INTRODUCTION

Under certain conditions of pressure and temperature, most substances can exist in any one of the three states of matter: solid, liquid, or gas. Water, for example, can be solid ice, liquid water, or steam or water vapor. The physical properties of a substance often depend on its state.

Gases, the subject of this chapter, are much simpler than liquids or solids in many ways. Molecular motion in gases is totally random, and the forces of attraction between gas molecules are so small that each molecule moves freely and essentially independently of other molecules. Subjected to changes in temperature and pressure, gases behave much more predictably than do solids and liquids. The laws that govern this behavior have played an important role in the development of the atomic theory of matter and the kinetic molecular theory of gases.

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5.2 PRESSURE OF A GAS
5.3 THE GAS LAWS
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5.5 GAS STOICHIOMETRY
5.6 DALTON’S LAW OF PARTIAL PRESSURES
5.7 THE KINETIC MOLECULAR THEORY OF GASES
5.8 DEVIATION FROM IDEAL BEHAVIOR
5.1 SUBSTANCES THAT EXIST AS GASES

We live at the bottom of an ocean of air whose composition by volume is roughly 78 percent \( \text{N}_2 \), 21 percent \( \text{O}_2 \), and 1 percent other gases, including \( \text{CO}_2 \). In the 1990s, the chemistry of this vital mixture of gases has become a source of great interest because of the detrimental effects of environmental pollution. The chemistry of the atmosphere and polluting gases is discussed in Chapter 17. Here we will focus generally on the behavior of substances that exist as gases under normal atmospheric conditions, which are defined as 25°C and 1 atmosphere (atm) pressure (see Section 5.2).

Figure 5.1 shows the elements that are gases under normal atmospheric conditions. Note that hydrogen, nitrogen, oxygen, fluorine, and chlorine exist as gaseous diatomic molecules: \( \text{H}_2 \), \( \text{N}_2 \), \( \text{F}_2 \), and \( \text{Cl}_2 \). An allotrope of oxygen, ozone \( (\text{O}_3) \), is also a gas at room temperature. All the elements in Group 8A, the noble gases, are monatomic gases: \( \text{He} \), \( \text{Ne} \), \( \text{Ar} \), \( \text{Kr} \), \( \text{Xe} \), and \( \text{Rn} \).

Ionic compounds do not exist as gases at 25°C and 1 atm, because cations and anions in an ionic solid are held together by very strong electrostatic forces. To overcome these attractions we must apply a large amount of energy, which in practice means strongly heating the solid. Under normal conditions, all we can do is melt the solid; for example, \( \text{NaCl} \) melts at the rather high temperature of 801°C. In order to boil it, we would have to raise the temperature to well above 1000°C.

The behavior of molecular compounds is more varied. Some—for example, \( \text{CO}, \) \( \text{CO}_2 \), \( \text{HCl} \), \( \text{NH}_3 \), and \( \text{CH}_4 \) (methane)—are gases, but the majority of molecular compounds are liquids or solids at room temperature. However, on heating they are converted to gases much more easily than ionic compounds. In other words, molecular compounds usually boil at much lower temperatures than ionic compounds do. There is no simple rule to help us determine whether a certain molecular compound is a gas under normal atmospheric conditions. To make such a determination we need to understand the nature and magnitude of the attractive forces among the molecules, called intermolecular forces (discussed in Chapter 11). In general, the stronger these attractions, the less likely a compound can exist as a gas at ordinary temperatures.

Of the gases listed in Table 5.1, only \( \text{O}_2 \) is essential for our survival. Hydrogen sulfide \( (\text{H}_2\text{S}) \) and hydrogen cyanide \( (\text{HCN}) \) are deadly poisons. Several others, such as \( \text{CO} \), \( \text{NO}_2 \), \( \text{O}_3 \), and \( \text{SO}_2 \), are somewhat less toxic. The gases \( \text{He} \), \( \text{Ne} \), and \( \text{Ar} \) are chemically inert; that is, they do not react with any other substance. Most gases are colorless. Exceptions are \( \text{F}_2 \), \( \text{Cl}_2 \), and \( \text{NO}_2 \). The dark-brown color of \( \text{NO}_2 \) is sometimes visible in polluted air. All gases have the following physical characteristics:

- Gases assume the volume and shape of their containers.
- Gases are the most compressible of the states of matter.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.

5.2 PRESSURE OF A GAS

Gases exert pressure on any surface with which they come in contact, because gas molecules are constantly in motion. We humans have adapted so well physiologically to the pressure of the air around us that we are usually unaware of it, perhaps as fish are not conscious of the water’s pressure on them.
A gas is a substance that is normally in the gaseous state at ordinary temperatures and pressures; a vapor is the gaseous form of any substance that is a liquid or a solid at normal temperatures and pressures. Thus, at 25°C and 1 atm pressure, we speak of water vapor and oxygen gas.

It is easy to demonstrate atmospheric pressure. One everyday example is the ability to drink a liquid through a straw. Sucking air out of the straw reduces the pressure inside the straw. The greater atmospheric pressure on the liquid pushes it up into the straw to replace the air that has been sucked out.

### SI UNITS OF PRESSURE

Pressure is one of the most readily measurable properties of a gas. In order to understand how we measure the pressure of a gas, it is helpful to know how the units of measurement are derived. We begin with velocity and acceleration.

*Velocity* is defined as the change in distance with elapsed time; that is

\[
\text{velocity} = \frac{\text{distance moved}}{\text{elapsed time}}
\]

### TABLE 5.1 Some Substances Found as Gases at 1 atm and 25°C

<table>
<thead>
<tr>
<th>ELEMENTS</th>
<th>COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (molecular hydrogen)</td>
<td>HF (hydrogen fluoride)</td>
</tr>
<tr>
<td>N₂ (molecular nitrogen)</td>
<td>HCl (hydrogen chloride)</td>
</tr>
<tr>
<td>O₂ (molecular oxygen)</td>
<td>HBr (hydrogen bromide)</td>
</tr>
<tr>
<td>O₃ (ozone)</td>
<td>HI (hydrogen iodide)</td>
</tr>
<tr>
<td>F₂ (molecular fluorine)</td>
<td>CO (carbon monoxide)</td>
</tr>
<tr>
<td>Cl₂ (molecular chlorine)</td>
<td>CO₂ (carbon dioxide)</td>
</tr>
<tr>
<td>He (helium)</td>
<td>NH₃ (ammonia)</td>
</tr>
<tr>
<td>Ne (neon)</td>
<td>NO (nitric oxide)</td>
</tr>
<tr>
<td>Ar (argon)</td>
<td>NO₂ (nitrogen dioxide)</td>
</tr>
<tr>
<td>Kr (krypton)</td>
<td>N₂O (nitrous oxide)</td>
</tr>
<tr>
<td>Xe (xenon)</td>
<td>SO₂ (sulfur dioxide)</td>
</tr>
<tr>
<td>Rn (radon)</td>
<td>H₂S (hydrogen sulfide)</td>
</tr>
<tr>
<td></td>
<td>HCN (hydrogen cyanide)*</td>
</tr>
</tbody>
</table>

*The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.*

---

**FIGURE 5.1** Elements that exist as gases at 25°C and 1 atm. The noble gases (the Group 8A elements) are monatomic species; the other elements exist as diatomic molecules. Ozone (O₃) is also a gas.
The SI unit for velocity is m/s, although we also use cm/s. Acceleration is the change in velocity with time, or

\[
\text{acceleration} = \frac{\text{change in velocity}}{\text{elapsed time}}
\]

Acceleration is measured in m/s² (or cm/s²).

The second law of motion, formulated by Sir Isaac Newton† in the late seventeenth century, defines another term, from which the units of pressure are derived, namely, force. According to this law,

\[
\text{force} = \text{mass} \times \text{acceleration}
\]

In this context, the SI unit of force is the newton (N), where

\[
1 \text{ N} = 1 \text{ kg m/s}^2
\]

Finally, we define pressure as force applied per unit area:

\[
\text{pressure} = \frac{\text{force}}{\text{area}}
\]

The SI unit of pressure is the pascal (Pa),‡ defined as one newton per square meter:

\[
1 \text{ Pa} = 1 \text{ N/m}^2
\]

**ATMOSPHERIC PRESSURE**

The atoms and molecules of the gases in the atmosphere, like those of all other matter, are subject to Earth’s gravitational pull. As a consequence, the atmosphere is much denser near the surface of Earth than at high altitudes. (The air outside the pressurized cabin of an airplane at 9 km is too thin to breathe.) In fact, the density of air decreases very rapidly with increasing distance from Earth (Figure 5.2). Measurements show that about 50 percent of the atmosphere lies within 6.4 km of Earth’s surface, 90 percent within 16 km, and 99 percent within 32 km. Not surprisingly the denser the air is, the greater the pressure it exerts. The force experienced by any area exposed to Earth’s atmosphere is equal to the weight of the column of air above it. Atmospheric pressure is the pressure exerted by Earth’s atmosphere. The actual value of atmospheric pressure depends on location, temperature, and weather conditions.

How is atmospheric pressure measured? The barometer is probably the most familiar instrument for measuring atmospheric pressure. A simple barometer consists of a long glass tube, closed at one end and filled with mercury. If the tube is carefully inverted in a dish of mercury so that no air enters the tube, some mercury will flow out of the tube into the dish, creating a vacuum at the top (Figure 5.3). The weight of the mercury remaining in the tube is supported by atmospheric pressure acting on the surface of the mercury in the dish. Standard atmospheric pressure (1 atm) is equal to the pressure that supports a column of mercury exactly 760 mm (or 76 cm) high at 0°C at sea level. In other words, the standard atmosphere equals a pressure of 760 mmHg, where mmHg represents the pressure exerted by a column of mercury 1 mm high. The

---

1 Sir Isaac Newton (1642–1726). English mathematician, physicist, and astronomer. Newton is regarded by many as one of the two greatest physicists the world has known (the other is Albert Einstein). There was hardly a branch of physics to which Newton did not make a significant contribution. His book *Principia*, published in 1687, marks a milestone in the history of science.

2 Blaise Pascal (1623–1662). French mathematician and physicist. Pascal’s work ranged widely in mathematics and physics, but his specialty was in the area of hydrodynamics (the study of the motion of fluids). He also invented a calculating machine.
The mmHg unit is also called the torr, after the Italian scientist Evangelista Torricelli,† who invented the barometer. Thus

\[ 1 \text{ torr} = 1 \text{ mmHg} \]

and

\[ 1 \text{ atm} = 760 \text{ mmHg} \]
\[ = 760 \text{ torr} \]

The relation between atmospheres and pascals (see Appendix 2) is

\[ 1 \text{ atm} = 101,325 \text{ Pa} \]
\[ = 1.01325 \times 10^5 \text{ Pa} \]

and since 1000 Pa = 1 kPa (kilopascal)

\[ 1 \text{ atm} = 1.01325 \times 10^2 \text{ kPa} \]

The following examples show the conversion from mmHg to atm and kPa.

**EXAMPLE 5.1**

The pressure outside a jet plane flying at high altitude falls considerably below standard atmospheric pressure. Therefore, the air inside the cabin must be pressurized to protect the passengers. What is the pressure in atmospheres in the cabin if the barometer reading is 688 mmHg?

**Answer** The pressure in atmospheres is calculated as follows:

\[ \text{pressure} = \frac{688 \text{ mmHg}}{760 \text{ mmHg}} = 0.905 \text{ atm} \]

**PRACTICE EXERCISE**

Convert 749 mmHg to atmospheres.

**EXAMPLE 5.2**

The atmospheric pressure in San Francisco on a certain day was 732 mmHg. What was the pressure in kPa?

**Answer** The conversion equations show that

\[ 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} \]

which allow us to calculate the atmospheric pressure in kPa:

\[ \text{pressure} = \frac{732 \text{ mmHg}}{760 \text{ mmHg}} \times 1.01325 \times 10^5 \text{ Pa} \]
\[ = 9.76 \times 10^4 \text{ Pa} \]
\[ = 97.6 \text{ kPa} \]

**PRACTICE EXERCISE**

Convert 295 mmHg to kilopascals.

---

†Evangelista Torricelli (1608–1674). Italian mathematician. Torricelli was supposedly the first person to recognize the existence of atmospheric pressure.
A manometer is a device used to measure the pressure of gases other than the atmosphere. The principle of operation of a manometer is similar to that of a barometer. There are two types of manometers, shown in Figure 5.4. The closed-tube manometer is normally used to measure pressures below atmospheric pressure [Figure 5.4(a)] while the open-tube manometer is better suited for measuring pressures equal to or greater than atmospheric pressure [Figure 5.4(b)].

Nearly all barometers and most manometers use mercury as the working fluid, despite the fact that it is a toxic substance with a harmful vapor. The reason is that mercury has a very high density (13.6 g/mL) compared with most other liquids. Since the height of the liquid in a column is inversely proportional to the liquid’s density, this property allows the construction of manageably small barometers and manometers.

5.3 THE GAS LAWS

The gas laws we will study in this chapter are the product of countless experiments on the physical properties of gases that were carried out over several centuries. Each of these generalizations regarding the macroscopic behavior of gaseous substances represents a milestone in the history of science. Together they have played a major role in the development of many ideas in chemistry.

THE PRESSURE-VOLUME RELATIONSHIP: BOYLE’S LAW

In the seventeenth century, Robert Boyle\(^\text{3}\) studied the behavior of gases systematically and quantitatively. In one series of studies, Boyle investigated the pressure-volume re-

\(^3\)Robert Boyle (1627–1691). British chemist and natural philosopher. Although Boyle is commonly associated with the gas law that bears his name, he made many other significant contributions in chemistry and physics. Although he was often at odds with contemporary scientists, his book *The Skeptical Chymist* (1661) influenced generations of chemists.
FIGURE 5.5 Apparatus for studying the relationship between pressure and volume of a gas. In (a) the pressure of the gas is equal to the atmospheric pressure. The pressure exerted on the gas increases from (a) to (d) as mercury is added, and the volume of the gas decreases, as predicted by Boyle’s law. The extra pressure exerted on the gas is shown by the difference in the mercury levels (h mmHg). The temperature of the gas is kept constant.

The pressure applied to a gas is equal to the gas pressure.

