5

Gases



The buildup of pressure, which results from the constant collisions of gas molecules with the surfaces around them, expels the cork in a bottle of champagne.

So many of the properties of matter, especially when in the gaseous form, can be deduced from the hypothesis that their minute parts are in rapid motion, the velocity increasing with the temperature, that the precise nature of this motion becomes a subject of rational curiosity.

—James Clerk Maxwell (1831–1879)

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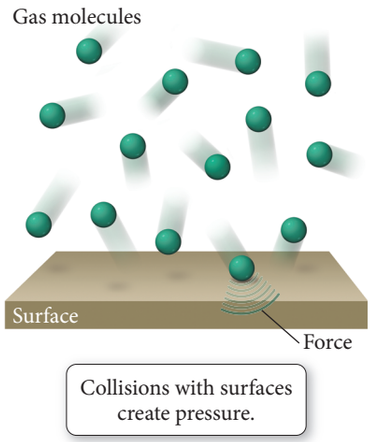
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WE CAN SURVIVE FOR WEEKS without food, days without water, but only minutes without air. Fortunately, we live at the bottom of a vast ocean of air, held to Earth by gravity. We inhale a lungful of this air every few seconds, keep some of the molecules for our own needs, add some molecules our bodies no longer have a use for, and exhale the mixture back into the surrounding air. The air around us is matter in the gaseous state. What are the fundamental properties of these gases? What laws describe their behaviour? What theory explains these properties and laws? The scientific method proceeds in this way—from observations to laws to theories—exactly the way we will proceed in this chapter. The gaseous state is the simplest and best-understood state of matter. In this chapter, we examine that state.

5.1 Breathing: Putting Pressure to Work

Every day, without even thinking about it, you move approximately 8500 litres of air into and out of your lungs. The total weight of this air is about 25 kilograms. How do you do it? The simple answer is *pressure*. You rely on your body's ability to create pressure differences to move air into and out of your lungs. **Pressure** is the force exerted per unit area by gas molecules as they strike the surfaces around them (Figure 5.1 ▼). Just as a ball exerts a force when it bounces against a wall, so

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▲ **FIGURE 5.1 Gas Pressure** Pressure is the force per unit area exerted by gas molecules colliding with the surfaces around them.

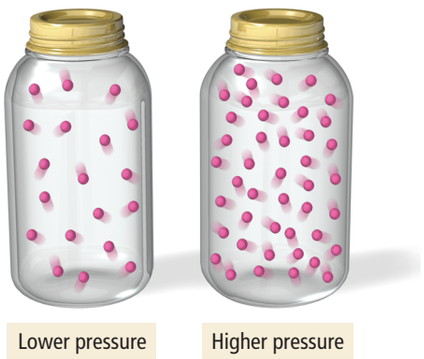
a gaseous atom or molecule exerts a force when it collides with a surface. The sum of all these molecular collisions is pressure—a constant force on the surfaces exposed to any gas. The total pressure exerted by a gas depends on several factors, including the concentration of gas molecules in the sample—the higher the concentration, the greater the pressure.

When you inhale, the muscles that surround your chest cavity expand the volume of your lungs. The expanded volume results in a lower concentration of gas molecules (the number of molecules does not change, but since the volume increases, the *concentration* goes down). This in turn results in fewer molecular collisions, which results in lower pressure. The external pressure (the pressure outside of your lungs) remains relatively constant and is now higher than the pressure within your lungs. As a result, gaseous molecules flow into your lungs, from the region of higher pressure to the region of lower pressure. When you exhale, the process is reversed. The chest cavity muscles relax, which *decreases* the lung volume, increasing the pressure within the lungs and forcing air back out. In this way, within the course of a normal human lifetime, you will take about half a billion breaths, and move about 250 million litres of air through your lungs. With each breath, you create pressure differences that allow you to obtain the oxygen that you need to live.

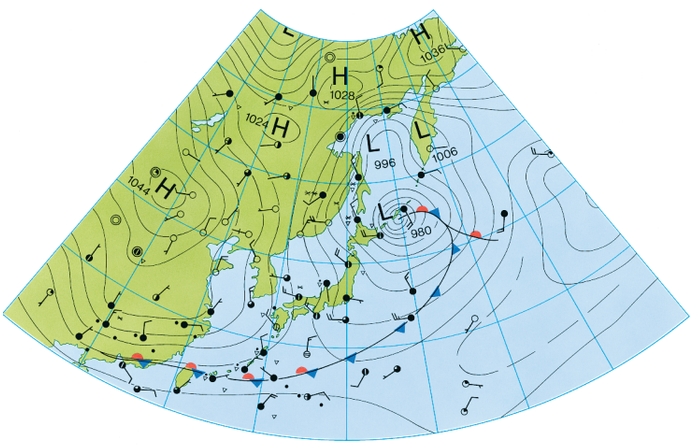
5.2 Pressure: The Result of Molecular Collisions

