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>
<thead>
<tr>
<th>Constituent</th>
<th>% Volume</th>
<th>% Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>78.08</td>
<td>75.52</td>
</tr>
<tr>
<td>O₂</td>
<td>20.95</td>
<td>23.14</td>
</tr>
<tr>
<td>Ar</td>
<td>0.93</td>
<td>1.29</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.040</td>
<td>0.060</td>
</tr>
<tr>
<td>Ne</td>
<td>1.82 × 10⁻³</td>
<td>1.27 × 10⁻³</td>
</tr>
<tr>
<td>He</td>
<td>5.24 × 10⁻⁴</td>
<td>7.24 × 10⁻⁵</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.7 × 10⁻⁴</td>
<td>9.4 × 10⁻⁵</td>
</tr>
<tr>
<td>Kr</td>
<td>1.14 × 10⁻⁴</td>
<td>3.3 × 10⁻⁵</td>
</tr>
</tbody>
</table>
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, \( a = 9.81 \text{ m/s}^2 \).

\[
\text{Pressure } P = \frac{F}{A} = \frac{ma}{A}.
\]

The SI unit for force is the newton (N), where \( 1 \text{ N} = 1 \text{ (kg \cdot m)}/\text{s}^2 \), and the SI unit for pressure is the pascal (Pa), where \( 1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ (kg \cdot m)}/(\text{m} \cdot \text{s}^2) \). 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 cm².

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

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 m² 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).

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

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).

\[
\frac{10,300 \text{ kg}}{1 \text{ m}^2} \times \frac{2.21 \text{ lb}}{1 \text{ kg}} \times \left( \frac{1 \text{ m}}{10^2 \text{ cm}} \right)^2 \times \left( \frac{2.54 \text{ cm}}{1 \text{ in.}} \right)^2 = 14.2 \text{ lb/in.}^2
\]

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 (1.359 51 × 10⁴ kg/m³ at 0°C) and the acceleration due to gravity (9.806 65 m/s²), 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:

\[
P = (0.760 \text{ m}) \left( 1.359 51 \times 10^4 \frac{\text{kg}}{\text{m}^3} \right) \left( 9.806 65 \frac{\text{m}}{\text{s}^2} \right) = 101,325 \text{ Pa}
\]

1 atm = 760 mm Hg = 101,325 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 bar = 100,000 Pa = 100 kPa = 0.986 923 atm

![FIGURE 10.3](image-url)

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.

*The empty space above the mercury in the sealed end of the tube is a vacuum.*

*The downward pressure of the mercury in the column is exactly balanced by the outside atmospheric pressure that presses down on the mercury in the dish and pushes it up the column.*

**TABLE 10.2** Conversions between Common Units of Pressure

<table>
<thead>
<tr>
<th>1 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa (1 N/m²)</td>
</tr>
<tr>
<td>kPa</td>
</tr>
<tr>
<td>bar</td>
</tr>
<tr>
<td>mm Hg</td>
</tr>
<tr>
<td>lb/in.$^2$ or psi</td>
</tr>
</tbody>
</table>

*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
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 $101,325 \text{ Pa} / 760 \text{ mm Hg}$, $1 \text{ atm} / 760 \text{ mm Hg}$, and $1 \text{ bar} / 10^5 \text{ Pa}$ to carry out the necessary calculations.

**SOLUTION**

\[
\begin{align*}
(265 \text{ mm Hg}) & \left( \frac{101,325 \text{ Pa}}{760 \text{ mm Hg}} \right) = 3.53 \times 10^4 \text{ Pa} \\
(265 \text{ mm Hg}) & \left( \frac{1 \text{ atm}}{760 \text{ mm Hg}} \right) = 0.349 \text{ atm} \\
(3.53 \times 10^4 \text{ Pa}) & \left( \frac{1 \text{ bar}}{10^5 \text{ Pa}} \right) = 0.353 \text{ bar}
\end{align*}
\]

**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**

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

▲ 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.

continued on next page


**Chapter 10  Gases: Their Properties and Behavior**

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.

(a) Draw a picture of the manometer similar to Figure 10.5.
(b) 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**  \( V = \frac{1}{P} \)  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.

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

At constant \( n \) and \( T \), the volume of an ideal gas decreases proportionately as its pressure increases.

If the pressure is doubled, the volume is halved.

If the pressure is halved, the volume is doubled.
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 \( y = mx + b \).

\[
V = k \left( \frac{1}{P} \right) + 0 \quad \text{(or } PV = k) \\
y = mx + b
\]

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.

\[
\text{Charles’s law } \quad V \propto T \quad \text{or } \quad V/T = k \quad \text{at constant } n \text{ and } P
\]

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.
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).