The relationship of a gas sample using an apparatus like that shown in Figure 5.5. In Figure 5.5(a) the pressure exerted on the gas by the mercury added to the tube is equal to atmospheric pressure. In Figure 5.5(b) an increase in pressure due to the addition of more mercury results in a decrease in the volume of the gas and in unequal levels of mercury in the tube. Boyle noticed that when temperature is held constant, the volume \( V \) of a given amount of a gas decreases as the total applied pressure \( P \)—atmospheric pressure plus the pressure due to the added mercury—is increased. This relationship between pressure and volume is evident in Figure 5.5(b), (c), and (d). Conversely, if the applied pressure is decreased, the gas volume becomes larger. The results of several pressure-volume measurements are given in Table 5.2.

The \( P-V \) data recorded in Table 5.2 are consistent with this mathematical expression showing an inverse relationship:

\[
V \propto \frac{1}{P}
\]

where the symbol \( \propto \) means proportional to. To change \( \propto \) to an equals sign, we must write

\[
V = k_1 \times \frac{1}{P} \quad \text{(5.1a)}
\]

where \( k_1 \) is a constant called the proportionality constant. Equation (5.1a) is an expression of Boyle’s law, which states that the volume of a fixed amount of gas maintained at constant temperature is inversely proportional to the gas pressure. We can rearrange Equation (5.1a) and obtain

\[
PV = k_1 \quad \text{(5.1b)}
\]

<table>
<thead>
<tr>
<th>( P ) (mmHg)</th>
<th>724</th>
<th>869</th>
<th>951</th>
<th>998</th>
<th>1230</th>
<th>1893</th>
<th>2250</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V ) (arbitrary units)</td>
<td>1.50</td>
<td>1.33</td>
<td>1.22</td>
<td>1.16</td>
<td>0.94</td>
<td>0.61</td>
<td>0.51</td>
</tr>
<tr>
<td>( PV )</td>
<td>( 1.09 \times 10^3 )</td>
<td>( 1.16 \times 10^3 )</td>
<td>( 1.16 \times 10^3 )</td>
<td>( 1.16 \times 10^3 )</td>
<td>( 1.2 \times 10^3 )</td>
<td>( 1.2 \times 10^3 )</td>
<td>( 1.1 \times 10^3 )</td>
</tr>
</tbody>
</table>
This form of Boyle’s law says that the product of the pressure and volume of a gas at constant temperature is a constant.

The concept of one quantity being proportional to another and the use of a proportionality constant can be clarified through the following analogy. The daily income of a movie theater depends on both the price of the tickets (in dollars per ticket) and the number of tickets sold. Assuming that the theater charges one price for all tickets, we write

\[
\text{income} = \text{(dollar/ticket)} \times \text{number of tickets sold}
\]

Since the number of tickets sold varies from day to day, the income on a given day is said to be proportional to the number of tickets sold:

\[
\text{income} \propto \text{number of tickets sold} = C \times \text{number of tickets sold}
\]

where \(C\), the proportionality constant, is the price per ticket.

Figure 5.6 shows two conventional ways of expressing Boyle’s findings graphically. Figure 5.6(a) is a graph of the equation \(PV = k_1\); Figure 5.6(b) is a graph of the equivalent equation \(P = k_1 / V\). Note that the latter is a linear equation of the form \(y = mx + b\), where \(b = 0\).

Although the individual values of pressure and volume can vary greatly for a given sample of gas, as long as the temperature is held constant and the amount of the gas does not change, \(P\) times \(V\) is always equal to the same constant. Therefore, for a given sample of gas under two different sets of conditions at constant temperature, we have

\[
P_1V_1 = k_1 = P_2V_2
\]

or

\[
P_1V_1 = P_2V_2 \quad (5.2)
\]

where \(V_1\) and \(V_2\) are the volumes at pressures \(P_1\) and \(P_2\), respectively.

One common application of Boyle’s law is predicting how the volume of a gas will be affected by a change in pressure or how the pressure exerted by a gas will be affected by a change in volume based on Equation (5.2). Example 5.3 illustrates the procedure for solving problems with Boyle’s law.

**FIGURE 5.6**  Graphs showing variation of the volume of a gas sample with the pressure exerted on the gas, at constant temperature. (a) \(P\) versus \(V\). Note that the volume of the gas doubles as the pressure is halved; (b) \(P\) versus \(1/V\).
EXAMPLE 5.3

An inflated balloon has a volume of 0.55 L at sea level (1.0 atm) and is allowed to rise to a height of 6.5 km, where the pressure is about 0.40 atm. Assuming that the temperature remains constant, what is the final volume of the balloon?

Answer

We use Equation (5.2):

\[ P_1 V_1 = P_2 V_2 \]

where

<table>
<thead>
<tr>
<th>INITIAL CONDITIONS</th>
<th>FINAL CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_1 = 1.0 \text{ atm} )</td>
<td>( P_2 = 0.40 \text{ atm} )</td>
</tr>
<tr>
<td>( V_1 = 0.55 \text{ L} )</td>
<td>( V_2 = ? )</td>
</tr>
</tbody>
</table>

Therefore

\[ V_2 = V_1 \times \frac{P_1}{P_2} \]

\[ = 0.55 \text{ L} \times \frac{1.0 \text{ atm}}{0.40 \text{ atm}} \]

\[ = 1.4 \text{ L} \]

Comment

When pressure is reduced (at constant temperature), volume increases. The final volume is greater than the initial volume, so the answer is reasonable.

PRACTICE EXERCISE

A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. Calculate the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL.

THE TEMPERATURE-VOLUME RELATIONSHIP: CHARLES’ AND GAY-LUSSAC’S LAW

Boyle’s law depends on the temperature of the system remaining constant. But suppose the temperature changes: How does a change in temperature affect the volume and pressure of a gas? Let us first look at the effect of temperature on the volume of a gas. The earliest investigators of this relationship were French scientists, Jacques Charles\(^1\) and Joseph Gay-Lussac.\(^2\) Their studies showed that, at constant pressure, the volume of a gas sample expands when heated and contracts when cooled (Figure 5.7). The quantitative relations involved in changes in gas temperature and volume turn out to be remarkably consistent. For example, we observe an interesting phenomenon when we study the temperature-volume relationship at various pressures. At any given pressure, the plot of volume versus temperature yields a straight line. By extending the line to zero volume, we find the intercept on the temperature axis to be \(-273.15^\circ\text{C}\). At any other pressure, we obtain a different straight line for the volume-temperature plot, but we get the same zero-volume temperature intercept at \(-273.15^\circ\text{C}\) (Figure 5.8). (In practice, we can measure the volume of a gas over only a limited temperature range, because all gases condense at low temperatures to form liquids.)

\(^1\)Jacques Alexandre Cesar Charles (1746–1823). French physicist. He was a gifted lecturer, an inventor of scientific apparatus, and the first person to use hydrogen to inflate balloons.

\(^2\)Joseph Louis Gay-Lussac (1778–1850). French chemist and physicist. Like Charles, Gay-Lussac was a balloon enthusiast. Once he ascended to an altitude of 20,000 feet to collect air samples for analysis.
In 1848 Lord Kelvin† realized the significance of this phenomenon. He identified \( -273.15 \, ^\circ C \) as absolute zero, theoretically the lowest attainable temperature. Then he set up an absolute temperature scale, now called the Kelvin temperature scale, with absolute zero as the starting point (see Section 1.6). On the Kelvin scale, one kelvin (K) is equal in magnitude to one degree Celsius. The only difference between the absolute temperature scale and the Celsius scale is that the zero position is shifted. Important points on the two scales match up as follows:

- Absolute zero: \( 0 \, K = -273.15 \, ^\circ C \)
- Freezing point of water: \( 273.15 \, K = 0 \, ^\circ C \)
- Boiling point of water: \( 373.15 \, K = 100 \, ^\circ C \)

The conversion between \(^\circ C\) and K is given on p. 18. In most calculations we will use 273 instead of 273.15 as the term relating K and \(^\circ C\). By convention, we use \( T \) to denote absolute (kelvin) temperature and \( t \) to indicate temperature on the Celsius scale.

The dependence of the volume of a gas on temperature is given by

\[
V \propto T
\]

or

\[
\frac{V}{T} = k_2
\]  

(5.3)

where \( k_2 \) is the proportionality constant. Equation (5.3) is known as Charles’ and Gay-Lussac’s law, or simply Charles’ law, which states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas.

Just as we did for pressure-volume relationships at constant temperature, we can compare two sets of volume-temperature conditions for a given sample of gas at constant pressure. From Equation (5.3) we can write

\[
\frac{V_1}{T_1} = k_2 = \frac{V_2}{T_2}
\]

or

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2}
\]  

(5.4)

where \( V_1 \) and \( V_2 \) are the volumes of the gases at temperatures \( T_1 \) and \( T_2 \) (both in kelvins), respectively. In all subsequent calculations we assume that the temperatures given in °C are exact, so that they do not affect the number of significant figures.

The following example illustrates the use of Charles’ law.

**EXAMPLE 5.4**

A 452-mL sample of fluorine gas is heated from 22°C to 187°C at constant pressure. What is its final volume?

**Answer** We use Equation (5.4),

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2}
\]

where

<table>
<thead>
<tr>
<th>INITIAL CONDITIONS</th>
<th>FINAL CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_1 = 452 \text{ mL} )</td>
<td>( V_2 = ? )</td>
</tr>
<tr>
<td>( T_1 = (22 + 273) \text{ K} )</td>
<td>( T_2 = (187 + 273) \text{ K} )</td>
</tr>
</tbody>
</table>

Hence

\[
V_2 = V_1 \times \frac{T_2}{T_1}
\]

\[
= 452 \text{ mL} \times \frac{460 \text{ K}}{295 \text{ K}}
\]

\[
= 705 \text{ mL}
\]

**Comment** As you can see, when the gas is heated at constant pressure, it expands.

**PRACTICE EXERCISE**

A sample of carbon monoxide gas occupies 3.20 L at 125°C. Calculate the temperature at which the gas will occupy 1.54 L if the pressure remains constant.

---

**THE VOLUME-AMOUNT RELATIONSHIP: AVOGADRO’S LAW**

The work of the Italian scientist Amedeo Avogadro complemented the studies of Boyle, Charles, and Gay-Lussac. In 1811 he published a hypothesis stating that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules (or atoms if the gas is monatomic). It follows that the volume of any given gas must be proportional to the number of moles of molecules present; that is,

\[
V \propto n
\]

\[
V = k_3 n
\]  

(5.5)

where \( n \) represents the number of moles and \( k_3 \) is the proportionality constant.

Equation (5.5) is the mathematical expression of **Avogadro’s law**, which states that at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present. From Avogadro’s law we learn that when two gases react with each other, their reacting volumes have a simple ratio to each other. If the product is a gas, its volume is related to the volume of the reactants by a simple ratio (a fact demonstrated earlier by Gay-Lussac). For example, consider the synthesis of ammonia from molecular hydrogen and molecular nitrogen:

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

3 mol 1 mol 2 mol
Since, at the same temperature and pressure, the volumes of gases are directly proportional to the number of moles of the gases present, we can now write

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

The volume ratio of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to molecular hydrogen and molecular nitrogen combined (the reactants) is 2:4, or 1:2 (Figure 5.9).

### 5.4 THE IDEAL GAS EQUATION

Let us summarize the gas laws we have discussed so far:

- **Boyle’s law:** \( V \propto \frac{1}{P} \) (at constant \( n \) and \( T \))
- **Charles’ law:** \( V \propto T \) (at constant \( n \) and \( P \))
- **Avogadro’s law:** \( V \propto n \) (at constant \( P \) and \( T \))

We can combine all three expressions to form a single master equation for the behavior of gases:

$$V \propto \frac{nT}{P}$$

or

$$PV = nRT$$

(5.6)

where \( R \), the proportionality constant, is called the **gas constant**. Equation (5.6), which is called the **ideal gas equation**, describes the relationship among the four variables \( P, V, T, \) and \( n \). An **ideal gas** is a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation. The molecules of an ideal gas do not attract or repel one another, and their volume is negligible compared with the volume of the container. Although there is no such thing in nature as an ideal gas, discrepancies in the behavior of real gases over reasonable temperature and pressure ranges do not significantly affect calculations. Thus we can safely use the ideal gas equation to solve many gas problems.

Before we can apply the ideal gas equation to a real system, we must evaluate the gas constant \( R \). At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an
ideal gas. Experiments show that under these conditions, 1 mole of an ideal gas occupies 22.414 L, which is somewhat greater than the volume of a basketball, as shown in Figure 5.10. The conditions 0°C and 1 atm are called standard temperature and pressure, often abbreviated STP. From Equation (5.6) we can write

\[
R = \frac{PV}{nT}
\]

\[
= \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})}
\]

\[
= 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}
\]

\[
= 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}
\]

The dots between L and atm and between K and mol remind us that both L and atm are in the numerator and both K and mol are in the denominator. For most calculations, we will round off the value of \( R \) to three significant figures (0.0821 \( \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \)) and use 22.41 L for the molar volume of a gas at STP.

The following example shows that if we know the quantity, volume, and temperature of a gas, we can calculate its pressure using the ideal gas equation.

**EXAMPLE 5.5**

Sulfur hexafluoride (SF\(_6\)) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C.

**Answer** Rearranging the ideal gas equation we write

\[
P = \frac{nRT}{V}
\]

\[
= \frac{(1.82 \text{ mol})(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}})(69.5 + 273) \text{ K}}{5.43 \text{ L}}
\]

\[
= 9.42 \text{ atm}
\]
**PRACTICE EXERCISE**

Calculate the volume (in liters) occupied by 2.12 moles of nitric oxide (NO) at 6.54 atm and 76°C.

By using the fact that the molar volume of a gas occupies 22.41 L at STP, we can calculate the volume of a gas at STP without using the ideal gas equation.

**EXAMPLE 5.6**

Calculate the volume (in liters) occupied by 7.40 g of CO₂ at STP.

**Answer**

Recognizing that 1 mole of an ideal gas occupies 22.41 L at STP, we write

\[
V = \frac{7.40 \text{ g CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol CO}_2}{22.41 \text{ L}} = 3.77 \text{ L}
\]

**PRACTICE EXERCISE**

What is the volume (in liters) occupied by 49.8 g of HCl at STP?

