes, ³⁵Cl and ³⁷Cl. What is the ratio of the diffusion rates of the three species (³⁵Cl)₂, ³⁵Cl³⁷Cl, and (³⁷Cl)₂?
- 10.140** What would the atmospheric pressure be in millimeters of mercury if our atmosphere were composed of pure CO₂ gas?
- 10.141** The surface temperature of Venus is about 1050 K, and the pressure is about 75 Earth atmospheres. Assuming that these conditions represent a Venusian "STP," what is the standard molar volume in liters of a gas on Venus?
- 10.142** When you look directly up at the sky, you are actually looking through a very tall, transparent column of air that extends from the surface of the Earth thousands of kilometers into space. If the air in this column were liquefied, how tall would it be? The density of liquid air is 0.89 g/mL.
- 10.143** Uranium hexafluoride, a molecular solid used for purification of the uranium isotope needed to fuel nuclear power plants, sublimates at 56.5 °C. Assume that you have a 22.9 L vessel that contains 512.9 g of UF₆ at 70.0 °C.
- What is the pressure in the vessel calculated using the ideal gas law?
 - What is the pressure in the vessel calculated using the van der Waals equation? (For UF₆, $a = 15.80 \text{ (L}^2 \cdot \text{atm)/mol}^2$; $b = 0.1128 \text{ L/mol}$.)
- 10.144** A driver with a nearly empty fuel tank may say she is "running on fumes." If a 15.0 gallon automobile gas tank had only gasoline vapor remaining in it, what is the farthest the vehicle could travel if it gets 20.0 miles per gallon on liquid gasoline? Assume the average molar mass of molecules in gasoline is 105 g/mol, the density of liquid gasoline is 0.75 g/mL, the pressure is 743 mm Hg, and the temperature is 25 °C.
- 10.145** Two 112 L tanks are filled with gas at 330 K. One contains 5.00 mol of Kr, and the other contains 5.00 mol of O₂. Considering the assumptions of kinetic-molecular theory, rank the gases from low to high for each of the following properties:
- | | |
|-------------------------|-------------------|
| (a) collision frequency | (b) density (g/L) |
| (c) average speed | (d) pressure |

10.146 Two identical 732.0 L tanks each contain 212.0 g of gas at 293 K, with neon in one tank and nitrogen in the other. Based on the assumptions of kinetic-molecular theory, rank the gases from low to high for each of the following properties:

- (a) average speed (b) pressure
(c) collision frequency (d) density (g/L)

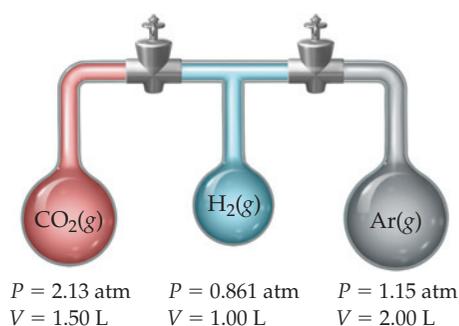
10.147 Pakistan's K2 is the world's second tallest mountain, with an altitude of 28,251 ft. Its base camp, where climbers stop to acclimate, is located about 16,400 ft above sea level.

- (a) Approximate atmospheric pressure P at different altitudes is given by the equation $P = e^{-h/7000}$, where P is in atmospheres and h is the altitude in meters. What is the approximate atmospheric pressure in mm Hg at K2 base camp?
(b) What is the atmospheric pressure in mm Hg at the summit of K2?
(c) Assuming the mole fraction of oxygen in air is 0.2095, what is the partial pressure of oxygen in mm Hg at the summit of K2?