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

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.
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.

\[ n = 1 \text{ mol} \quad V = 22.4 \text{ L} \]
\[ n = 2 \text{ mol} \quad V = 44.8 \text{ L} \]

The volume of an ideal gas changes proportionately with its molar amount. If the molar amount doubles, the volume doubles. If the molar amount is halved, the volume is halved.

\[ \text{Avogadro’s law} \quad V \propto n \quad \text{or} \quad \frac{V}{n} = k \text{ at constant } T \text{ and } P \]

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.
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 laws 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.
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**

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

**Boyle’s law:**

\[ PV = nRT = k \] (When \( n \) and \( T \) are constant)

**Charles’s law:**

\[ \frac{V}{T} = \frac{nR}{P} = k \] (When \( n \) and \( P \) are constant)

**Avogadro’s law:**

\[ \frac{V}{n} = \frac{RT}{P} = k \] (When \( T \) and \( P \) 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 \( \text{L·atm} \)/(K·mol), or 8.3145 \( J/(\text{K}·\text{mol}) \) in SI units:

\[
R = \frac{P \cdot V}{n \cdot T} = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} = 0.082 058 \frac{\text{L·atm}}{\text{K·mol}}
\]

\[
= 8.3145 \frac{\text{J}}{\text{K}·\text{mol}} \quad (\text{When } P \text{ is in pascals and } V \text{ is in cubic meters})
\]

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**

\( T = 0 \degree \text{C} \quad P = 1 \text{ atm} \)

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

<table>
<thead>
<tr>
<th>Molar volume (L)</th>
<th>H₂</th>
<th>He</th>
<th>NH₃</th>
<th>N₂</th>
<th>F₂</th>
<th>Ar</th>
<th>CO₂</th>
<th>Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.43</td>
<td>22.41</td>
<td>22.40</td>
<td>22.40</td>
<td>22.38</td>
<td>22.09</td>
<td>22.40</td>
<td>22.06</td>
<td></td>
</tr>
</tbody>
</table>

---

*370  CHAPTER 10  Gases: Their Properties and Behavior*
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

<table>
<thead>
<tr>
<th>Known</th>
<th>Unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume ( (V = 3.8 \text{ L}) )</td>
<td>Moles of gas ( (n) )</td>
</tr>
<tr>
<td>Pressure ( (P = 1.00 \text{ atm}) )</td>
<td></td>
</tr>
<tr>
<td>Temperature ( (T = 37°C) )</td>
<td></td>
</tr>
</tbody>
</table>

STRATEGY

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

SOLUTION

\[
n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(3.8 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(310 \text{ K})} = 0.15 \text{ mol}
\]

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, \( \text{CH}_4 \), 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 \( (\text{C}_3\text{H}_8) \) as propellant. What is the pressure in atmospheres of gas in the can at 20 °C?

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

<table>
<thead>
<tr>
<th>Known</th>
<th>Unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pressure ( (P_i = 1.0 \text{ atm}) )</td>
<td>Final volume ( (V_f) )</td>
</tr>
<tr>
<td>Final pressure ( (P_f = 9.5 \text{ atm}) )</td>
<td></td>
</tr>
<tr>
<td>Initial volume ( (V_i = 410 \text{ mL}) )</td>
<td></td>
</tr>
</tbody>
</table>

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.

\[
PV = nRT = k
\]

continued on next page
Because pressure times volume is a constant (Boyle’s law), the equation \( P_1V_1 = P_2V_2 \) can be used to solve for the final volume:

\[
V_f = \frac{P_fV_i}{P_i} = \frac{(1.0 \text{ atm})(410 \text{ mL})}{(9.5 \text{ atm})} = 43 \text{ mL}
\]

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.

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

\[
3 \text{ H}_2(g) + \text{ N}_2(g) \rightarrow 2 \text{ NH}_3(g)
\]

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, \( \text{NaN}_3 \), to produce \( \text{N}_2 \) 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 \( \text{N}_2 \) gas at 1.15 atm and 30 °C are produced by decomposition of 45.0 g of \( \text{NaN}_3 \)?

\[
2 \text{NaN}_3(s) \rightarrow 2 \text{Na}(s) + 3 \text{N}_2(g)
\]

IDENTIFY

<table>
<thead>
<tr>
<th>Known</th>
<th>Unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure ( (P = 1.15 \text{ atm}) )</td>
<td>Volume of ( \text{N}_2 ) ( (V) )</td>
</tr>
<tr>
<td>Temperature ( (T = 30 \text{ °C}) )</td>
<td></td>
</tr>
<tr>
<td>Mass of ( \text{NaN}_3 ) (45.0 g)</td>
<td></td>
</tr>
</tbody>
</table>

STRATEGY

Use stoichiometric relationships to find the number of moles of \( \text{N}_2 \) produced from 45.0 g of \( \text{NaN}_3 \) and then use the ideal gas law to find the volume of \( \text{N}_2 \).