The ideal gas equation is useful for problems that do not involve changes in \( P, V, T, \) and \( n \) for a gas sample. At times, however, we need to deal with changes in pressure, volume, and temperature, or even in the amount of a gas. When conditions change, we must employ a modified form of the ideal gas equation that takes into account the initial and final conditions. We derive the modified equation as follows. From Equation (5.6),

\[
R = \frac{P_1V_1}{n_1T_1} \quad \text{(before change)}
\]

and

\[
R = \frac{P_2V_2}{n_2T_2} \quad \text{(after change)}
\]

so that

\[
\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}
\]

If \( n_1 = n_2 \), as is usually the case because the amount of gas normally does not change, the equation then becomes

\[
\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{(5.7)}
\]

Applications of Equation (5.7) are the subject of the following two examples.

**EXAMPLE 5.7**

A small bubble rises from the bottom of a lake, where the temperature and pressure are 8°C and 6.4 atm, to the water’s surface, where the temperature is 25°C and pressure is 1.0 atm. Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL.
We can use any appropriate units for volume (or pressure) as long as we use the same units on both sides of the equation.

**Answer** We start by writing

<table>
<thead>
<tr>
<th>INITIAL CONDITIONS</th>
<th>FINAL CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1 = 6.4 \text{ atm}$</td>
<td>$P_2 = 1.0 \text{ atm}$</td>
</tr>
<tr>
<td>$V_1 = 2.1 \text{ mL}$</td>
<td>$V_2 = ?$</td>
</tr>
<tr>
<td>$T_1 = (8 + 273) \text{ K} = 281 \text{ K}$</td>
<td>$T_2 = (25 + 273) \text{ K} = 298 \text{ K}$</td>
</tr>
</tbody>
</table>

The amount of the gas in the bubble remains constant, so that $n_1 = n_2$. To calculate the final volume, $V_2$, we rearrange Equation (5.7) as follows:

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$$= 2.1 \text{ mL} \times \frac{6.4 \text{ atm}}{1.0 \text{ atm}} \times \frac{298 \text{ K}}{281 \text{ K}}$$

$$= 14 \text{ mL}$$

Thus, the bubble’s volume increases from 2.1 mL to 14 mL because of the decrease in water pressure and the increase in temperature.

**PRACTICE EXERCISE**

A gas initially at 4.0 L, 1.2 atm, and $66{^\circ}\text{C}$ undergoes a change so that its final volume and temperature become 1.7 L and $42{^\circ}\text{C}$. What is its final pressure? Assume the number of moles remains unchanged.

**EXAMPLE 5.8**

Argon is an inert gas used in light bulbs to retard the vaporization of the filament. A certain light bulb containing argon at 1.20 atm and $18{^\circ}\text{C}$ is heated to $85{^\circ}\text{C}$ at constant volume. Calculate its final pressure (in atm).

**Answer** The volume and amount of the gas are unchanged, so $V_1 = V_2$ and $n_1 = n_2$. Equation (5.7) can therefore be written as

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Next we write

<table>
<thead>
<tr>
<th>INITIAL CONDITIONS</th>
<th>FINAL CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1 = 1.20 \text{ atm}$</td>
<td>$P_2 = ?$</td>
</tr>
<tr>
<td>$T_1 = (18 + 273) \text{ K} = 291 \text{ K}$</td>
<td>$T_2 = (85 + 273) \text{ K} = 358 \text{ K}$</td>
</tr>
</tbody>
</table>

The final pressure is given by

$$P_2 = P_1 \times \frac{T_2}{T_1}$$

$$= 1.20 \text{ atm} \times \frac{358 \text{ K}}{291 \text{ K}}$$

$$= 1.48 \text{ atm}$$

**Comment** At constant volume, the pressure of a given amount of gas is directly proportional to its absolute temperature. Therefore the increase in pressure is reasonable here.

---

Electric light bulbs are usually filled with argon.

One practical consequence of this relationship is that automobile tire pressures should be checked only when the tires are at normal temperatures. After a long drive (especially in the summer), tires become quite hot, and the air pressure inside them rises.

Similar problem: 5.34.
PRACTICE EXERCISE
A sample of oxygen gas initially at 0.97 atm is cooled from 21°C to −68°C at constant volume. What is its final pressure (in atm)?

DENSITY CALCULATIONS
If we rearrange the ideal gas equation, we can calculate the density of a gas:

\[ \frac{n}{V} = \frac{P}{RT} \]

The number of moles of the gas, \( n \), is given by

\[ n = \frac{m}{M} \]

where \( m \) is the mass of the gas in grams and \( M \) is its molar mass. Therefore

\[ \frac{m}{M} = \frac{P}{RT} \]

Since density, \( d \), is mass per unit volume, we can write

\[ d = \frac{m}{V} = \frac{P \cdot M}{RT} \quad (5.8) \]

Unlike molecules in condensed matter (that is, in liquids and solids), gaseous molecules are separated by distances that are large compared with their size. Consequently, the density of gases is very low under atmospheric conditions. For this reason, gas densities are usually expressed in grams per liter (g/L) rather than grams per milliliter (g/mL), as the following example shows.

EXAMPLE 5.9
Calculate the density of ammonia (NH₃) in grams per liter (g/L) at 752 mmHg and 55°C.

Answer To convert the pressure to atmospheres, we write

\[ P = 752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \]

\[ = \left( \frac{752}{760} \right) \text{ atm} \]

Using Equation (5.8) and \( T = 273 + 55 = 328 \) K, we have

\[ d = \frac{P \cdot M}{RT} \]

\[ = \frac{(752/760) \text{ atm}(17.03 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(328 \text{ K})} \]

\[ = 0.626 \text{ g/L} \]

Comment In units of grams per milliliter, the gas density would be \( 6.26 \times 10^{-4} \) g/mL, which is a very small number.
**PRACTICE EXERCISE**

What is the density (in g/L) of uranium hexafluoride (UF₆) at 779 mmHg and 62°C?

---

**THE MOLAR MASS OF A GASEOUS SUBSTANCE**

From what we have said so far, you may have the impression that the molar mass of a substance is found by examining its formula and summing the molar masses of its component atoms. However, this procedure works only if the actual formula of the substance is known. In practice, chemists often deal with substances of unknown or only partially defined composition. If the unknown substance is gaseous, its molar mass can nevertheless be found thanks to the ideal gas equation. All that is needed is an experimentally determined density value (or mass and volume data) for the gas at a known temperature and pressure. By rearranging Equation (5.8) we get

\[
\frac{d}{P} = \frac{dRT}{P}
\]  

(5.9)

In a typical experiment, a bulb of known volume is filled with the gaseous substance under study. The temperature and pressure of the gas sample are recorded, and the total mass of the bulb plus gas sample is determined (Figure 5.11). The bulb is then evacuated (emptied) and weighed again. The difference in mass is the mass of the gas. The density of the gas is equal to its mass divided by the volume of the bulb. Once we know the density of a gas, we can calculate the molar mass of the substance using Equation (5.9). Example 5.10 shows this calculation.

---

**EXAMPLE 5.10**

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.

**Answer** We substitute in Equation (5.9):

\[
\frac{d}{P} = \frac{dRT}{P} = \frac{(7.71 \text{ g/L})(0.0821 \text{ L \cdot atm/K \cdot mol})(36 + 273) \text{ K}}{2.88 \text{ atm}}
\]

= 67.9 g/mol

We can determine the molecular formula of the compound by trial and error, using only the knowledge of the molar masses of chlorine (35.45 g) and oxygen (16.00 g). We know that a compound containing one Cl atom and one O atom would have a molar mass of 51.45 g, which is too low, while the molar mass of a compound made up of two Cl atoms and one O atom is 86.90 g, which is too high. Thus the compound must contain one Cl atom and two O atoms and have the formula ClO₂, which has a molar mass of 67.45 g.

**PRACTICE EXERCISE**

The density of a gaseous organic compound is 3.38 g/L at 40°C and 1.97 atm. What is its molar mass?
Since Equation (5.9) is derived from the ideal gas equation, we can also calculate the molar mass of a gaseous substance using the ideal gas equation, as shown below.

**EXAMPLE 5.11**

Chemical analysis of a gaseous compound showed that it contained 33.0 percent silicon and 67.0 percent fluorine by mass. At 35°C, 0.210 L of the compound exerted a pressure of 1.70 atm. If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

**Answer** First we determine the empirical formula of the compound.

\[
\begin{align*}
  n_{\text{Si}} &= 33.0 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 1.17 \text{ mol Si} \\
  n_{\text{F}} &= 67.0 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 3.53 \text{ mol F}
\end{align*}
\]

Therefore, the formula is Si\(_{1.17}\)F\(_{3.53}\), or SiF\(_3\). Next, we calculate the number of moles contained in 2.38 g of the compound. From the idea gas equation

\[
(n) = \frac{PV}{RT} = \frac{(1.70 \text{ atm})(0.210 \text{ L})}{(0.0821 \text{ L·atm/K·mol})(308 \text{ K})} = 0.0141 \text{ mol}
\]

Therefore, the molar mass of the compound is

\[
M = \frac{2.38 \text{ g}}{0.0141 \text{ mol}} = 169 \text{ g/mol}
\]

The empirical molar mass of SiF\(_3\) (empirical formula) is 85.09 g. Therefore the molecular formula of the compound must be Si\(_2\)F\(_6\), because \(2 \times 85.09\), or 170.2 g, is very close to 169 g.

**PRACTICE EXERCISE**

A gaseous compound is 78.14 percent boron and 21.86 percent hydrogen. At 27°C, 74.3 mL of the gas exerted a pressure of 1.12 atm. If the mass of the gas was 0.0934 g, what is its molecular formula?

---

**5.5 GAS STOICHIOMETRY**

In Chapter 3 we used relationships between amounts (in moles) and masses (in grams) of reactants and products to solve stoichiometry problems. When the reactants and/or products are gases, we can also use the relationships between amounts (moles, \(n\)) and volume (\(V\)) to solve such problems (Figure 5.12). The following examples show how the gas laws are used in these calculations.
EXAMPLE 5.12

Calculate the volume of O₂ (in liters) at STP required for the complete combustion of 2.64 L of acetylene (C₂H₂) at STP:

\[ 2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]

**Answer** Since both C₂H₂ and O₂ are gases measured at the same temperature and pressure, according to Avogadro’s law their reacting volumes are related to their coefficients in the balanced equation; that is, 2 L of C₂H₂ react with 5 L of O₂. Knowing this ratio we can calculate the volume (in liters) of O₂ that will react with 2.64 L of C₂H₂.

\[
\text{volume of } \text{O}_2 = \frac{2.64 \text{ L C}_2\text{H}_2}{2} \times \frac{5 \text{ L O}_2}{5} = 6.60 \text{ L O}_2
\]

PRACTICE EXERCISE

Assuming no change in temperature and pressure, calculate the volume of O₂ (in liters) required for the complete combustion of 14.9 L of butane (C₄H₁₀):

\[ 2\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 10\text{H}_2\text{O}(l) \]

EXAMPLE 5.13

Sodium azide (NaN₃) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN₃ as follows:

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

The nitrogen gas produced quickly inflates the bag between the driver and the windshield. Calculate the volume of N₂ generated at 21°C and 823 mmHg by the decomposition of 60.0 g of NaN₃.

**Answer** From the balanced equation we see that 2 mol NaN₃ ⊆ 3 mol N₂. The number of moles of N₂ produced by 60.0 g NaN₃ is

\[
\text{moles of } \text{N}_2 = \frac{60.0 \text{ g NaN}_3}{65.02 \text{ g NaN}_3} \times \frac{1 \text{ mol NaN}_3}{2 \text{ mol NaN}_3} \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} = 1.38 \text{ moles of } \text{N}_2
\]

The volume of 1.38 moles of N₂ can be obtained by using the ideal gas equation:

\[
V = \frac{nRT}{P} = \frac{(1.38 \text{ mol})(0.0821 \text{ L atm/K mol})(294 \text{ K})}{(823/760) \text{ atm}} = 30.8 \text{ L}
\]

PRACTICE EXERCISE

The equation for the metabolic breakdown of glucose (C₆H₁₂O₆) is the same as the equation for the combustion of glucose in air:

\[ \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

Calculate the volume of CO₂ produced at 37°C and 1.00 atm when 5.60 g of glucose are used up in the reaction.
The air in submerged submarines and space vehicles needs to be purified continuously.

Similar problem: 5.93.

EXAMPLE 5.14

Aqueous lithium hydroxide solution is used to purify air in spacecrafts and submarines because it absorbs carbon dioxide according to the equation

\[ 2\text{LiOH}(aq) + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \]

The pressure of carbon dioxide in a cabin having a volume of \(2.4 \times 10^5\) L is \(7.9 \times 10^{-3}\) atm at 312 K. A solution of lithium hydroxide (LiOH) of negligible volume is introduced into the cabin. Eventually the pressure of \(\text{CO}_2\) is reduced to \(1.2 \times 10^{-3}\) atm. How many grams of lithium carbonate are formed by this process?

**Answer**

First we calculate the number of moles of \(\text{CO}_2\) consumed in the reaction. The drop in pressure, which is \(7.9 \times 10^{-3}\) atm \(- 1.2 \times 10^{-4}\) atm, or \(7.8 \times 10^{-3}\) atm, corresponds to the consumption of \(\text{CO}_2\). Using the ideal gas equation, we write

\[ n = \frac{PV}{RT} \]

\[ = \frac{(7.8 \times 10^{-3}\text{ atm})(2.4 \times 10^5\text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(312\text{ K})} = 73\text{ mol} \]

From the equation we see that 1 mol \(\text{CO}_2\) \(\rightarrow 1\) mol \(\text{Li}_2\text{CO}_3\), so the amount of \(\text{Li}_2\text{CO}_3\) formed is also 73 moles. Then, with the molar mass of \(\text{Li}_2\text{CO}_3\) (73.89 g) we calculate its mass:

\[ \text{mass of } \text{Li}_2\text{CO}_3 \text{ formed} = 73\text{ mol} \times \frac{73.89\text{ g}}{1\text{ mol}} = 5.4 \times 10^3\text{ g} \]

PRACTICE EXERCISE

A 2.14-L sample of hydrogen chloride gas at 2.61 atm and 28°C is completely dissolved in 668 mL of water to form hydrochloric acid solution. Calculate the molarity of the acid solution.