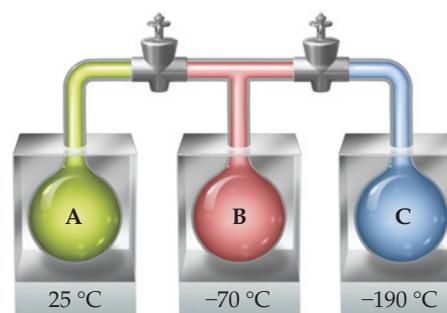
10.148 When a 10.00 L vessel containing 42.189 g of I_2 is heated to 1173 K, some I_2 dissociates: $I_2(g) \rightarrow 2I(g)$. If the final pressure in the vessel is 1.733 atm, what are the mole fractions of the two components $I_2(g)$ and $I(g)$ after the reaction?

10.149 Assume that you take a flask, evacuate it to remove all the air, and find its mass to be 478.1 g. You then fill the flask with argon to a pressure of 2.15 atm and reweigh it. What would the balance read in grams if the flask has a volume of 7.35 L and the temperature is 20.0 °C?

10.150 The apparatus shown consists of three bulbs connected by stopcocks. What is the pressure inside the system when the stopcocks are opened? Assume that the lines connecting the bulbs have zero volume and that the temperature remains constant.

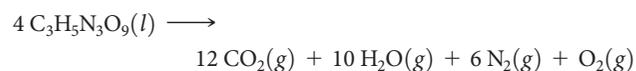


10.151 The apparatus shown consists of three temperature-jacketed 1.000 L bulbs connected by stopcocks. Bulb A contains a mixture of $H_2O(g)$, $CO_2(g)$, and $N_2(g)$ at 25 °C and a total pressure of 564 mm Hg. Bulb B is empty and is held at a temperature of -70 °C. Bulb C is also empty and is held at a temperature of -190 °C. The stopcocks are closed, and the volume of the lines connecting the bulbs is zero. CO_2 sublimates at -78 °C, and N_2 boils at -196 °C.



- (a) The stopcock between A and B is opened, and the system is allowed to come to equilibrium. The pressure in A and B is now 219 mm Hg. What do bulbs A and B contain?
(b) How many moles of H_2O are in the system?
(c) Both stopcocks are opened, and the system is again allowed to come to equilibrium. The pressure throughout the system is 33.5 mm Hg. What do bulbs A, B, and C contain?
(d) How many moles of N_2 are in the system?
(e) How many moles of CO_2 are in the system?

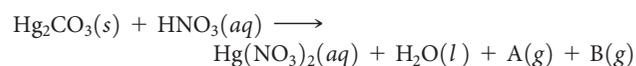
10.152 Assume that you have 1.00 g of nitroglycerin in a 500.0 mL steel container at 20.0 °C and 1.00 atm pressure. An explosion occurs, raising the temperature of the container and its contents to 425 °C. The balanced equation is



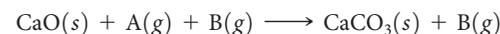
- (a) How many moles of nitroglycerin and how many moles of gas (air) were in the container originally?
(b) How many moles of gas are in the container after the explosion?
(c) What is the pressure in atmospheres inside the container after the explosion according to the ideal gas law?

10.153 Use both the ideal gas law and the van der Waals equation to calculate the pressure in atmospheres of 45.0 g of NH_3 gas in a 1.000 L container at 0 °C, 50 °C, and 100 °C. For NH_3 , $a = 4.17 (L^2 \cdot atm)/mol^2$ and $b = 0.0371 L/mol$.

10.154 When solid mercury(I) carbonate, Hg_2CO_3 , is added to nitric acid, HNO_3 , a reaction occurs to give mercury(II) nitrate, $Hg(NO_3)_2$, water, and two gases A and B:



- (a) When the gases are placed in a 500.0 mL bulb at 20 °C, the pressure is 258 mm Hg. How many moles of gas are present?
(b) When the gas mixture is passed over $CaO(s)$, gas A reacts, forming $CaCO_3(s)$:



- The remaining gas B is collected in a 250.0 mL container at 20 °C and found to have a pressure of 344 mm Hg. How many moles of B are present?
(c) The mass of gas B collected in part (b) was found to be 0.218 g. What is the density of B in g/L?
(d) What is the molecular weight of B, and what is its formula?
(e) Write a balanced equation for the reaction of mercury(I) carbonate with nitric acid.