SOLUTION

To find \( n \), the number of moles of \( \text{N}_2 \) gas produced, we first need to find how many moles of \( \text{NaN}_3 \) are in 45.0 g:

\[
\text{Molar mass of } \text{NaN}_3 = 65.0 \text{ g/mol} \\
\text{Moles of } \text{NaN}_3 = \frac{45.0 \text{ g } \text{NaN}_3}{65.0 \text{ g } \text{NaN}_3} = 0.692 \text{ mol } \text{NaN}_3
\]
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 $N_2$:

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

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.

$$V = \frac{nRT}{P} = \frac{(1.04 \text{ mol } N_2) \times (0.08206 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times 303 \text{ K}}{1.15 \text{ atm}} = 22.5 \text{ L}$$

**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

$$CaCO_3(s) + 2 \text{HCl(aq)} \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

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

$$3 \text{H}_2(g) + N_2(g) \rightarrow 2 \text{NH}_3(g)$$

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

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

![Determining the density of an unknown gas.](image-url)
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.

\[
n = \frac{PV}{RT}_{\text{measured}} = \frac{PV}{RT}_{\text{STP}} \quad \text{or} \quad V_{\text{STP}} = \frac{PV}{RT}_{\text{measured}} = \frac{PV}{RT}_{\text{STP}}
\]

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

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.

\[
PV(M) = n(M)RT
\]

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

\[
PV(M) = mRT
\]

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

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

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

\[
\text{Gas density} \quad d = \frac{m}{V} = \frac{PM}{RT}
\]

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?
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.

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

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,

\[
P_1 = n_1 \left( \frac{RT}{V} \right) \quad P_2 = n_2 \left( \frac{RT}{V} \right) \quad P_3 = n_3 \left( \frac{RT}{V} \right) \ldots \quad \text{and so forth}
\]
But because all the gases in the mixture have the same temperature and volume, we can rewrite 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:

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

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:

$$ X_i = \frac{n_i}{n_{\text{total}}} $$

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

$$ X_i = \frac{P_i \left( \frac{V}{RT} \right)}{P_{\text{total}} \left( \frac{V}{RT} \right)} = \frac{P_i}{P_{\text{total}}} $$

which can be rearranged to solve for $P_i$.

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

$$ \text{Partial pressure} \quad P_i = X_i \cdot P_{\text{total}} $$

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 $\text{N}_2$, $\text{O}_2$, $\text{Ar}$, and $\text{CO}_2$ are 0.7808, 0.2095, 0.0093, and 0.0004, respectively (Table 10.1), and the total pressure of the air is the sum of the individual partial pressures:

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

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

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

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**

<table>
<thead>
<tr>
<th>Known</th>
<th>Unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of each gas</td>
<td>Partial pressure ( P_{H_2}, P_{N_2}, P_{NH_3} )</td>
</tr>
<tr>
<td>Volume ( V = 1.50 \text{ L} )</td>
<td>Total pressure ( P_{\text{tot}} )</td>
</tr>
<tr>
<td>Temperature ( T = 90 \text{ °C} )</td>
<td></td>
</tr>
</tbody>
</table>

**STRATEGY**

Convert the mass of each gas into moles using molar mass. Find the partial pressure of each gas using the general formula \( P_i = n_i \frac{RT}{V} \). Find the total pressure of the gas mixture by summing the partial pressure of each gas.

**SOLUTION**

Moles of each gas:

\[
\begin{align*}
5.50 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0 \text{ g H}_2} &= 2.75 \text{ mol H}_2 \\
7.31 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2} &= 0.261 \text{ mol N}_2 \\
2.42 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} &= 0.142 \text{ mol NH}_3
\end{align*}
\]

Partial pressure of each gas:

\[
\begin{align*}
P_{H_2} &= \frac{(2.75 \text{ mol H}_2) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(363 \text{ K})}{1.50 \text{ L}} = 54.6 \text{ atm} \\
P_{N_2} &= \frac{(0.261 \text{ mol N}_2) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(363 \text{ K})}{1.50 \text{ L}} = 5.18 \text{ atm} \\
P_{NH_3} &= \frac{(0.142 \text{ mol NH}_3) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(363 \text{ K})}{1.50 \text{ L}} = 2.81 \text{ atm}
\end{align*}
\]

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

\[
P_{\text{tot}} = P_{H_2} + P_{N_2} + P_{NH_3} = 54.6 \text{ atm} + 5.18 \text{ atm} + 2.81 \text{ atm} = 62.6 \text{ atm}
\]

**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 \( O_2 \) is 0.36, and the mole fraction of \( N_2 \) is 0.64 in a 10.0 L tank with a pressure of 50 atm at 25 °C.

(a) Calculate the partial pressure of \( O_2 \) and \( N_2 \).