5.6 DALTON’S LAW OF PARTIAL PRESSURES

Thus far we have concentrated on the behavior of pure gaseous substances, but experimental studies very often involve mixtures of gases. For example, for a study of air pollution, we may be interested in the pressure-volume-temperature relationship of a sample of air, which contains several gases. In this case, and all cases involving mixtures of gases, the total gas pressure is related to partial pressures, that is, the pressures of individual gas components in the mixture. In 1801 Dalton formulated a law, now known as Dalton’s law of partial pressures, which states that the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone.

Consider a case in which two gases, A and B, are in a container of volume V. The pressure exerted by gas A, according to the ideal gas equation, is

\[ P_A = \frac{n_A RT}{V} \]
where \( n_A \) is the number of moles of A present. Similarly, the pressure exerted by gas B is

\[
P_B = \frac{n_B RT}{V}
\]

In a mixture of gases A and B, the total pressure \( P_T \) is the result of the collisions of both types of molecules, A and B, with the walls of the container. Thus, according to Dalton’s law,

\[
P_T = P_A + P_B
\]

\[
= \frac{n_A RT}{V} + \frac{n_B RT}{V}
\]

\[
= \frac{RT}{V} (n_A + n_B)
\]

\[
= \frac{nRT}{V}
\]

where \( n \), the total number of moles of gases present, is given by \( n = n_A + n_B \), and \( P_A \) and \( P_B \) are the partial pressures of gases A and B, respectively. For a mixture of gases, then, \( P_T \) depends only on the total number of moles of gas present, not on the nature of the gas molecules.

In general, the total pressure of a mixture of gases is given by

\[
P_T = P_1 + P_2 + P_3 + \ldots
\]

where \( P_1, P_2, P_3, \ldots \) are the partial pressures of components 1, 2, 3, \ldots. To see how each partial pressure is related to the total pressure, consider again the case of a mixture of two gases A and B. Dividing \( P_A \) by \( P_T \), we obtain

\[
\frac{P_A}{P_T} = \frac{n_A RT/V}{(n_A + n_B)RT/V}
\]

\[
= \frac{n_A}{n_A + n_B}
\]

\[
= X_A
\]

where \( X_A \) is called the mole fraction of gas A. The mole fraction is a dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present. It is always smaller than 1, except when A is the only component present. In that case, \( n_B = 0 \) and \( X_A = n_A/n_A = 1 \). We can express the partial pressure of A as

\[
P_A = X_A P_T
\]

Similarly,

\[
P_B = X_B P_T
\]

Note that the sum of the mole fractions for a mixture of gases must be unity. If only two components are present, then

\[
X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1
\]

If a system contains more than two gases, then the partial pressure of the \( i \)th component is related to the total pressure by
\[ P_i = X_i P_T \]  

(5.10)

where \( X_i \) is the mole fraction of substance \( i \).

How are partial pressures determined? A manometer can measure only the total pressure of a gaseous mixture. To obtain the partial pressures, we need to know the mole fractions of the components, which would involve elaborate chemical analyses. The most direct method of measuring partial pressures is using a mass spectrometer. The relative intensities of the peaks in a mass spectrum are directly proportional to the amounts, and hence to the mole fractions, of the gases present.

From mole fractions and total pressure, we can calculate the partial pressures of individual components, as Example 5.15 shows. A direct application of Dalton’s law of partial pressures to scuba diving is discussed in the Chemistry in Action essay on p. 179.

**EXAMPLE 5.15**

A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe). Calculate the partial pressures of the gases if the total pressure is 2.00 atm at a certain temperature.

**Answer** The mole fraction of Ne is

\[
X_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} = \frac{4.46 \text{ mol}}{4.46 \text{ mol} + 0.74 \text{ mol} + 2.15 \text{ mol}} = 0.607
\]

From Equation (5.10)

\[
P_{\text{Ne}} = X_{\text{Ne}} P_T = 0.607 \times 2.00 \text{ atm} = 1.21 \text{ atm}
\]

Similarly,

\[
P_{\text{Ar}} = 0.10 \times 2.00 \text{ atm} = 0.20 \text{ atm}
\]

and

\[
P_{\text{Xe}} = 0.293 \times 2.00 \text{ atm} = 0.586 \text{ atm}
\]

**PRACTICE EXERCISE**

A sample of natural gas contains 8.24 moles of methane (CH\(_4\)), 0.421 mole of ethane (C\(_2\)H\(_6\)), and 0.116 mole of propane (C\(_3\)H\(_8\)). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?

Dalton’s law of partial pressures is useful for calculating volumes of gases collected over water. For example, when potassium chlorate (KClO\(_3\)) is heated, it decomposes to KCl and O\(_2\):

\[ 2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g) \]

The oxygen gas can be collected over water, as shown in Figure 5.13. Initially, the inverted bottle is completely filled with water. As oxygen gas is generated, the gas bubbles rise to the top and displace water from the bottle. This method of collecting a gas is based on the assumptions that the gas does not react with water and that it is not appreciably soluble in it. These assumptions are valid for oxygen gas, but not for gases
FIGURE 5.13 An apparatus for collecting gas over water. The oxygen generated by heating potassium chlorate (KClO₃) in the presence of a small amount of manganese dioxide (MnO₂), which speeds up the reaction, is bubbled through water and collected in a bottle as shown. Water originally present in the bottle is pushed into the trough by the oxygen gas.

TABLE 5.3 Pressure of Water Vapor at Various Temperatures

<table>
<thead>
<tr>
<th>TEMPERATURE (°C)</th>
<th>WATER VAPOR PRESSURE (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.58</td>
</tr>
<tr>
<td>5</td>
<td>6.54</td>
</tr>
<tr>
<td>10</td>
<td>9.21</td>
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<td>15</td>
<td>12.79</td>
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<td>525.76</td>
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<td>95</td>
<td>633.90</td>
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<tr>
<td>100</td>
<td>760.00</td>
</tr>
</tbody>
</table>

such as NH₃, which dissolves readily in water. The oxygen gas collected in this way is not pure, however, because water vapor is also present in the bottle. The total gas pressure is equal to the sum of the pressures exerted by the oxygen gas and the water vapor:

\[ P_T = P_{O_2} + P_{H_2O} \]

Consequently, we must allow for the pressure caused by the presence of water vapor when we calculate the amount of O₂ generated. Table 5.3 shows the pressure of water vapor at various temperatures. These data are plotted in Figure 5.14.

Example 5.16 shows how to use Dalton’s law to calculate the amount of a gas collected over water.

EXAMPLE 5.16

Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in Figure 5.13. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24°C is 22.4 mmHg.

**Answer** Our first step is to calculate the partial pressure of O₂. We know that

\[ P_T = P_{O_2} + P_{H_2O} \]

Therefore
FIGURE 5.14 The pressure of water vapor as a function of temperature. Note that at the boiling point of water (100°C) the pressure is 760 mmHg, which is exactly equal to 1 atm.

\[ P_{O_2} = P_T - P_{H_2O} \]
\[ = 762 \text{ mmHg} - 22.4 \text{ mmHg} \]
\[ = 740 \text{ mmHg} \]
\[ = 740 \frac{\text{mmHg}}{1 \text{ atm}} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \]
\[ = 0.974 \text{ atm} \]

From the ideal gas equation we write

\[ PV = nRT = \frac{m}{\mu}RT \]

where \( m \) and \( \mu \) are the mass of O\(_2\) collected and the molar mass of O\(_2\), respectively. Rearranging the equation we get

\[ m = \frac{PV \cdot \mu}{RT} = \frac{(0.974 \text{ atm})(0.128 \text{ L})(32.00 \text{ g/mol})}{(0.0821 \text{ L \cdot atm/K \cdot mol}(273 + 24) \text{ K}} \]
\[ = 0.164 \text{ g} \]

**PRACTICE EXERCISE**

Hydrogen gas generated when calcium metal reacts with water is collected as shown in Figure 5.13. The volume of gas collected at 30°C and pressure of 988 mmHg is 641 mL. What is the mass (in grams) of the hydrogen gas obtained? The pressure of water vapor at 30°C is 31.82 mmHg.

**5.7 THE KINETIC MOLECULAR THEORY OF GASES**

The gas laws help us to predict the behavior of gases, but they do not explain what happens at the molecular level to cause the changes we observe in the macroscopic world. For example, why does a gas expand upon heating?
Scuba diving is an exhilarating sport, and, thanks in part to the gas laws, it is also a safe activity for trained individuals who are in good health. ("Scuba" is an acronym for self-contained underwater breathing apparatus.) Two applications of the gas laws to this popular pastime are the development of guidelines for returning safely to the surface after a dive and the determination of the proper mix of gases to prevent a potentially fatal condition during a dive.

A typical dive might be 40 to 65 ft, but dives to 90 ft are not uncommon. Because seawater has a slightly higher density than fresh water—about 1.03 g/mL, compared with 1.00 g/mL—the pressure exerted by a column of 33 ft of seawater is equivalent to 1 atm pressure. Pressure increases with increasing depth, so at a depth of 66 ft the pressure of the water will be 2 atm, and so on.

What would happen if a diver rose to the surface from a depth of, say, 20 ft rather quickly without breathing? The total decrease in pressure for this change in depth would be \((20 \text{ ft})/33 \text{ ft}) \times 1 \text{ atm}, or 0.6 \text{ atm}. When the diver reached the surface, the volume of air trapped in the lungs would have increased by a factor of \((1 + 0.6) \text{ atm}/1 \text{ atm}, or 1.6 times. This sudden expansion of air can fatally rupture the membranes of the lungs. Another serious possibility is that an air embolism might develop. As air expands in the lungs, it is forced into tiny blood vessels called capillaries. The presence of air bubbles in these vessels can block normal blood flow to the brain. As a result, the diver might lose consciousness before reaching the surface. The only cure for an air embolism is recompression. For this painful process, the victim is placed in a chamber filled with compressed air. Here bubbles in the blood are slowly squeezed down to harmless size over the course of several hours to a day. To avoid these unpleasant complications, divers know they must ascend slowly, pausing at certain points to give their bodies time to adjust to the falling pressure.

Our second example is a direct application of Dalton’s law. Oxygen gas is essential for our survival, so it is hard to believe that an excess of oxygen could be harmful. Nevertheless, the toxicity of too much oxygen is well established. For example, newborn infants placed in oxygen tents often sustain damage to the retinal tissue, which can cause partial or total blindness.

Our bodies function best when oxygen gas has a partial pressure of about 0.20 atm, as it does in the air we breathe. The oxygen partial pressure is given by

\[
P_{O_2} = X_{O_2} P_T = \frac{n_{O_2}}{n_{O_2} + n_{N_2}} P_T
\]

where \(P_T\) is the total pressure. However, since volume is directly proportional to the number of moles of gas present (at constant temperature and pressure), we can now write

\[
P_{O_2} = \frac{V_{O_2}}{V_{O_2} + V_{N_2}} P_T
\]

Thus the composition of air is 20 percent oxygen gas and 80 percent nitrogen gas by volume. When a diver is submerged, the pressure of the water on the diver is greater than atmospheric pressure. The air pressure inside the body cavities (for example, lungs, sinuses) must be the same as the pressure of the surrounding water; otherwise they would collapse. A special valve...
In the nineteenth century, a number of physicists, notably Ludwig Boltzmann\(^\dagger\) and James Clerk Maxwell,\(^\ddagger\) found that the physical properties of gases can be explained in terms of the motion of individual molecules. This molecular movement is a form of energy, which we define as the capacity to do work or to produce change. In mechanics, work is defined as force times distance. Since energy can be measured as work, we can write

\[
\text{energy} = \text{work done} = \text{force} \times \text{distance}
\]

The joule (J) is the SI unit of energy

\[1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2 = 1 \text{ N m}\]

Alternatively, energy can be expressed in kilojoules (kJ):

\[1 \text{ kJ} = 1000 \text{ J}\]

As we will see in Chapter 6, there are many different kinds of energy. Kinetic energy (KE) is the type of energy expended by a moving object, or energy of motion.

The findings of Maxwell, Boltzmann, and others resulted in a number of generalizations about gas behavior that have since been known as the kinetic molecular theory of gases, or simply the kinetic theory of gases. Central to the kinetic theory are the following assumptions:

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be “points”; that is, they possess mass but have negligible volume.
2. Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic.

Although nitrogen gas may seem to be the obvious choice to mix with oxygen gas, there is a serious problem with it. When the partial pressure of nitrogen gas exceeds 1 atm, enough of the gas dissolves in the blood to cause a condition known as nitrogen narcosis. The effects on the diver resemble those associated with alcohol intoxication. Divers suffering from nitrogen narcosis have been known to do strange things, such as dancing on the sea floor and chasing sharks. For this reason, helium is often used to dilute oxygen gas. An inert gas, helium is much less soluble in blood than nitrogen and produces no narcotic effects.

\(^\dagger\)Ludwig Eduard Boltzmann (1844–1906). Austrian physicist. Although Boltzmann was one of the greatest theoretical physicists of all time, his work was not recognized by other scientists in his own lifetime. Suffering from poor health and great depression, he committed suicide in 1906.

\(^\ddagger\)James Clerk Maxwell (1831–1879). Scottish physicist. Maxwell was one of the great theoretical physicists of the nineteenth century; his work covered many areas in physics, including kinetic theory of gases, thermodynamics, and electricity and magnetism.
words, energy can be transferred from one molecule to another as a result of a collision. Nevertheless, the total energy of all the molecules in a system remains the same.

3. Gas molecules exert neither attractive nor repulsive forces on one another.

4. The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins. Any two gases at the same temperature will have the same average kinetic energy. The average kinetic energy of a molecule is given by

$$KE = \frac{1}{2}mu^2$$

where $m$ is the mass of the molecule and $u$ is its speed. The horizontal bar denotes an average value. The quantity $u^2$ is called mean square speed; it is the average of the square of the speeds of all the molecules:

$$u^2 = \frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}$$

where $N$ is the number of molecules.

Assumption 4 allows us to write

$$\overline{KE} \propto T$$

$$\frac{1}{2}mu^2 \propto T$$

$$\frac{1}{2}mu^2 = CT$$

(5.11)

where $C$ is the proportionality constant and $T$ is the absolute temperature.