10.155 Dry ice (solid CO_2) has occasionally been used as an “explosive” in mining. A hole is drilled, dry ice and a small amount of gunpowder are placed in the hole, a fuse is added, and the hole is plugged. When lit, the exploding gunpowder rapidly vaporizes the dry ice, building up an immense pressure. Assume that 500.0 g of dry ice is placed in a cavity with a volume of 0.800 L and the ignited gunpowder heats the CO_2 to 700 K. What is the final pressure inside the hole?

10.156 Consider the combustion reaction of 0.148 g of a hydrocarbon having formula $\text{C}_n\text{H}_{2n+2}$ with an excess of O_2 in a 400.0 mL steel container. Before reaction, the gaseous mixture had a temperature of 25.0 °C and a pressure of 2.000 atm. After complete combustion and loss of considerable heat, the mixture of products and excess O_2 had a temperature of 125.0 °C and a pressure of 2.983 atm.

- What is the formula and molar mass of the hydrocarbon?
- What are the partial pressures in atmospheres of the reactants?
- What are the partial pressures in atmospheres of the products and the excess O_2 ?

10.157 Natural gas is a mixture of hydrocarbons, primarily methane (CH_4) and ethane (C_2H_6). A typical mixture might have $X_{\text{methane}} = 0.915$ and $X_{\text{ethane}} = 0.085$. Let's assume that we have a 15.50 g sample of natural gas in a volume of 15.00 L at a temperature of 20.00 °C.

- How many total moles of gas are in the sample?
- What is the pressure of the sample in atmospheres?
- What is the partial pressure of each component in the sample in atmospheres?
- When the sample is burned in an excess of oxygen, how much heat in kilojoules is liberated?

10.158 A mixture of $\text{CS}_2(g)$ and excess $\text{O}_2(g)$ is placed in a 10.0 L reaction vessel at 100.0 °C and a pressure of 3.00 atm. A spark causes the CS_2 to ignite, burning it completely, according to the equation



After reaction, the temperature returns to 100.0 °C, and the mixture of product gases (CO_2 , SO_2 , and unreacted O_2) is found to have a pressure of 2.40 atm. What is the partial pressure of each gas in the product mixture?

10.159 Gaseous compound **Q** contains only xenon and oxygen. When 0.100 g of **Q** is placed in a 50.0 mL steel vessel at 0 °C, the pressure is 0.229 atm.

- What is the molar mass of **Q**, and what is a likely formula?
- When the vessel and its contents are warmed to 100 °C, **Q** decomposes into its constituent elements. What is the total pressure, and what are the partial pressures of xenon and oxygen in the container?

10.160 When 10.0 g of a mixture of $\text{Ca}(\text{ClO}_3)_2$ and $\text{Ca}(\text{ClO})_2$ is heated to 700 °C in a 10.0 L vessel, both compounds decompose, forming $\text{O}_2(g)$ and $\text{CaCl}_2(s)$. The final pressure inside the vessel is 1.00 atm.

- Write balanced equations for the decomposition reactions.
- What is the mass of each compound in the original mixture?

10.161 A 5.00 L vessel contains 25.0 g of PCl_3 and 3.00 g of O_2 at 15 °C. The vessel is heated to 200.0 °C, and the contents react to give POCl_3 . What is the final pressure in the vessel, assuming that the reaction goes to completion and that all reactants and products are in the gas phase?

10.162 When 2.00 mol of $\text{NOCl}(g)$ was heated to 225 °C in a 400.0 L steel reaction vessel, the NOCl partially decomposed according to the equation $2 \text{NOCl}(g) \longrightarrow 2 \text{NO}(g) + \text{Cl}_2(g)$. The pressure in the vessel after reaction is 0.246 atm.

- What is the partial pressure of each gas in the vessel after reaction?
- What percent of the NOCl decomposed?