(b) Calculate the number of moles of \( O_2 \) and \( N_2 \).

**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?

\[\text{The partial pressure of oxygen in the scuba tanks must be the same underwater as in air at atmospheric pressure.}\]
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** ($P_{\text{total}} = P_1 + P_2 + \ldots$): 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

$$E_K = \frac{3}{2} \frac{RT}{N_A} = \frac{1}{2} mu^2$$
which can be rearranged to give

\[ u^2 = \frac{3RT}{mn_A} \]

or

\[ u = \sqrt{\frac{3RT}{mn_A}} = \sqrt{\frac{3RT}{M}} \]

where \( M \) is the molar mass.

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

\[
\begin{align*}
u &= \sqrt{\frac{(3)(8.314 \frac{\text{J}}{\text{K \cdot mol}})(298 \text{ K})}{4.00 \times 10^{-3} \frac{\text{kg}}{\text{mol}}}} \\
&= \sqrt{\frac{1.86 \times 10^6 \frac{\text{J}}{\text{kg}}}{\text{kg} \cdot \text{m}^2/\text{kg}}} \\
&= \sqrt{1.36 \times 10^3 \frac{\text{m}^2}{\text{s}^2/\text{kg}}} \\
&= 1.36 \times 10^3 \text{ m/s}
\end{align*}
\]

\[ \text{A FIGURE 10.12} \]

A kinetic–molecular view of the gas laws.
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 $2 \times 10^{-7}$ m, or 1000 atomic diameters, and there are approximately $10^{10}$ collisions per second. For a larger O$_2$ molecule, the mean free path is about $6 \times 10^{-8}$ 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).

### Table 10.6 Average Speeds (m/s) of Some Gas Molecules at 25 °C

<table>
<thead>
<tr>
<th>Molar mass (g/mol)</th>
<th>Average speed (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1960 H$_2$</td>
</tr>
<tr>
<td>4.0</td>
<td>1360 He</td>
</tr>
<tr>
<td>18.0</td>
<td>650 H$_2$O</td>
</tr>
<tr>
<td>28.0</td>
<td>320 N$_2$</td>
</tr>
<tr>
<td>32.0</td>
<td>490 O$_2$</td>
</tr>
<tr>
<td>44.0</td>
<td>415 CO$_2$</td>
</tr>
</tbody>
</table>

**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.
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.

\[ \text{Rate}_1 \cdot \frac{1}{\sqrt{m_1}} = \text{Rate}_2 \cdot \frac{1}{\sqrt{m_2}} \]

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:

\[ \frac{1}{2} m u^2 = \frac{3 RT}{2 N_A} \text{ for any gas} \]

then \( \left( \frac{1}{2} m u^2 \right)_{\text{gas 1}} = \left( \frac{1}{2} m u^2 \right)_{\text{gas 2}} \) at the same \( T \)

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:

\[ \frac{u_{\text{gas 1}}}{u_{\text{gas 2}}} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{m_2}{m_1}} \]

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.
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 $^{235}\text{U}$ (0.72%) and $^{238}\text{U}$ (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:

For $^{235}\text{UF}_6$, $m = 349.03$
For $^{238}\text{UF}_6$, $m = 352.04$

so

\[
\frac{\text{Rate of }^{235}\text{UF}_6\text{ diffusion}}{\text{Rate of }^{238}\text{UF}_6\text{ diffusion}} = \sqrt{\frac{352.04}{349.03}} = 1.0043
\]

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? (H = $^1\text{H}$) and (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

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

Comparing H$_2$ with D$_2$, we have

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

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$_2$H$_2$)

**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?
At lower pressure, the volume of the gas particles is negligible compared to the total volume.

At higher pressure, the volume of the gas particles is more significant compared to the total volume. As a result, the volume of a real gas at high pressure is somewhat larger than the ideal value.

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 \( \frac{an^2}{V^2} \) to the pressure.

\[
\begin{align*}
\text{van der Waals equation} \\
\text{Correction for intermolecular attractions} & \quad \text{Correction for molecular volume} \\
\left( P + \frac{an^2}{V^2} \right) (V - nb) &= nRT \\
or P &= \frac{nRT}{V - nb} - \frac{an^2}{V^2}
\end{align*}
\]
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
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:

- Percent by volume = \( (X_a) \times 100 \)
- Parts per million (ppm) by volume = \( (X_a) \times 10^6 \)
- 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.

(a) Express the concentration of CO as a percentage.

(b) Find the number of CO molecules inhaled in one breath if an average breath of air contains \( 3.3 \times 10^{-2} \) total moles of gas.