According to the kinetic molecular theory, gas pressure is the result of collisions between molecules and the walls of their container. It depends on the frequency of collision per unit area and on how “hard” the molecules strike the wall. The theory also provides a molecular interpretation of temperature. According to Equation (5.11), the absolute temperature of a gas is a measure of the average kinetic energy of the molecules. In other words, the absolute temperature is an index of the random motion of the molecules—the higher the temperature, the more energetic the molecules. Because it is related to the temperature of the gas sample, random molecular motion is sometimes referred to as thermal motion.

APPLICATION TO THE GAS LAWS

Although the kinetic theory of gases is based on a rather simple model, the mathematical details involved are very complex. However, on a qualitative basis, it is possible to use the theory to account for the general properties of substances in the gaseous state. The following examples illustrate the range of its utility.

- **Compressibility of gases.** Since molecules in the gas phase are separated by large distances (assumption 1), gases can be compressed easily to occupy less volume.
- **Boyle’s law.** The pressure exerted by a gas results from the impact of its molecules on the walls of the container. The collision rate, or the number of molecular collisions with the walls per second, is proportional to the number density (that is, number of molecules per unit volume) of the gas. Decreasing the volume of a given amount of gas increases its number density and hence its collision rate. For this reason, the pressure of a gas is inversely proportional to the volume it occupies; as volume decreases, pressure increases and vice versa.
- **Charles’ law.** Since the average kinetic energy of gas molecules is proportional to the sample’s absolute temperature (assumption 4), raising the temperature increases
Another way of stating Avogadro’s law is that at the same pressure and temperature, equal volumes of gases, whether they are the same or different gases, contain equal numbers of molecules.

- **Avogadro’s law.** We have shown that the pressure of a gas is directly proportional to both the density and the temperature of the gas. Since the mass of the gas is directly proportional to the number of moles \((n)\) of the gas, we can represent density by \(n/V\). Therefore

\[
P \propto \frac{n}{V} T
\]

For two gases, 1 and 2, we write

\[
P_1 \propto \frac{n_1 T_1}{V_1} = C \frac{n_1 T_1}{V_1}
\]

\[
P_2 \propto \frac{n_2 T_2}{V_2} = C \frac{n_2 T_2}{V_2}
\]

where \(C\) is the proportionality constant. Thus, for two gases under the same conditions of pressure, volume, and temperature (that is, when \(P_1 = P_2\), \(T_1 = T_2\), and \(V_1 = V_2\)), it follows that \(n_1 = n_2\), which is a mathematical expression of Avogadro’s law.

- **Dalton’s law of partial pressures.** If molecules do not attract or repel one another (assumption 3), then the pressure exerted by one type of molecule is unaffected by the presence of another gas. Consequently, the total pressure is given by the sum of individual gas pressures.

**DISTRIBUTION OF MOLECULAR SPEEDS**

The kinetic theory of gases allows us to investigate molecular motion in more detail. Suppose we have a large number of gas molecules, say, 1 mole, in a container. As long as we hold the temperature constant, the average kinetic energy and the mean-square speed will remain unchanged as time passes. As you might expect, the motion of the molecules is totally random and unpredictable. At a given instant, how many molecules are moving at a particular speed? To answer this question Maxwell analyzed the behavior of gas molecules at different temperatures.

Figure 5.15 shows typical Maxwell speed distribution curves for an ideal gas at two different temperatures. At a given temperature, the distribution curve tells us the number of molecules moving at a certain speed. The peak of each curve represents the average kinetic energy. Consequently, molecules will collide with the walls of the container more frequently and with greater impact if the gas is heated, and thus the pressure increases. The volume of gas will expand until the gas pressure is balanced by the constant external pressure (see Figure 5.7).

**FIGURE 5.15** Maxwell’s speed distribution for a gas at (a) temperature \(T_1\) and (b) a higher temperature \(T_2\). Note that the curve flattens out at the higher temperature. The shaded areas represent the number of molecules traveling at a speed equal to or greater than a certain speed \(u_1\). The higher the temperature, the greater the number of molecules moving at high speed.
most probable speed, that is, the speed of the largest number of molecules. Note that at the higher temperature [Figure 5.15(b)] the most probable speed is greater than that at the lower temperature [Figure 5.15(a)]. Comparing parts (a) and (b), we see that as temperature increases, not only does the peak shift toward the right, but the curve also flattens out, indicating that larger numbers of molecules are moving at greater speeds.

The distribution of molecular speeds can be demonstrated with the apparatus shown in Figure 5.16. A beam of atoms (or molecules) exits from an oven at a known temperature and passes through a pinhole (to collimate the beam). Two circular plates mounted on the same shaft are rotated by a motor. The first plate is called the “chopper” and the second is the detector. The purpose of the chopper is to allow small bursts of atoms (or molecules) to pass through it whenever the slit is aligned with the beam. Within each burst, the faster-moving molecules will reach the detector earlier than the slower-moving ones. Eventually, a layer of deposit will accumulate on the detector. Since the two plates are rotating at the same speed, molecules in the next burst will hit the detector plate at approximately the same place as molecules from the previous burst having the same speed. In time, the molecular deposition will become visible. The density of the deposition indicates the distribution of molecular speeds at that particular temperature.

ROOT-MEAN-SQUARE SPEED

How fast does a molecule move, on the average, at any temperature $T$? One way to estimate molecular speed is to calculate the root-mean-square (rms) speed ($u_{\text{rms}}$), which is an average molecular speed. One of the results of the kinetic theory of gases is that the total kinetic energy of a mole of any gas equals $\frac{3}{2}RT$. Earlier we saw that the average kinetic energy of one molecule is $\frac{1}{2}mu^2$ and so we can write

$$N_A \left(\frac{1}{2}mu^2\right) = \frac{3}{2}RT$$

where $N_A$ is Avogadro’s number. Since $N_A m = \frac{M}{\mu}$ the above equation can be rearranged to give

$$\bar{u^2} = \frac{3RT}{\mu}$$
Taking the square root of both sides gives

$$
\sqrt{u^2} = u_{\text{rms}} = \sqrt{\frac{3RT}{M}}
$$

Equation (5.12) shows that the root-mean-square speed of a gas increases with the square root of its temperature (in kelvins). Because \(M\) appears in the denominator, it follows that the heavier the gas, the more slowly its molecules move. If we substitute 8.314 J/K \cdot mol for \(R\) (see Appendix 2) and convert the molar mass to kg/mol, then \(u_{\text{rms}}\) will be calculated in meters per second (m/s). This procedure is illustrated in Example 5.17.

**EXAMPLE 5.17**

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in m/s at 25°C.

**Answer** We need Equation (5.12) for this calculation. For He the molar mass is 4.003 g/mol, or \(4.003 \times 10^{-3}\) kg/mol:

\[
u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J/K \cdot mol})(298 \text{ K})}{4.003 \times 10^{-3} \text{ kg/mol}}} = \sqrt{1.86 \times 10^6 \text{ J/kg}}
\]

Using the conversion factor,

\[1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2\]

we get

\[u_{\text{rms}} = \sqrt{1.86 \times 10^6 \text{ kg m}^2/\text{kg} \cdot \text{s}^2} = 1.36 \times 10^3 \text{ m/s}\]

The procedure is the same for \(N_2\), which has a molar mass of 28.02 g/mol, or \(2.802 \times 10^{-2}\) kg/mol:

\[
u_{\text{rms}} = \sqrt{\frac{3(8.314 \text{ J/K \cdot mol})(298 \text{ K})}{2.802 \times 10^{-2} \text{ kg/mol}}} = \sqrt{2.65 \times 10^5 \text{ m}^2/\text{s}^2} = 515 \text{ m/s}
\]

**Comment** Because of its smaller mass, a helium atom, on the average, moves about 2.6 times faster than a nitrogen molecule at the same temperature \((1360 \div 515 = 2.64)\).

**PRACTICE EXERCISE**

Calculate the root-mean-square speed of molecular chlorine in m/s at 20°C.

The calculation in Example 5.17 has an interesting relationship to the composition of Earth’s atmosphere. Earth, unlike, say, Jupiter, does not have appreciable amounts of hydrogen or helium in its atmosphere. Why is this the case? A smaller
FIGURE 5.17  The path traveled by a single gas molecule. Each change in direction represents a collision with another molecule.

planet than Jupiter, Earth has a weaker gravitational attraction for these lighter molecules. A fairly straightforward calculation shows that to escape Earth’s gravitational field, a molecule must possess an escape velocity equal to or greater than \(1.1 \times 10^4\) m/s. Because the average speed of helium is considerably greater than that of molecular nitrogen or molecular oxygen, more helium atoms escape from Earth’s atmosphere into outer space. Consequently, only a trace amount of helium is present in our atmosphere. On the other hand, Jupiter, with a mass about 320 times greater than that of Earth, retains both heavy and light gases in its atmosphere.

The Chemistry in Action Essay on p. 186 describes a fascinating phenomenon involving gases at extremely low temperatures.

GAS DIFFUSION

A direct demonstration of random motion is provided by diffusion, the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties. Diffusion always proceeds from a region of higher concentration to one of lower concentration. Despite the fact that molecular speeds are very great, the diffusion process takes a relatively long time to complete. For example, when a bottle of concentrated ammonia solution is opened at one end of a lab bench, it takes some time before a person at the other end of the bench can smell it. The reason is that a molecule experiences numerous collisions while moving from one end of the bench to the other, as shown in Figure 5.17. Thus, diffusion of gases always happens gradually, and not instantly as molecular speeds seem to suggest. Furthermore, because the root-mean-square speed of a light gas is greater than that of a heavier gas (see Example 5.17), a lighter gas will diffuse through a certain space more quickly than will a heavier gas. Figure 5.18 illustrates gaseous diffusion.

5.8 DEVIATION FROM IDEAL BEHAVIOR

The gas laws and the kinetic molecular theory assume that molecules in the gaseous state do not exert any force, either attractive or repulsive, on one another. The other assumption is that the volume of the molecules is negligibly small compared with that

FIGURE 5.18  A demonstration of gas diffusion. \(\text{NH}_3\) gas (from a bottle containing aqueous ammonia) combines with \(\text{HCl}\) gas (from a bottle containing hydrochloric acid) to form solid \(\text{NH}_4\text{Cl}\). Because \(\text{NH}_3\) is lighter and therefore diffuses faster, solid \(\text{NH}_4\text{Cl}\) first appears nearer the \(\text{HCl}\) bottle (on the right).
What happens to a gas when cooled to nearly absolute zero? More than seventy years ago, Albert Einstein, extending work by the Indian physicist Satyendra Nath Bose, predicted that at extremely low temperatures gaseous atoms of certain elements would “merge” or “condense” to form a single entity and a new form of matter. Unlike ordinary gases, liquids, and solids, this super-cooled substance, which was named the Bose-Einstein condensate (BEC), would contain no individual atoms because the original atoms would overlap one another, leaving no space in between.

Einstein’s hypothesis inspired an international effort to produce the BEC. But, as sometimes happens in science, the necessary technology was not available until fairly recently, and so early investigations were fruitless. Lasers, which use a process based on another of Einstein’s ideas, were not designed specifically for BEC research, but they became a critical tool for this work.

Finally, in 1995, physicists found the evidence they had sought for so long. A team at the University of Colorado was the first to report success. They created a BEC by cooling a sample of gaseous rubidium (Rb) atoms to about $1.7 \times 10^{-7}$ K using a technique called “laser cooling,” a process in which a laser light is directed at a beam of atoms, hitting them head on and dramatically slowing them down. The Rb atoms were further cooled in an “optical molasses” produced by the intersection of six lasers. The slowest, coolest atoms were trapped in a magnetic field while the faster-moving, “hotter” atoms escaped, thereby removing more energy from the gas. Under these conditions, the kinetic energy of the trapped atoms was virtually zero, which accounts for the extremely low temperature of the gas. At this point the Rb atoms formed the condensate, just as Einstein had predicted. Although this BEC was invisible to the naked eye (it measured only $5 \times 10^{-3}$ cm across), the scientists were able to capture its image on a computer screen by focusing another laser beam on it. The laser caused the BEC to break up after about 15 seconds, but that was long enough to record its existence.

The figure shows the Maxwell velocity distribution* of the Rb atoms at this temperature. The colors indicate the number of atoms having velocity specified by the two horizontal axes. The red color represents the lowest number of Rb atoms and the white color the highest. The average speed in the white region is about 0.5 mm/s.

The Maxwell velocity distribution differs from speed distribution in that velocity has both magnitude and direction. Thus velocity can have both positive and negative values but speed can have only zero or positive values.
Within weeks of the Colorado team’s discovery, a group of scientists at Rice University, using similar techniques, succeeded in producing a BEC with lithium atoms. At present, we can only guess at the significance of these discoveries for the future. It is expected that studies of the BEC will shed light on atomic properties that are still not fully understood (see Chapter 7) and on the mechanism of superconductivity (see the Chemistry in Action essay on this topic in Chapter 11). An additional benefit might be the development of better lasers. Other applications will depend on further study of the BEC itself. Nevertheless, the discovery of a new form of matter has to be one of the foremost scientific achievements of the twentieth century.

Of the container. A gas that satisfies these two conditions is said to exhibit ideal behavior.

Although we can assume that real gases behave like an ideal gas, we cannot expect them to do so under all conditions. For example, without intermolecular forces, gases could not condense to form liquids. The important question is: Under what conditions will gases most likely exhibit nonideal behavior?

Figure 5.19 shows \( \frac{PV}{RT} \) plotted against \( P \) for three real gases and an ideal gas at a given temperature. This graph provides a test of ideal gas behavior. According to the ideal gas equation (for 1 mole of gas), \( \frac{PV}{RT} = 1 \), regardless of the actual gas pressure. (When \( n = 1 \), \( PV = nRT \) becomes \( PV = RT \), or \( PV/RT = 1 \).) For real gases, this is true only at moderately low pressures (\( \leq 5 \) atm); significant deviations occur as pressure increases. Attractive forces operate among molecules at relatively short distances. At atmospheric pressure, the molecules in a gas are far apart and the attractive forces are negligible. At high pressures, the density of the gas increases; the molecules are much closer to one another. Intermolecular forces can then be significant enough to affect the motion of the molecules, and the gas will not behave ideally.

Another way to observe the nonideal behavior of gases is to lower the temperature. Cooling a gas decreases the molecules’ average kinetic energy, which in a sense deprives molecules of the drive they need to break from their mutual attraction.