10.163 Ozone (O_3) can be prepared in the laboratory by passing an electrical discharge through oxygen gas: $3 \text{O}_2(g) \longrightarrow 2 \text{O}_3(g)$. Assume that an evacuated steel vessel with a volume of 10.00 L is filled with 32.00 atm of O_2 at 25 °C and an electric discharge is passed through the vessel, causing some of the oxygen to be converted into ozone. As a result, the pressure inside the vessel drops to 30.64 atm at 25.0 °C. What is the final mass percent of ozone in the vessel?

10.164 A steel container with a volume of 500.0 mL is evacuated, and 25.0 g of CaCO_3 is added. The container and contents are then heated to 1500 K, causing the CaCO_3 to decompose completely, according to the equation $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$.

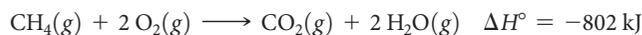
- Using the ideal gas law and ignoring the volume of any solids remaining in the container, calculate the pressure inside the container at 1500 K.
- Now make a more accurate calculation of the pressure inside the container. Take into account the volume of solid CaO (density = 3.34 g/mL) in the container, and use the van der Waals equation to calculate the pressure. The van der Waals constants for $\text{CO}_2(g)$ are $a = 3.59 \text{ (L}^2 \cdot \text{atm)/mol}^2$ and $b = 0.0427 \text{ L/mol}$.

10.165 Nitrogen dioxide dimerizes to give dinitrogen tetroxide: $2 \text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$. At 298 K, 9.66 g of an $\text{NO}_2/\text{N}_2\text{O}_4$ mixture exerts a pressure of 0.487 atm in a volume of 6.51 L. What are the mole fractions of the two gases in the mixture?

10.166 A certain nonmetal reacts with hydrogen at 440 °C to form a poisonous, foul-smelling gas. The density of the gas at 25 °C and 1.00 atm is 3.309 g/L. What is the formula of the gas?

MULTICONCEPT PROBLEMS

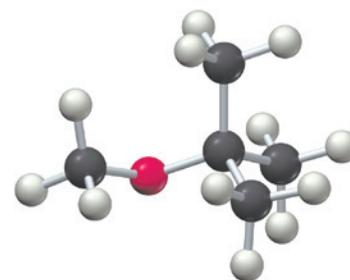
10.167 An empty 4.00 L steel vessel is filled with 1.00 atm of $\text{CH}_4(g)$ and 4.00 atm of $\text{O}_2(g)$ at 300 °C. A spark causes the CH_4 to burn completely, according to the equation:



- What mass of $\text{CO}_2(g)$ is produced in the reaction?
- What is the final temperature inside the vessel after combustion, assuming that the steel vessel has a mass of 14.500 kg, the mixture of gases has an average molar heat capacity of 21 J/(mol · °C), and the heat capacity of steel is 0.449 J/(g · °C)?
- What is the partial pressure of $\text{CO}_2(g)$ in the vessel after combustion?

10.168 When a gaseous compound **X** containing only C, H, and O is burned in O_2 , 1 volume of the unknown gas reacts with 3 volumes of O_2 to give 2 volumes of CO_2 and 3 volumes of gaseous H_2O . Assume all volumes are measured at the same temperature and pressure.