**IDENTIFY**

<table>
<thead>
<tr>
<th>Known</th>
<th>Unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of CO (155 ppm)</td>
<td>Concentration in units of percent</td>
</tr>
<tr>
<td>Moles of gas (( 3.3 \times 10^{-2} ))</td>
<td>Number of CO molecules</td>
</tr>
</tbody>
</table>

**STRATEGY**

(a) 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.

(b) 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) \( 155 \text{ ppm} = (X_{CO}) \times 10^6 \)

\[
X_{CO} = \frac{155}{1 \times 10^6} = 1.55 \times 10^{-4}
\]

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

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

\[
= 3.00 \times 10^{18} \text{ molecules CO}
\]
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 $3.3 \times 10^{-2}$ 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$_2$O. The balanced combustion reaction for natural gas (CH$_4$) is:

$$\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$$

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:

$$\text{CH}_4(g) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{CO}(g) + 2 \text{H}_2\text{O}(l)$$

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 μg/dL...
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 PM₁₀ classification corresponds to “inhalable coarse particles” (such as those found near roadways and industry), which have diameters between 2.5 and 10 µm. PM₂.₅ 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 (SO₂) is a highly reactive gas that is a major contributor to particulate pollution and acid rain. The largest sources of SO₂ 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 (FeS₂). When coal is burned, sulfur is converted in gaseous SO₂, which is emitted directly to the atmosphere unless it is removed by a process called scrubbing. A smaller source of SO₂ emissions is smelting which extracts metals from their ores.

SO₂ is very irritating to tissues and damaging to vegetation. Exposure to SO₂(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 (NO₂) and ozone (O₃) 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.

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

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.
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.

\[
\ce{N2 + O2 + heat -> 2 NO} \tag{1}
\]

The NO is further oxidized by reaction with oxygen to yield nitrogen dioxide, NO₂, which splits into NO plus free oxygen atoms (O) in the presence of sunlight (symbolized by \( \text{hv} \)). Highly reactive oxygen atoms then combine with oxygen molecules to make ozone (O₃).

\[
\ce{NO2 + hv (\lambda < 400nm) -> NO + O(g)} \tag{2}
\]

\[
\ce{O(g) + O2 -> O3} \tag{3}
\]

These two reactions alone would not necessarily produce unhealthy levels of ozone because the amount of ozone depends on the initial amount of NO₂. An additional reaction that regenerates NO₂, however, can initiate a cyclic process in which one molecule of NO₂ forms many molecules of ozone. Volatile organic compounds (VOCs) participate in reactions that regenerate NO₂ 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 NO₂ which can produce more ozone. The cycle continues as long as there is nitric oxide from combustion, sunlight, and VOCs.

\[
\text{VOCs}
\]

\[
\ce{NO2 + hv (\lambda < 400nm) -> NO + O(g)}
\]
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 NO$_2$. By noon NO$_2$ begins to decline as sunlight breaks the nitrogen–oxygen bond, forming O atoms which react with O$_2$ to form O$_3$. O$_3$ 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 SO$_2$, 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

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Percent Change (1980–2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide (CO)</td>
<td>-83%</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>-91%</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO$_2$)</td>
<td>-60%</td>
</tr>
<tr>
<td>Ozone (O$_3$)</td>
<td>-25%</td>
</tr>
<tr>
<td>Sulfur dioxide (SO$_2$)</td>
<td>-78%</td>
</tr>
<tr>
<td>Particulate Pollution</td>
<td></td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>-33% (2000–2012)</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>-39% (1990–2012)</td>
</tr>
</tbody>
</table>

#### Figure 10.18
Time profile for pollutants in a photochemical smog event.

**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.
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).
A hot electric burner emits black body radiation.
Why are some atmospheric gases classified as greenhouse gases and others are not? The two most concentrated gases in the atmosphere N₂ (∼80% by volume) and O₂ (∼20% by volume) do not absorb infrared radiation and therefore are not classified as greenhouse gases. In contrast, CO₂ 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 CO₂ is a greenhouse gas and N₂ and O₂ 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.

In the symmetric stretch, both oxygen atoms carry 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.

\[
\mu = Q \times r
\]

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 CO₂ to a bent geometry. Once the atoms reach their new positions the motion is reversed and the atoms oscillate around their original position. Every CO₂ 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 CO₂ 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 CO₂ 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 CO₂ molecule creating a net dipole moment. Therefore, the asymmetric stretch absorbs IR radiation.

**Bending (scissoring) vibration:** The bending vibration changes CO₂ 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 CO₂ 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.

**REMEMBER…**

The measure of net molecular polarity is a quantity called the dipole moment, \( \mu \) (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\(_2\)O), methane (CH\(_3\)), 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 (CH\(_2\)ClF\(_2\)) 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 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\(_2\)O 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 CO₂ and CH₄ 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 CO₂ 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, N₂O 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 (²H:¹H) in H₂O in ice core samples helps scientists estimate long-term shifts in average global temperature. Figure 10.25 shows the correlation between past carbon dioxide (CO₂)
carbon dioxide concentration (ppm) and methane concentration (ppb) over the past 800,000 years.