To study real gases accurately, then, we need to modify the ideal gas equation, taking into account intermolecular forces and finite molecular volumes. Such an analy-
sis was first made by the Dutch physicist J. D. van der Waals† in 1873. Besides being mathematically simple, van der Waals’ treatment provides us with an interpretation of real gas behavior at the molecular level.

Consider the approach of a particular molecule toward the wall of a container (Figure 5.20). The intermolecular attractions exerted by its neighbors tend to soften the impact made by this molecule against the wall. The overall effect is a lower gas pressure than we would expect for an ideal gas. Van der Waals suggested that the pressure exerted by an ideal gas, $P_{\text{ideal}}$, is related to the experimentally measured pressure, $P_{\text{real}}$, by the equation

$$P_{\text{ideal}} = P_{\text{real}} + \frac{a n^2}{V^2}$$

where $a$ is a constant and $n$ and $V$ are the number of moles and volume of the gas, respectively. The correction term for pressure ($an^2/V^2$) can be understood as follows. The intermolecular interaction that gives rise to nonideal behavior depends on how frequently any two molecules approach each other closely. The number of such “encounters” increases with the square of the number of molecules per unit volume, $(n/V)^2$, because the presence of each of the two molecules in a particular region is proportional to $n/V$. The quantity $P_{\text{ideal}}$ is the pressure we would measure if there were no intermolecular attractions, and so $a$ is just a proportionality constant.

Another correction concerns the volume occupied by the gas molecules. In the ideal gas equation, $V$ represents the volume of the container. However, each molecule does occupy a finite, although small, intrinsic volume, so the effective volume of the gas becomes $(V - nb)$, where $n$ is the number of moles of the gas and $b$ is a constant. The term $nb$ represents the volume occupied by $n$ moles of the gas.

Having taken into account the corrections for pressure and volume, we can rewrite the ideal gas equation as follows:

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

Equation (5.13), relating $P$, $V$, $T$, and $n$ for a nonideal gas, is known as the van der Waals equation. The van der Waals constants $a$ and $b$ are selected to give the best possible agreement between Equation (5.13) and observed behavior of a particular gas.

Table 5.4 lists the values of $a$ and $b$ for a number of gases. The value of $a$ indicates how strongly molecules of a given type of gas attract one another. We see that helium atoms have the weakest attraction for one another, because helium has the smallest $a$ value. There is also a rough correlation between molecular size and $b$. Generally,

---

†Johannes Diderick van der Waals (1837–1923). Dutch physicist. Van der Waals received the Nobel Prize in Physics in 1910 for his work on the properties of gases and liquids.
the larger the molecule (or atom), the greater \( b \) is, but the relationship between \( b \) and molecular (or atomic) size is not a simple one.

The following example compares the pressure of a gas calculated using the ideal gas equation and the van der Waals equation.

**EXAMPLE 5.18**

Given that 3.50 moles of \( \text{NH}_3 \) occupy 5.20 L at 47°C, calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the van der Waals equation.

**Answer**

(a) We have the following data:

\[
V = 5.20 \text{ L} \\
T = (47 + 273) \text{ K} = 320 \text{ K} \\
n = 3.50 \text{ mol} \\
R = 0.0821 \text{ L} \cdot \text{ atm/K} \cdot \text{ mol}
\]

We substitute these values in the ideal gas equation:

\[
P = \frac{nRT}{V} \\
= \frac{(3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{ atm/K} \cdot \text{ mol})(320 \text{ K})}{5.20 \text{ L}} \\
= 17.7 \text{ atm}
\]

(b) From Table 5.4, we have

\[
a = 4.17 \text{ atm} \cdot \text{L}^2/\text{mol}^2 \\
b = 0.0371 \text{ L/mol}
\]

It is convenient to calculate the correction terms for Equation (5.13) first. They are

\[
\frac{an^2}{V^2} = \frac{(4.17 \text{ atm} \cdot \text{L}^2/\text{mol}^2)(3.50 \text{ mol})^2}{(5.20 \text{ L})^2} = 1.89 \text{ atm} \\
 nb = (3.50 \text{ mol})(0.0371 \text{ L/mol}) = 0.130 \text{ L}
\]

Finally, substituting in the van der Waals equation, we write

\[(P + 1.89 \text{ atm})(5.20 \text{ L} - 0.130 \text{ L}) = (3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{ atm/K} \cdot \text{ mol})(320 \text{ K})
\]

\[P = 16.2 \text{ atm}
\]

**Comment**

The actual pressure measured under these conditions is 16.0 atm. Thus, the pressure calculated by the van der Waals equation (16.2 atm) is closer to the actual value than that calculated by the ideal gas equation (17.7 atm).

**PRACTICE EXERCISE**

Using the data shown in Table 5.4, calculate the pressure exerted by 4.37 moles of molecular chlorine confined in a volume of 2.45 L at 38°C. Compare the pressure with that calculated using the ideal gas equation.
### SUMMARY OF KEY EQUATIONS

<table>
<thead>
<tr>
<th>Equation</th>
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<td>$PV = k_1$</td>
<td>(5.1) Boyle’s law. Constant $T$ and $n$.</td>
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<td>$P_1V_1 = P_2V_2$</td>
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<td>$\frac{V}{T} = k_2$</td>
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<td>$V = k_3n$</td>
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<td>$KE = \frac{1}{2}mv^2 = CT$</td>
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### SUMMARY OF FACTS AND CONCEPTS

1. At 25°C and 1 atm, a number of elements and molecular compounds exist as gases. Ionic compounds are solids rather than gases under atmospheric conditions.
2. Gases exert pressure because their molecules move freely and collide with any surface with which they make contact. Units of gas pressure include millimeters of mercury (mmHg), torr, pascals, and atmospheres. One atmosphere equals 760 mmHg, or 760 torr.
3. The pressure-volume relationships of ideal gases are governed by Boyle’s law: Volume is inversely proportional to pressure (at constant $T$ and $n$).
4. The temperature-volume relationships of ideal gases are described by Charles’ and Gay-Lussac’s law: Volume is directly proportional to temperature (at constant $P$ and $n$).
5. Absolute zero ($-273.15°C$) is the lowest theoretically attainable temperature. The Kelvin temperature scale takes 0 K as absolute zero. In all gas law calculations, temperature must be expressed in kelvins.
6. The amount-volume relationships of ideal gases are described by Avogadro’s law: Equal volumes of gases contain equal numbers of molecules (at the same $T$ and $P$).
7. The ideal gas equation, $PV = nRT$, combines the laws of Boyle, Charles, and Avogadro. This equation describes the behavior of an ideal gas.
8. Dalton’s law of partial pressures states that each gas in a mixture of gases exerts the same pressure that it would if it were alone and occupied the same volume.
9. The kinetic molecular theory, a mathematical way of describing the behavior of gas molecules, is based on the following assumptions: Gas molecules are separated by distances far greater than their own dimensions, they possess mass but have negligible volume, they are in constant motion, and they frequently collide with one another. The molecules neither attract nor repel one another.
10. A Maxwell speed distribution curve shows how many gas molecules are moving at various speeds at a given temperature. As temperature increases, more molecules move at greater speeds.
12. The van der Waals equation is a modification of the ideal gas equation that takes into account the nonideal behavior of real gases. It corrects for the fact that real gas molecules do exert forces on each other and that they do have volume. The van der Waals constants are determined experimentally for each gas.

KEY WORDS
Absolute temperature scale, p. 164
Absolute zero, p. 164
Atmospheric pressure, p. 158
Avogadro’s law, p. 165
Barometer, p. 158
Boyle’s law, p. 161
Charles’ and Gay-Lussac’s law, p. 164
KINETIC ENERGY (KE), p. 180
Root-mean-square speed, p. 183
STANDARD ATMOSPHERIC PRESSURE (1 atm), p. 158
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QUESTIONS AND PROBLEMS

SUBSTANCES THAT EXIST AS GASES

Review Questions
5.1 Name five elements and five compounds that exist as gases at room temperature.
5.2 List the physical characteristics of gases.

PRESSURE OF A GAS

Review Questions
5.3 Define pressure and give the common units for pressure.
5.4 Describe how a barometer and a manometer are used to measure pressure.
5.5 Why is mercury a more suitable substance to use in a barometer than water?
5.6 Explain why the height of mercury in a barometer is independent of the cross-sectional area of the tube. Would the barometer still work if the tubing were tilted at an angle, say 15° (see Figure 5.3)?
5.7 Would it be easier to drink water with a straw on top of Mt. Everest or at the foot? Explain.
5.8 Is the atmospheric pressure in a mine that is 500 m below sea level greater or less than 1 atm?
5.9 What is the difference between a gas and a vapor? At 25°C, which of the following substances in the gas phase should be properly called a gas and which should be called a vapor: molecular nitrogen (N₂), mercury?
5.10 If the maximum distance that water may be brought up a well by a suction pump is 34 ft (10.3 m), how is it possible to obtain water and oil from hundreds of feet below the surface of Earth?

5.11 Why is it that if the barometer reading falls in one part of the world, it must rise somewhere else?
5.12 Why do astronauts have to wear protective suits when they are on the surface of the moon?

Problems
5.13 Convert 562 mmHg to kPa and 2.0 kPa to mmHg.
5.14 The atmospheric pressure at the summit of Mt. McKinley is 606 mmHg on a certain day. What is the pressure in atm and in kPa?

THE GAS LAWS

Review Questions
5.15 State the following gas laws in words and also in the form of an equation: Boyle’s law, Charles’ law, Avogadro’s law. In each case, indicate the conditions under which the law is applicable, and give the units for each quantity in the equation.
5.16 Explain why a helium weather balloon expands as it rises in the air. Assume that the temperature remains constant.

Problems
5.17 A gas occupying a volume of 725 mL at a pressure of 0.970 atm is allowed to expand at constant temperature until its pressure reaches 0.541 atm. What is its final volume?
5.18 At 46°C a sample of ammonia gas exerts a pressure of 5.3 atm. What is the pressure when the volume of the gas is reduced to one-tenth (0.10) of the original value at the same temperature?
5.19 The volume of a gas is 5.80 L, measured at 1.00 atm. What is the pressure of the gas in mmHg if the volume is changed to 9.65 L? (The temperature remains constant.)

5.20 A sample of air occupies 3.8 L when the pressure is 1.2 atm. (a) What volume does it occupy at 6.6 atm? (b) What pressure is required in order to compress it to 0.075 L? (The temperature is kept constant.)

5.21 A 36.4-L volume of methane gas is heated from 25°C to 88°C at constant pressure. What is the final volume of the gas?

5.22 Under constant-pressure conditions a sample of hydrogen gas initially at 88°C and 9.6 L is cooled until its final volume is 3.4 L. What is its final temperature?

5.23 Ammonia burns in oxygen gas to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?

5.24 Molecular chlorine and molecular fluorine combine to form a gaseous product. Under the same conditions of temperature and pressure it is found that one volume of Cl₂ reacts with three volumes of F₂ to yield two volumes of the product. What is the formula of the product?

**THE IDEAL GAS EQUATION**

**Review Questions**

5.25 List the characteristics of an ideal gas.

5.26 Write the ideal gas equation and also state it in words. Give the units for each term in the equation.

5.27 What are standard temperature and pressure (STP)? What is the significance of STP in relation to the volume of 1 mole of an ideal gas?

5.28 Why is the density of a gas much lower than that of a liquid or solid under atmospheric conditions? What units are normally used to express the density of gases?

**Problems**

5.29 A sample of nitrogen gas kept in a container of volume 2.3 L and at a temperature of 32°C exerts a pressure of 4.7 atm. Calculate the number of moles of gas present.

5.30 Given that 6.9 moles of carbon monoxide gas are present in a container of volume 30.4 L, what is the pressure of the gas (in atm) if the temperature is 62°C?

5.31 What volume will 5.6 moles of sulfur hexafluoride (SF₆) gas occupy if the temperature and pressure of the gas are 128°C and 9.4 atm?

5.32 A certain amount of gas at 25°C and at a pressure of 0.800 atm is contained in a glass vessel. Suppose that the vessel can withstand a pressure of 2.00 atm. How high can you raise the temperature of the gas without bursting the vessel?

5.33 A gas-filled balloon having a volume of 2.50 L at 1.2 atm and 25°C is allowed to rise to the stratosphere (about 30 km above the surface of Earth), where the temperature and pressure are −23°C and 3.00 × 10⁻³ atm, respectively. Calculate the final volume of the balloon.

5.34 The temperature of 2.5 L of a gas initially at STP is raised to 250°C at constant volume. Calculate the final pressure of the gas in atm.

5.35 The pressure of 6.0 L of an ideal gas in a flexible container is decreased to one-third of its original pressure, and its absolute temperature is decreased by one-half. What is the final volume of the gas?

5.36 A gas evolved during the fermentation of glucose (wine making) has a volume of 0.78 L at 20.1°C and 1.00 atm. What was the volume of this gas at the fermentation temperature of 36.5°C and 1.00 atm pressure?

5.37 An ideal gas originally at 0.85 atm and 66°C was allowed to expand until its final volume, pressure, and temperature were 94 mL, 0.60 atm, and 45°C, respectively. What was its initial volume?

5.38 The volume of a gas at STP is 488 mL. Calculate its volume at 22.5 atm and 150°C.

5.39 A gas at 772 mmHg and 35.0°C occupies a volume of 6.85 L. Calculate its volume at STP.

5.40 Dry ice is solid carbon dioxide. A 0.050-g sample of dry ice is placed in an evacuated 4.6-L vessel at 30°C. Calculate the pressure inside the vessel after all the dry ice has been converted to CO₂ gas.

5.41 At STP, 0.280 L of a gas weighs 0.400 g. Calculate the molar mass of the gas.

5.42 At 741 torr and 44°C, 7.10 g of a gas occupy a volume of 5.40 L. What is the molar mass of the gas?

5.43 Ozone molecules in the stratosphere absorb much of the harmful radiation from the sun. Typically, the temperature and pressure of ozone in the stratosphere are 250 K and 1.0 × 10⁻³ atm, respectively. How many ozone molecules are present in 1.0 L of air under these conditions?

5.44 Assuming that air contains 78 percent N₂, 21 percent O₂, and 1 percent Ar, all by volume, how many molecules of each type of gas are present in 1.0 L of air at STP?