- (a) Calculate a formula for the unknown gas, and write a balanced equation for the combustion reaction.
- (b) Is the formula you calculated an empirical formula or a molecular formula? Explain.
- (c) Draw two different possible electron-dot structures for the compound **X**.
- (d) Combustion of 5.000 g of **X** releases 144.2 kJ heat. Look up ΔH_f° values for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ in Appendix B, and calculate ΔH_f° for compound **X**.
- 10.169** Isooctane, C_8H_{18} , is the component of gasoline from which the term *octane rating* derives.
- (a) Write a balanced equation for the combustion of isooctane to yield CO_2 and H_2O .
- (b) Assuming that gasoline is 100% isooctane, that isooctane burns to produce only CO_2 and H_2O , and that the density of isooctane is 0.792 g/mL, what mass of CO_2 in kilograms is produced each year by the annual U.S. gasoline consumption of 4.6×10^{10} L?
- (c) What is the volume in liters of this CO_2 at STP?
- (d) How many moles of air are necessary for the combustion of 1 mol of isooctane, assuming that air is 21.0% O_2 by volume? What is the volume in liters of this air at STP?
- 10.170** The *Rankine* temperature scale used in engineering is to the Fahrenheit scale as the Kelvin scale is to the Celsius scale. That is, 1 *Rankine* degree is the same size as 1 Fahrenheit degree, and $0^\circ\text{R} = \text{absolute zero}$.
- (a) What temperature corresponds to the freezing point of water on the Rankine scale?
- (b) What is the value of the gas constant R on the Rankine scale in $(\text{L} \cdot \text{atm})/(\text{R} \cdot \text{mol})$?
- (c) Use the van der Waals equation to determine the pressure inside a 400.0 mL vessel that contains 2.50 mol of CH_4 at a temperature of 525°R . For CH_4 , $a = 2.253 (\text{L}^2 \cdot \text{atm})/\text{mol}^2$ and $b = 0.04278 \text{ L/mol}$.
- 10.171** Chemical explosions are characterized by the instantaneous release of large quantities of hot gases, which set up a shock wave of enormous pressure (up to 700,000 atm) and velocity (up to 20,000 mi/h). For example, explosion of nitroglycerin ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$) releases four gases, **A**, **B**, **C**, and **D**:
- $$n \text{C}_3\text{H}_5\text{N}_3\text{O}_9(\text{l}) \longrightarrow a \text{A}(\text{g}) + b \text{B}(\text{g}) + c \text{C}(\text{g}) + d \text{D}(\text{g})$$
- Assume that the explosion of 1 mol (227 g) of nitroglycerin releases gases with a temperature of 1950°C and a volume of 1323 L at 1.00 atm pressure.
- (a) How many moles of hot gas are released by the explosion of 0.004 00 mol of nitroglycerin?
- (b) When the products released by explosion of 0.004 00 mol of nitroglycerin were placed in a 500.0 mL flask and the flask was cooled to -10°C , product **A** solidified and the pressure inside the flask was 623 mm Hg. How many moles of **A** were present, and what is its likely identity?
- (c) When gases **B**, **C**, and **D** were passed through a tube of powdered Li_2O , gas **B** reacted to form Li_2CO_3 . The remaining gases, **C** and **D**, were collected in another 500.0 mL flask and found to have a pressure of 260 mm Hg at 25°C . How many moles of **B** were present, and what is its likely identity?
- (d) When gases **C** and **D** were passed through a hot tube of powdered copper, gas **C** reacted to form CuO . The remaining gas, **D**, was collected in a third 500.0 mL flask and found to have a mass of 0.168 g and a pressure of 223 mm Hg at 25°C . How many moles each of **C** and **D** were present, and what are their likely identities?
- (e) Write a balanced equation for the explosion of nitroglycerin.
- 10.172** Combustion analysis of 0.1500 g of methyl *tert*-butyl ether, an octane booster used in gasoline, gave 0.3744 g of CO_2 and 0.1838 g of H_2O . When a flask having a volume of 1.00 L was evacuated and then filled with methyl *tert*-butyl ether vapor at a pressure of 100.0 kPa and a temperature of 54.8°C , the mass of the flask increased by 3.233 g.

Methyl *tert*-butyl ether

- (a) What is the empirical formula of methyl *tert*-butyl ether?
- (b) What is the molecular weight and molecular formula of methyl *tert*-butyl ether?
- (c) Write a balanced equation for the combustion reaction.
- (d) The enthalpy of combustion for methyl *tert*-butyl ether is $\Delta H_{\text{combustion}}^\circ = -3368.7 \text{ kJ/mol}$. What is its standard enthalpy of formation, ΔH_f° ?