**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.

**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.

**Source:**

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

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
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.
### STUDY GUIDE

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<td>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.</td>
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<td>The behavior of gases can be accounted for using a model called the kinetic–molecular theory, a group of five postulates: 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.</td>
<td>10.6 Calculate the density or molar mass of a gas using the formula for gas density.</td>
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Section Concept Summary

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.

Learning Objectives
10.10 Visualize the processes of effusion and diffusion.
10.11 Use Graham’s Law to estimate relative rates of diffusion for two gases.

Test Your Understanding
Problems 10.35, 10.37

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.

Learning Objectives
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.

Test Your Understanding
Problems 10.106, 10.107

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.

Learning Objectives
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.

Test Your Understanding
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.

Learning Objectives
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.

Test Your Understanding
Problems 10.130–10.132

KEY TERMS

atmosphere (atm) 361
diffusion 380
dalton’s law 364
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**KEY EQUATIONS**

- **Boyle's law (Section 10.2)**
  \[ V \propto \frac{1}{P} \text{ or } PV = k \text{ at constant } n \text{ and } T \]

- **Charles's law (Section 10.2)**
  \[ V \propto T \text{ or } \frac{V}{T} = k \text{ at constant } n \text{ and } P \]

- **Avogadro's law (Section 10.2)**
  \[ V \propto n \text{ or } \frac{V}{n} = k \text{ at constant } T \text{ and } P \]

- **Ideal gas law (Section 10.3)**
  \[ V = \frac{nRT}{P} \text{ or } PV = nRT \]

- **Standard temperature and pressure (STP) for gases (Section 10.3)**
  \[ T = 0^\circ C \quad P = 1 \text{ atm} \]

- **Gas density (Section 10.4)**
  \[ d = \frac{m}{V} = \frac{PM}{RT} \]

- **Dalton's law of partial pressures (Section 10.5)**
  \[ P_{\text{total}} = P_1 + P_2 + P_3 + \ldots \]
  where \( P_1, P_2, \ldots \) 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)**
  \[ P_i = X_i \cdot P_{\text{total}} \]

- **Average speed of gas particle at temperature \( T \) (Section 10.6)**
  \[ u = \sqrt{\frac{3RT}{mN_A}} = \sqrt{\frac{3RT}{M}} \text{ where } M \text{ is the molar mass.} \]

- **Graham's law (Section 10.7)**
  \[ \text{Rate of effusion} \propto \frac{1}{\sqrt{m}} \]

- **van der Waals equation (Section 10.8)**
  \[ \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT \text{ or } P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \]
  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.

![Diagram of gas particles]

**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)?

(a) ![Diagram of blue and red circles]
(b) ![Diagram of blue circles]
(c) ![Diagram of red circles]
(d) ![Diagram of blue circles]

**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?

![Diagram of four gases]

**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.

![Diagram of three bulbs]

**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.

(a) ![Diagram of green gas with piston](initial) 
   - $T = 25 \, ^\circ\text{C}$
   - $n = 0.075 \, \text{mol}$
   - $P = 0.92 \, \text{atm}$

(b) ![Diagram of green gas with piston](a) 
   - $T = 50 \, ^\circ\text{C}$
   - $n = 0.075 \, \text{mol}$
   - $P = 0.92 \, \text{atm}$

(c) ![Diagram of green gas with piston](b) 
   - $T = 175 \, ^\circ\text{C}$
   - $n = 0.22 \, \text{mol}$
   - $P = 2.7 \, \text{atm}$

(d) ![Diagram of green gas with piston](c) 
   - $T = 25 \, ^\circ\text{C}$
   - $n = 0.075 \, \text{mol}$
   - $P = 2.7 \, \text{atm}$
**Gases and Gas Pressure (Section 10.1)**

10.37 Effusion of a 1:1 mixture of two gases through a small pinhole produces the results shown below.

(a) Which gas molecules—yellow or blue—have a higher average speed?

(b) 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:

(a) 352 torr to kPa

(b) 0.255 atm to mm Hg

(c) 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?

---

**The Gas Laws (Sections 10.2 and 10.3)**

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?