5.45 A 2.10-L vessel contains 4.65 g of a gas at 1.00 atm and 27.0°C. (a) Calculate the density of the gas in
grams per liter. (b) What is the molar mass of the gas? Assume ideal behavior.

5.46 Calculate the density of hydrogen bromide (HBr) gas in grams per liter at 733 mmHg and 46°C.

5.47 A certain anesthetic contains 64.9 percent C, 13.5 percent H, and 21.6 percent O by mass. At 120°C and 750 mmHg, 1.00 L of the gaseous compound weighs 2.30 g. What is the molecular formula of the compound?

5.48 A compound has the empirical formula SF₄. At 20°C, 0.100 g of the gaseous compound occupies a volume of 22.1 mL and exerts a pressure of 1.02 atm. What is the molecular formula of the gas?

GAS STOICHIOMETRY

Problems

5.49 A compound of P and F was analyzed as follows: Heating 0.232 g of the compound in a 378-cm³ container turned all of it to gas, which had a pressure of 97.3 mmHg at 77°C. Then the gas was mixed with calcium chloride solution, which turned all of the F to 0.2631 g of CaF₂. Determine the molecular formula of the compound.

5.50 A quantity of 0.225 g of a metal M (molar mass = 27.0 g/mol) liberated 0.303 L of molecular hydrogen (measured at 17°C and 741 mmHg) from an excess of hydrochloric acid. Deduce from these data the corresponding equation and write formulas for the oxide and sulfate of M.

5.51 What is the mass of the solid NH₄Cl formed when 73.0 g of NH₃ are mixed with an equal mass of HCl? What is the volume of the gas remaining, measured at 14.0°C and 752 mmHg? What gas is it?

5.52 Dissolving 3.00 g of an impure sample of calcium carbonate in hydrochloric acid produced 0.656 L of carbon dioxide (measured at 20.0°C and 792 mmHg). Calculate the percent by mass of calcium carbonate in the sample.

5.53 Calculate the mass in grams of hydrogen chloride produced when 5.6 L of molecular hydrogen measured at STP react with an excess of molecular chlorine gas.

5.54 Ethanol (C₂H₅OH) burns in air:

\[
\text{C}_2\text{H}_5\text{OH}(l) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)
\]

Balance the equation and determine the volume of air in liters at 35.0°C and 790 mmHg required to burn 227 g of ethanol. Assume that air is 21.0 percent O₂ by volume.

5.55 State Dalton's law of partial pressures and explain what mole fraction is. Does mole fraction have units?

5.56 A sample of air contains only nitrogen and oxygen gases whose partial pressures are 0.80 atm and 0.20 atm, respectively. Calculate the total pressure and the mole fractions of the gases.

Problems

5.57 A mixture of gases contains 0.31 mole CH₄, 0.25 mole C₂H₆, and 0.29 mole C₃H₈. The total pressure is 1.50 atm. Calculate the partial pressures of the gases.

5.58 A 2.5-L flask at 15°C contains a mixture of N₂, He, and Ne at partial pressures of 0.32 atm for N₂, 0.15 atm for He, and 0.42 atm for Ne. (a) Calculate the total pressure of the mixture. (b) Calculate the volume in liters at STP occupied by He and Ne if the N₂ is removed selectively.

5.59 Dry air near sea level has the following composition by volume: N₂, 78.08 percent; O₂, 20.94 percent; Ar, 0.93 percent; CO₂, 0.05 percent. The atmospheric pressure is 1.00 atm. Calculate (a) the partial pressure of each gas in atm and (b) the concentration of each gas in moles per liter at 0°C. (Hint: Since volume is proportional to the number of moles present, mole fractions of gases can be expressed as ratios of volumes at the same temperature and pressure.)

5.60 A mixture of helium and neon gases is collected over water at 28.0°C and 745 mmHg. If the partial pressure of helium is 368 mmHg, what is the partial pressure of neon? (Vapor pressure of water at 28°C = 28.3 mmHg.)

5.61 A piece of sodium metal reacts completely with water as follows:

\[2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g)\]

The hydrogen gas generated is collected over water at 25.0°C. The volume of the gas is 246 mL measured at 1.00 atm. Calculate the number of grams of sodium used in the reaction. (Vapor pressure of water at 25°C = 0.0313 atm.)

5.62 A sample of zinc metal reacts completely with an excess of hydrochloric acid:

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

The hydrogen gas produced is collected over water at 25.0°C using an arrangement similar to that shown in Figure 5.13. The volume of the gas is 7.80 L, and
the pressure is 0.980 atm. Calculate the amount of zinc metal in grams consumed in the reaction. (Vapor pressure of water at 25°C = 23.8 mmHg.)

5.63 Helium is mixed with oxygen gas for deep-sea divers. Calculate the percent by volume of oxygen gas in the mixture if the diver has to submerge to a depth where the total pressure is 4.2 atm. The partial pressure of oxygen is maintained at 0.20 atm at this depth.

5.64 A sample of ammonia (NH₃) gas is completely decomposed to nitrogen and hydrogen gases over heated iron wool. If the total pressure is 866 mmHg, calculate the partial pressures of N₂ and H₂.

KINETIC MOLECULAR THEORY OF GASES

Review Questions
5.65 What are the basic assumptions of the kinetic molecular theory of gases?
5.66 How does the kinetic molecular theory explain Boyle’s law, Charles’ law, Avogadro’s law, and Dalton’s law of partial pressures?
5.67 What does the Maxwell speed distribution curve tell us? Does Maxwell’s theory work for a sample of 200 molecules? Explain.
5.68 Write the expression for the root-mean-square speed for a gas at temperature T. Define each term in the equation and show the units that are used in the calculation.
5.69 Which of the following statements is correct? (a) Heat is produced by the collision of gas molecules against one another. (b) When a gas is heated, the molecules collide with one another more often.
5.70 Uranium hexafluoride (UF₆) is a much heavier gas than helium, yet at a given temperature, the average kinetic energies of the samples of the two gases are the same. Explain.

Problems
5.71 Compare the root-mean-square speeds of O₂ and UF₆ at 65°C.
5.72 The temperature in the stratosphere is −23°C. Calculate the root-mean-square speeds of N₂, O₂, and O₃ molecules in this region.
5.73 The average distance traveled by a molecule between successive collisions is called mean free path. For a given amount of a gas, how does the mean free path of a gas depend on (a) density, (b) temperature at constant volume, (c) pressure at constant temperature, (d) volume at constant temperature, and (e) size of the atoms?
5.74 At a certain temperature the speeds of six gaseous molecules in a container are 2.0 m/s, 2.2 m/s, 2.6 m/s, 2.7 m/s, 3.3 m/s, and 3.5 m/s. Calculate the root-mean-square speed and the average speed of the molecules. These two average values are close to each other, but the root-mean-square value is always the larger of the two. Why?

DEVIAION FROM IDEAL BEHAVIOR

Review Questions
5.75 Cite two pieces of evidence to show that gases do not behave ideally under all conditions.
5.76 Under what set of conditions would a gas be expected to behave most ideally? (a) High temperature and low pressure, (b) high temperature and high pressure, (c) low temperature and high pressure, (d) low temperature and low pressure.
5.77 Write the van der Waals equation for a real gas. Explain the corrective terms for pressure and volume.
5.78 (a) A real gas is introduced into a flask of volume V. Is the corrected volume of the gas greater or less than V? (b) Ammonia has a larger a value than neon does (see Table 5.4). What can you conclude about the relative strength of the attractive forces between molecules of ammonia and between atoms of neon?

Problems
5.79 Using the data shown in Table 5.4, calculate the pressure exerted by 2.50 moles of CO₂ confined in a volume of 5.00 L at 450 K. Compare the pressure with that predicted by the ideal gas equation.
5.80 At 27°C, 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

ADDITIONAL PROBLEMS
5.81 Discuss the following phenomena in terms of the gas laws: (a) the pressure increase in an automobile tire on a hot day, (b) the “popping” of a paper bag, (c) the expansion of a weather balloon as it rises in the air, (d) the loud noise heard when a light bulb shatters.
5.82 Under the same conditions of temperature and pressure, which of the following gases would behave most ideally: Ne, N₂, or CH₄? Explain.
5.83 Nitroglycerin, an explosive compound, decomposes according to the equation

\[ 4C_3H_5(NO_3)_3(s) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g) \]

Calculate the total volume of gases when collected at 1.2 atm and 25°C from 2.6 × 10² g of nitroglycerin.
What are the partial pressures of the gases under these conditions?

5.84 The empirical formula of a compound is CH. At 200°C, 0.145 g of this compound occupies 97.2 mL at a pressure of 0.74 atm. What is the molecular formula of the compound?

5.85 When ammonium nitrite (NH₄NO₂) is heated, it decomposes to give nitrogen gas. This property is used to inflate some tennis balls. (a) Write a balanced equation for the reaction. (b) Calculate the quantity (in grams) of NH₄NO₂ needed to inflate a tennis ball to a volume of 86.2 mL at 1.20 atm and 22°C.

5.86 The percent by mass of bicarbonate (HCO₃⁻) in a certain Alka-Seltzer product is 32.5 percent. Calculate the volume of CO₂ generated (in mL) at 37°C and 1.00 atm when a person ingests a 3.29-g tablet. (Hint: The reaction is between HCO₃⁻ and HCl acid in the stomach.)

5.87 The boiling point of liquid nitrogen is −196°C. On the basis of this information alone, do you think nitrogen is an ideal gas?

5.88 In the metallurgical process of refining nickel, the metal is first combined with carbon monoxide to form tetracarbonylnickel, which is a gas at 43°C:

Ni(s) + 4CO(g) → Ni(CO)₄(g)

This reaction separates nickel from other solid impurities. (a) Starting with 86.4 g of Ni, calculate the pressure of Ni(CO)₄ in a container of volume 4.00 L. (Assume the above reaction goes to completion.) (b) At temperatures above 43°C, the pressure of the gas is observed to increase much more rapidly than predicted by the ideal gas equation. Explain.

5.89 The partial pressure of carbon dioxide varies with seasons. Would you expect the partial pressure in the Northern Hemisphere to be higher in the summer or winter? Explain.

5.90 A healthy adult exhales about 5.0 × 10² mL of a gaseous mixture with each breath. Calculate the number of molecules present in this volume at 37°C and 1.1 atm. List the major components of this gaseous mixture.

5.91 Sodium bicarbonate (NaHCO₃) is called baking soda because when heated, it releases carbon dioxide gas, which is responsible for the rising of cookies, doughnuts, and bread. (a) Calculate the volume (in liters) of CO₂ produced by heating 5.0 g of NaHCO₃ at 180°C and 1.3 atm. (b) Ammonium bicarbonate (NH₄HCO₃) has also been used for the same purpose. Suggest one advantage and one disadvantage of using NH₄HCO₃ instead of NaHCO₃ for baking.

5.92 A barometer having a cross-sectional area of 1.00 cm² at sea level measures a pressure of 76.0 cm of mercury. The pressure exerted by this column of mercury is equal to the pressure exerted by all the air on 1 cm² of Earth’s surface. Given that the density of mercury is 13.6 g/mL and the average radius of Earth is 6371 km, calculate the total mass of Earth’s atmosphere in kilograms. (Hint: The surface area of a sphere is 4πr² where r is the radius of the sphere.)

5.93 Some commercial drain cleaners contain a mixture of sodium hydroxide and aluminum powder. When the mixture is poured down a clogged drain, the following reaction occurs:

2NaOH(aq) + 2Al(s) + 6H₂O(l) → 2NaAl(OH)₄(aq) + 3H₂(g)

The heat generated in this reaction helps melt away obstructions such as grease, and the hydrogen gas released stirs up the solids clogging the drain. Calculate the volume of H₂ formed at STP if 3.12 g of Al are treated with an excess of NaOH.

5.94 The volume of a sample of pure HCl gas was 189 mL at 25°C and 108 mmHg. It was completely dissolved in about 60 mL of water and titrated with a NaOH solution; 15.7 mL of the NaOH solution were required to neutralize the HCl. Calculate the molarity of the NaOH solution.

5.95 Propane (C₃H₈) burns in oxygen to produce carbon dioxide gas and water vapor. (a) Write a balanced equation for this reaction. (b) Calculate the number of liters of carbon dioxide measured at STP that could be produced from 7.45 g of propane.

5.96 Consider the following apparatus. Calculate the partial pressures of helium and neon after the stopcock is open. The temperature remains constant at 16°C.

5.97 Nitric oxide (NO) reacts with molecular oxygen as follows:

2NO(g) + O₂(g) → 2NO₂(g)

Initially NO and O₂ are separated as shown below. When the valve is opened, the reaction quickly goes to completion. Determine what gases remain at the
end and calculate their partial pressures. Assume that the temperature remains constant at 25°C.

5.98 Consider the apparatus shown below. When a small amount of water is introduced into the flask by squeezing the bulb of the medicinal dropper, water is squirted upward out of the long glass tubing. Explain this observation. (Hint: Hydrogen chloride gas is soluble in water.)

5.99 Describe how you would measure, by either chemical or physical means, the partial pressures of a mixture of gases of the following composition: (a) CO₂ and H₂, (b) He and N₂.

5.100 A certain hydrate has the formula MgSO₄ · xH₂O. A quantity of 54.2 g of the compound is heated in an oven to drive off the water. If the steam generated exerts a pressure of 3.55 atm in a 2.00-L container at 120°C, calculate x.

5.101 A mixture of Na₂CO₃ and MgCO₃ of mass 7.63 g is reacted with an excess of hydrochloric acid. The CO₂ gas generated occupies a volume of 1.67 L at 1.24 atm and 26°C. From these data, calculate the percent composition by mass of Na₂CO₃ in the mixture.

5.102 The following apparatus can be used to measure atomic and molecular speed. Suppose that a beam of metal atoms is directed at a rotating cylinder in a vacuum. A small opening in the cylinder allows the atoms to strike a target area. Because the cylinder is rotating, atoms traveling at different speeds will strike the target at different positions. In time, a layer of the metal will deposit on the target area, and the variation in its thickness is found to correspond to Maxwell’s speed distribution. In one experiment it is found that at 850°C some bismuth (Bi) atoms struck the target at a point 2.80 cm from the spot directly opposite the slit. The diameter of the cylinder is 15.0 cm and it is rotating at 130 revolutions per second. (a) Calculate the speed (m/s) at which the target is moving. (Hint: The circumference of a circle is given by 2πr, where r is the radius.) (b) Calculate the time (in seconds) it takes for the target to travel 2.80 cm. (c) Determine the speed of the Bi atoms. Compare your result in (c) with the u_rms of Bi at 850°C. Comment on the difference.