---

**Calculate the average molecular weight of air from the data given in Table 10.1.**

**What is the average molecular weight of a diving-gas mixture that contains 2.0% by volume O₂ and 98.0% by volume He?**

---

**Carry out the following conversions:**

(a) 352 torr to kPa

(b) 0.255 atm to mm Hg

(c) 0.0382 mm Hg to Pa

---

**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?**

---

**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?**

---

**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?**

---

**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?**

---

**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?**

(a) Triple the Kelvin temperature while holding the volume constant

(b) Reduce the amount of gas by one-third while holding the temperature and volume constant

(c) Decrease the volume by 45% at constant T

(d) Halve the Kelvin temperature and triple the volume

---

**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?**

(a) Halve the Kelvin temperature while holding the pressure constant

(b) Increase the amount of gas by one-fourth while holding the temperature and pressure constant

(c) Decrease the pressure by 75% at constant T

(d) Double the Kelvin temperature and double the pressure

---

**Which sample contains more molecules: 2.50 L of air at STP, or 1.00 L of He at STP?**

**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?**

**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?**

**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?**

**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?**

**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 70.4% H₂O by volume. At 714 mm Hg and 1111 mm Hg pressure or 11.07 g of Cl₂? What is the density in g/L of a gas mixture that contains 27.0% O₂ and 1111 mm Hg pressure or 11.07 g of Cl₂?

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:

\[
2 \text{HgO} (s) \rightarrow 2 \text{Hg}(l) + \text{O}_2 (g)
\]

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:

\[
\text{Zn}(s) + 2 \text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)
\]

(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

\[
2 \text{NH}_4\text{NO}_3(s) \rightarrow 2 \text{N}_2(g) + 4 \text{H}_2\text{O}(g) + \text{O}_2(g)
\]

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:

\[
2 \text{Na}_2\text{O}_2(s) + \text{CO}_2(g) \rightarrow 2 \text{Na}_2\text{CO}_3(s) + \text{O}_2(g)
\]

(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:

\[
2 \text{TiCl}_4(g) + \text{H}_2(g) \rightarrow 2 \text{TiCl}_3(s) + \text{HCl}(g)
\]

(a) How many grams of TiCl₃ 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 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

\[
\text{C}_3\text{H}_8(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)
\]

(a) How many liters of CO₂ would be formed at 742 mm Hg and 15°C if 43.8 g of propane is burned at STP?
(b) How many grams of zinc would you start with if you wanted to prepare 2.3 L of CO₂ at 350 mm Hg and 30.0°C?

### 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?
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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:

\[ \text{Mg}(s) + 2 \text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g) \]

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:

\[ 2 \text{NaCl}(s) + 2 \text{H}_2\text{SO}_4(l) + \text{MnO}_2(s) \rightarrow \text{Na}_2\text{SO}_4(s) + 2 \text{H}_2\text{O}(g) + \text{Cl}_2(g) \]

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 °C) and on a cold day in winter (T = -25 °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 (L²·atm)/mol² and b = 0.0387 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 (L²·atm)/mol² and b = 0.0387 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 × 10¹⁵ 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 g/mol) + 0.80 (28.0 g/mol) = 28.8 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 (PM₁₀ or PM₂.₅)? 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 (N₂O) in dry air at sea level is $5 \times 10^{-5}\%$. What is the concentration of N₂O in units of ppm and ppb?

10.118 The concentration of SO₂ in the air was measured to be 0.26 μg/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 SO₂ to the atmosphere is coal-fired power plants. Calculate the volume of SO₂ in L produced by burning 1 kg of coal that contains 2% sulfur. Assume all the sulfur is converted to SO₂.

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 (PbSO₃). Lead(II) sulfite is then thermally decomposed into lead(II) oxide and sulfur dioxide gas. Balance the following equation.

PbSO₃(s) $\underset{\text{heat}}{\rightarrow}$ PbO(s) + SO₂(g)

(b) How many liters of SO₂ are produced at 1 atm and 300 °C, if 250 g of PbSO₃ 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 NO₂ 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 O₃, NO₂, 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.

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.
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Daily Peak AQI (Combined PM$_{2.5}$ and O$_3$) August 8, 2012

Daily Peak AQI (Combined PM$_{2.5}$ and O$_3$) 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)
(a) The sun most strongly emits in the _______ and _______ regions of electromagnetic radiation.
(b) The atmosphere filters out biologically damaging _______ radiation from incoming solar radiation and prevents it from reaching Earth.
(c) The Earth most strongly emits _______ radiation.
(d) Greenhouse gases absorb _______ radiation.

10.131 (a) 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.
(b) 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.
(c) 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 (O$_3$) is a harmful pollutant in the troposphere. Draw the electron-dot structure for ozone (O$_3$) 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 CO$_2$ and CH$_4$ 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.

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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, $^{35}$Cl and $^{37}$Cl. What is the ratio of the diffusion rates of the three species ($^{35}$Cl)$_2$, $^{35}$Cl$^{37}$Cl, and ($^{37}$Cl)$_2$?

10.140 What would the atmospheric pressure be in millimeters of mercury if our atmosphere were composed of pure CO$_2$ 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, sublimes at 56.5 °C. Assume that you have a 22.9 L vessel that contains 512.9 g of UF$_6$ at 70.0 °C.
(a) What is the pressure in the vessel calculated using the ideal gas law?
(b) What is the pressure in the vessel calculated using the van der Waals equation? (For UF$_6$, $a = 15.80$ (L$^2$ atm)/mol$^2$; $b = 0.1128$ 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 O$_2$. 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 \( P = e^{-h/7600} \), 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: \( I_2(g) \rightarrow 2 I(g) \). 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\(_2\)O(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\(_2\) sublimes at −78 °C, and N\(_2\) boils at −196 °C.

10.152 Assume that you have 1.00 g of nitroglycerin in a 500.0 mL steel container at 200.0 °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

\[
4 C_3H_5N_3O_9(l) \rightarrow 12 CO_2(g) + 10 H_2O(l) + 6 N_2(g) + O_2(g)
\]

(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\(_3\), \( a = 4.17 \text{ (L}^2\text{ atm)} \text{/mol}^2 \) and \( b = 0.0371 \text{ L/mol} \).

10.154 When solid mercury(I) carbonate, Hg\(_2\)CO\(_3\), 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:

\[
\text{Hg}_2\text{CO}_3(s) + \text{HNO}_3(aq) \rightarrow \text{Hg(NO}_3)_2(aq) + \text{H}_2\text{O(l)} + \text{A(g)} + \text{B(g)}
\]

(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):

\[
\text{CaO(s)} + \text{A(g)} \rightarrow \text{CaCO}_3(s)
\]

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 C$_n$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 2.00 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.

(a) What is the formula and molar mass of the hydrocarbon?
(b) What are the partial pressures in atmospheres of the reactants?
(c) 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$_2$H$_6$). 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.

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

10.158 A mixture of CS$_2$(g) and excess 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

$$\text{CS}_2(g) + 3 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{SO}_2(g)$$

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.

(a) What is the molar mass of Q, and what is a likely formula?
(b) 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 Ca(ClO$_3$)$_2$ and Ca(ClO$_4$)$_2$ is heated to 700 °C in a 10.0 L vessel, both compounds decompose, forming O$_2$(g) and CaCl$_2$(s). The final pressure inside the vessel is 1.00 atm.

(a) Write balanced equations for the decomposition reactions.
(b) 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 POCI$_5$. 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 NOCl(g) was heated to 225 °C in a 400.0 L steel reaction vessel, the NOCl partially decomposed according to the equation

$$2 \text{NOCl}(g) \rightarrow 2 \text{NO}(g) + \text{Cl}_2(g)$$

The pressure in the vessel after reaction is 0.246 atm.

(a) What is the partial pressure of each gas in the vessel after reaction?
(b) 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 O$_2$(g) → 2 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 °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

$$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$$

(a) 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.
(b) 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 CO$_2$(g) are $a = 3.59 \text{ (L}^2 \cdot \text{atm})/\text{mol}^2$ and $b = 0.0427 \text{ L/mol}$.

10.165 Nitrogen dioxide dimerizes to give dinitrogen tetroxide: 2 NO$_2$(g) → N$_2$O$_4$(g). At 298 K, 9.66 g of an NO$_2$/N$_2$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 CH$_4$(g) and 4.00 atm of O$_2$(g) at 300 °C. A spark causes the CH$_4$ to burn completely, according to the equation:

$$\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \quad \Delta H^\circ = -802 \text{ kJ}$$

(a) What mass of CO$_2$(g) is produced in the reaction?
(b) 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)?
(c) What is the partial pressure of 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$_2$O. 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 $\Delta H_r^\circ$ values for CO$_2$(g) and H$_2$O(g) in Appendix B, and calculate $\Delta H_r^\circ$ for compound X.

10.169 Isooctane, C$_8$H$_{18}$, is the component of gasoline from which the term octave rating derives.
(a) Write a balanced equation for the combustion of isoctane to yield CO$_2$ and H$_2$O.
(b) Assuming that gasoline is 100% isoctane, that isoctane burns to produce only CO$_2$ and H$_2$O, and that the density of isoctane 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 x 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 isoctane, 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 °R = 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 (L · atm)/(°R · 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$_4$, $a = 2.253$ (L$^2$ · atm)/mol$^2$ and $b = 0.04278$ 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 (C$_5$H$_{11}$N$_3$O$_7$) releases four gases, A, B, C, and D:

$$n \text{C}_5\text{H}_{11}\text{N}_3\text{O}_7(l) \rightarrow a \text{A}(g) + b \text{B}(g) + c \text{C}(g) + d \text{D}(g)$$

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$_2$O, gas B reacted to form Li$_2$CO$_3$. 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 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$_2$O. 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.

(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 $\Delta H_{\text{combustion}}^\circ = -3368.7$ kJ/mol. What is its standard enthalpy of formation, $\Delta H_f^\circ$?