5.103 If 10.00 g of water are introduced into an evacuated flask of volume 2.500 L at 65°C, calculate the mass of water vaporized. (Hint: Assume that the volume of the remaining liquid water is negligible; the vapor pressure of water at 65°C is 187.5 mmHg.)

5.104 Commercially, compressed oxygen is sold in metal cylinders. If a 120-L cylinder is filled with oxygen to a pressure of 132 atm at 22°C, what is the mass of O₂ present? How many liters of O₂ gas at 1.00 atm and 22°C could the cylinder produce? (Assume ideal behavior.)

5.105 The shells of hard-boiled eggs sometimes crack due to the rapid thermal expansion of the shells at high temperatures. Suggest another reason why the shells may crack.

5.106 Ethylene gas (C₂H₄) is emitted by fruits and is known to be responsible for their ripening. Based on this information, explain why a bunch of bananas ripens faster in a closed paper bag than in a bowl.

5.107 About 8.0 × 10⁶ tons of urea [(NH₂)₂CO] are used annually as a fertilizer. The urea is prepared at 200°C and under high-pressure conditions from carbon dioxide and ammonia (the products are urea and steam). Calculate the volume of ammonia (in liters) measured at 150 atm needed to prepare 1.0 ton of urea.

5.108 Some ballpoint pens have a small hole in the main body of the pen. What is the purpose of this hole?
5.109 The gas laws are vitally important to scuba divers. The pressure exerted by 33 ft of seawater is equivalent to 1 atm pressure. (a) A diver ascends quickly to the surface of the water from a depth of 36 ft without exhaling gas from his lungs. By what factor will the volume of his lungs increase by the time he reaches the surface? Assume that the temperature is constant. (b) The partial pressure of oxygen in air is about 0.20 atm. (Air is 20% oxygen by volume.) In deep-sea diving, the composition of air the diver breathes must be changed to maintain this partial pressure. What must the oxygen content (in percent by volume) be when the total pressure exerted on the diver is 4.0 atm? (At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of gases.) (Hint: See Chemistry in Action essay on p. 179.)

5.110 Nitrous oxide (N₂O) can be obtained by the thermal decomposition of ammonium nitrate (NH₄NO₃). (a) Write a balanced equation for the reaction. (b) In a certain experiment, a student obtains 0.340 L of the NH₃ gas at 718 mmHg and 24°C. If the gas weighs 0.580 g, calculate the value of the gas constant.

5.111 Two vessels are labeled A and B. Vessel A contains NH₃ gas at 70°C, and vessel B contains Ne gas at the same temperature. If the average kinetic energy of NH₃ is 7.1 × 10⁻²¹ J/molecule, calculate the mean-square speed of Ne atoms in m²/s².

5.112 Which of the following molecules has the largest a value: CH₄, F₂, C₆H₆, Ne?

5.113 The following procedure is a simple though somewhat crude way to measure the molar mass of a gas. A liquid of mass 0.0184 g is introduced into a syringe 2.2 m high at 20°C. (a) Calculate the rate of CO production in moles per minute. (b) How long would it take to build up a lethal concentration of CO of 1000 ppmv (parts per million by volume)?

5.114 In 1995 a man suffocated as he walked by an aban-

5.115 Acidic oxides such as carbon dioxide react with basic oxides like calcium oxide (CaO) and barium oxide (BaO) to form salts (metal carbonates). (a) Write equations representing these two reactions. (b) A student placed a mixture of BaO and CaO of combined mass 4.88 g in a 1.46-L flask containing carbon dioxide gas at 35°C and 746 mmHg. After the reactions were complete, she found that the CO₂ pressure had dropped to 252 mmHg. Calculate the percent composition by mass of the mixture.

5.116 (a) What volume of air at 1.0 atm and 22°C is needed to fill a 0.98-L bicycle tire to a pressure of 5.0 atm at the same temperature? (Note that the 5.0 atm is the gauge pressure, which is the difference between the pressure in the tire and atmospheric pressure. Before filling, the pressure in the tire was 1.0 atm.) (b) What is the total pressure in the tire when the gauge pressure reads 5.0 atm? (c) The tire is pumped by filling the cylinder of a hand pump with air at 1.0 atm and then, by compressing the gas in the cylinder, adding all the air in the pump to the air in the tire. If the volume of the pump is 33 percent of the tire's volume, what is the gauge pressure in the tire after 3 full strokes of the pump? Assume constant temperature.

5.117 The running engine of an automobile produces carbon monoxide (CO), a toxic gas, at the rate of about 188 g CO per hour. A car is left idling in a poorly ventilated garage that is 6.0 m long, 4.0 m wide, and 2.2 m high at 20°C. (a) Calculate the rate of CO production in moles per minute. (b) How long would it take to build up a lethal concentration of CO of 1000 ppmv (parts per million by volume)?

5.118 Interstellar space contains mostly hydrogen atoms at a concentration of about 1 atom/cm³. (a) Calculate the pressure of the H atoms. (b) Calculate the volume (in liters) that contains 1.0 g of H atoms. The temperature is 3 K.

5.119 Atop Mt. Everest, the atmospheric pressure is 210 mmHg and the air density is 0.426 kg/m³. (a) Calculate the air temperature, given that the molar mass of air is 29.0 g/mol. (b) Assuming no change in air composition, calculate the percent decrease in oxygen gas from sea level to the top of Mt. Everest.

5.120 Relative humidity is defined as the ratio (expressed as a percentage) of the partial pressure of water vapor in the air to the equilibrium vapor pressure (see Table 5.3) at a given temperature. On a certain sum-
Lithium hydride reacts with water as follows:

\[
\text{LiH(s) + H}_2\text{O(l)} \rightarrow \text{LiOH(aq) + H}_2(g)
\]

During World War II, U.S. pilots carried LiH tablets. In the event of a crash landing at sea, the LiH would react with the seawater and fill their life belts and lifeboats with hydrogen gas. How many grams of LiH are needed to fill a 4.1-L life belt at 0.97 atm and 12°C?

The atmosphere on Mars is composed mainly of carbon dioxide. The surface temperature is 220 K and the atmospheric pressure is about 6.0 mmHg. Taking these values as Martian “STP,” calculate the molar volume in liters of an ideal gas on Mars.

Venus’s atmosphere is composed of 96.5 percent CO₂, 3.5 percent N₂, and 0.015 percent SO₂ by volume. Its standard atmospheric pressure is \(9.0 \times 10^6\) Pa. Calculate the partial pressures of the gases in pascals.

A student tries to determine the volume of a bulb like the one shown on p. 171. These are her results: Mass of the bulb filled with dry air at 23°C and 744 mmHg = 91.6843 g; mass of evacuated bulb = 91.4715 g. Assume the composition of air is 78 percent N₂, 21 percent O₂, and 1 percent argon. What is the volume (in milliliters) of the bulb? (Hint: First calculate the average molar mass of air, as shown in Problem 3.130.)

Apply your knowledge of the kinetic theory of gases to the following situations. (a) Two flasks of volumes \(V_1\) and \(V_2\) (where \(V_2 > V_1\)) contain the same number of helium atoms at the same temperature. (i) Compare the root-mean-square (rms) speeds and average kinetic energies of the helium (He) atoms in the flasks. (ii) Compare the frequency and the force with which the He atoms collide with the walls of their containers. (b) Equal numbers of He atoms are placed in two flasks of the same volume at temperatures \(T_1\) and \(T_2\) (where \(T_2 > T_1\)). (i) Compare the rms speeds of the atoms in the two flasks. (ii) Compare the frequency and the force with which the He atoms collide with the walls of their containers. (c) Equal numbers of He and neon (Ne) atoms are placed in two flasks of the same volume, and the temperature of both gases is 74°C. Comment on the validity of the following statements: (i) The rms speed of He is equal to that of Ne. (ii) The average kinetic energies of the two gases are equal. (iii) The rms speed of each He atom is \(1.47 \times 10^3\) m/s.

It has been said that every breath we take, on average, contains molecules that were once exhaled by Wolfgang Amadeus Mozart (1756–1791). The following calculations demonstrate the validity of this statement. (a) Calculate the total number of molecules in the atmosphere. (Hint: Use the result in Problem 5.92 and 29.0 g/mol as the molar mass of air.) (b) Assuming the volume of every breath (inhaler or exhaler) is 500 mL, calculate the number of molecules exhaled in each breath at 37°C, which is the body temperature. (c) If Mozart’s lifespan was exactly 35 years, what is the number of molecules he exhaled in that period? (Given that an average person breathes 12 times per minute.) (d) Calculate the fraction of molecules in the atmosphere that were breathed out.
by Mozart. How many of Mozart’s molecules do we
breathe in with every inhale of air? Round off your
answer to one significant figure. (e) List three im-
portant assumptions in these calculations.

**Answers to Practice Exercises:**

5.1 0.986 atm. 5.2 39.3 kPa. 5.3 $4.46 \times 10^2$ mmHg. 5.4 192 K, or $-81^\circ$C. 5.5 9.29 L.
5.6 30.6 L. 5.7 2.6 atm. 5.8 0.68 atm. 5.9 13.1 g/L. 5.10 44.1 g/mol. 5.11 B$_2$H$_6$. 5.12 96.9 L. 5.13 4.75 L. 5.14 0.338 M.
5.15 CH$_4$: 1.29 atm; C$_2$H$_6$: 0.0657 atm; C$_3$H$_8$: 0.0181 atm.
5.16 0.0653 g. 5.17 321 m/s. 5.18 30.0 atm; 45.5 atm using the
ideal gas equation.
In September 1991 four men and four women entered the world’s largest glass bubble, known as Biosphere II, to test the idea that humans could design and build a totally self-contained ecosystem, a model for some future colony on another planet. Biosphere II (Earth is considered Biopshere I) was a 3-acre mini-world, complete with a tropical rain forest, savanna, marsh, desert, and working farm that was intended to be fully self-sufficient. This unique experiment was to continue for 2 to 3 years, but almost immediately there were signs that the project could be in jeopardy.

Soon after the bubble had been sealed, sensors inside the facility showed that the concentration of oxygen in Biosphere II’s atmosphere had fallen from its initial level of 21 percent (by volume), while the amount of carbon dioxide had risen from a level of 0.035 percent (by volume), or 350 ppm (parts per million). Alarmingly, the oxygen level continued to fall at a rate of about 0.5 percent a month and the level of carbon dioxide kept rising, forcing the crew to turn on electrically powered chemical scrubbers, similar to those on submarines, to remove some of the excess CO₂. Gradually the CO₂ level stabilized around 4000 ppm, which is high but not dangerous. The loss of oxygen did not stop, though. By January 1993—16 months into the experiment—the oxygen concentration had dropped to 14 percent, which is equivalent to the O₂ concentration in air at an elevation of 4360 meters (14,300 ft). The crew began having trouble performing normal tasks. For their safety it was necessary to pump pure oxygen into Biosphere II.

With all the plants present in Biosphere II, the production of oxygen should have been greater as a consequence of photosynthesis. Why had the oxygen concentration declined to such a low level? A small part of the loss was blamed on unusually cloudy weather, which had slowed down plant growth. The possibility that iron in the soil was reacting with oxygen to form iron(III) oxide or rust was ruled out along with several other explanations for lack of evidence. The most plausible hypothesis was that microbes (microorganisms) were using oxygen to metabolize the excess organic matter that had been added to the soils to promote plant growth. This turned out to be the case.

Identifying the cause of oxygen depletion raised another question. Metabolism produces carbon dioxide. Based on the amount of oxygen consumed by the microbes, the CO₂ level should be at 40,000 ppm, ten times what was measured. What happened to the excess gas? After ruling out leakage to the outside world and reactions between CO₂ with compounds in the soils and in water, scientists found that concrete inside Biosphere II was consuming large amounts of CO₂!

Concrete is a mixture of sand and gravel held together by a binding agent which is a mixture of calcium silicate hydrates and calcium hydroxide. The calcium hydrox-

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Carbon dioxide is the key ingredient in the CO$_2$ mystery. Carbon dioxide diffuses into the porous structure of concrete, then reacts with calcium hydroxide to form calcium carbonate and water:

$$\text{Ca(OH)}_2(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$$

Under normal conditions, this reaction goes on slowly. But CO$_2$ concentrations in Biosphere II were much higher than normal, so the reaction proceeded much faster. In fact, in just over 2 years, CaCO$_3$ had accumulated to a depth of more than 2 cm in Biosphere II’s concrete. Some 10,000 m$^2$ of exposed concrete was hiding 500,000 to 1,500,000 moles of CO$_2$.

The water produced in the reaction between Ca(OH)$_2$ and CO$_2$ created another problem: CO$_2$ also reacts with water to form carbonic acid (H$_2$CO$_3$), and hydrogen ions produced by the acid promote the corrosion of the reinforcing iron bars in the concrete, thereby weakening its structure. This situation was dealt with effectively by painting all concrete surfaces with an impermeable coating.

In the meantime the decline in oxygen (and hence also the rise in carbon dioxide) slowed, perhaps because there was now less organic matter in the soils and also because new lights in the agricultural areas may have boosted photosynthesis. The project was terminated prematurely, and as of 1996, the facility was transformed into an science education and research center.

The Biosphere II experiment is an interesting project from which we can learn a lot about Earth and its inhabitants. If nothing else, it has shown us how complex Earth’s ecosystems are and how difficult it is to mimic nature, even on a small scale.

**CHEMICAL CLUES**

1. What solution would you use in a chemical scrubber to remove carbon dioxide?
2. Photosynthesis converts carbon dioxide and water to carbohydrates and oxygen gas, while metabolism is the process by which carbohydrates react with oxygen to form carbon dioxide and water. Using glucose (C$_6$H$_{12}$O$_6$) to represent carbohydrates, write equations for these two processes.
3. Why was diffusion of O$_2$ from Biosphere II to the outside world not considered a possible cause for the depletion in oxygen?
4. Carbonic acid is a diprotic acid. Write equations for the stepwise ionization of the acid in water.
5. What are the factors to consider in choosing a planet on which to build a structure like Biosphere II?