Air can hold up a jumbo jet or knock down a building. How? As we just discussed, air contains gaseous atoms and molecules in constant motion. The particles collide with each other and with the surfaces around them. Each collision exerts only a small force, but when the forces of the many particles are summed, they quickly add up. The result of the constant collisions between the atoms or molecules in a gas and the surfaces around them is *pressure*. Because of pressure, we can drink from straws, inflate basketballs, and move air into and out of our lungs. Variation in pressure in Earth's atmosphere creates wind, and changes in pressure help us to predict weather. Pressure is all around us and even inside of us. The pressure that a gas sample exerts is the force per unit area that results from the collisions of gas particles with the surrounding surfaces:

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{F}{A} \qquad [5.1]$$

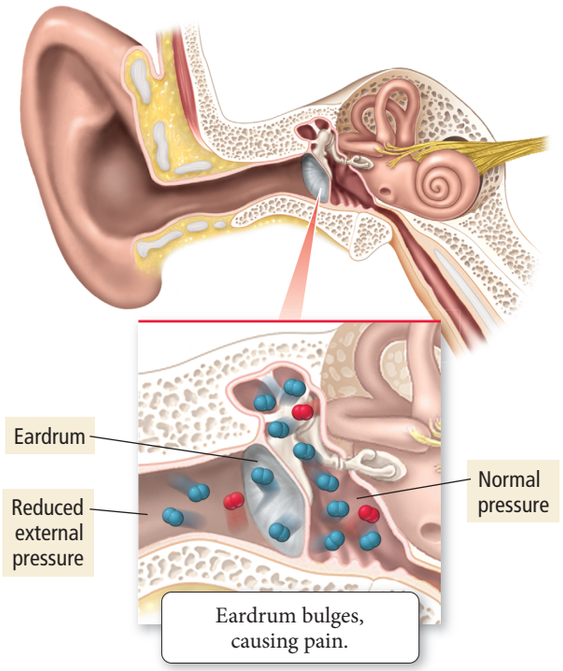


▲ **FIGURE 5.2 Pressure and Particle Density** A low density of gas particles results in low pressure. A high density of gas particles results in high pressure.



▲ Pressure variations in Earth's atmosphere create wind and weather. The H's in this map indicate regions of high pressure, usually associated with clear weather. The L's indicate regions of low pressure, usually associated with unstable weather. The map shows a typhoon off the northeast coast of Japan. The isobars, or lines of constant pressure, are labelled in hectopascals (100 Pa).

The pressure of a gas sample depends on several factors, including the number of gas particles in a given volume—the fewer the gas particles, the lower the pressure (Figure 5.2 ◂). Pressure decreases with increasing altitude because there are fewer molecules per unit



◀ **FIGURE 5.3 Pressure Imbalance**
The discomfort you may feel in your ears upon ascending a mountain is caused by a pressure imbalance between the cavities in your ears and the outside air.

volume of air. Above 9100 m for example, where most commercial airplanes fly, the pressure is so low that you could pass out due to a lack of oxygen. For this reason, most airplane cabins are artificially pressurized.

You can often feel the effect of a drop in pressure as a brief pain in your ears. This pain arises within the air-containing cavities in your ear (Figure 5.3 ▲). When you ascend a mountain, the external pressure (the pressure that surrounds you) drops, while the pressure within your ear cavities (the internal pressure) remains the same. This creates an imbalance—the greater internal pressure forces your eardrum to bulge outward, causing pain. With time, and with the help of a yawn or two, the excess air within your ear's cavities escapes, equalizing the internal and external pressures and relieving the pain.

Pressure Units

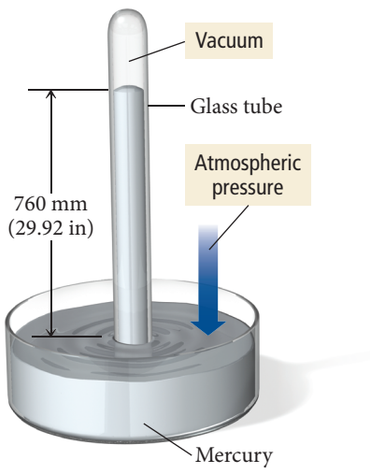
Pressure can be measured in several different units. A common unit of pressure, the **millimetre of mercury (mmHg)**, originates from how pressure is measured with a **barometer** (Figure 5.4 ▶). A barometer is an evacuated glass tube, the tip of which is submerged in a pool of mercury. Liquid in an evacuated tube is forced upward by atmospheric gas pressure on the liquid's surface. Because mercury is so dense (13.5 times more dense than water), atmospheric pressure can support a column of Hg that is only about 0.760 m or 760 mm tall. This makes a column of mercury a convenient way to measure pressure.

In a barometer, when the atmospheric pressure rises, the height of the mercury column rises as well. Similarly, when atmospheric pressure falls, the height of the column falls. The unit *millimetre of mercury* is often called a **torr**, after the Italian physicist Evangelista Torricelli (1608–1647) who invented the barometer.

$$1 \text{ mmHg} = 1 \text{ Torr}$$

The SI unit of pressure is the **pascal (Pa)**. Average sea level pressures are 101 325 Pa. This amount of pressure pushes a column of mercury to a height of 760 mmHg. The **atmosphere (atm)** is another unit of pressure that equals 760 mmHg and 101 325 Pa.

$$101\,325 \text{ Pa} = 101.325 \text{ kPa} = 760 \text{ Torr} = 1 \text{ atm}$$



▲ **FIGURE 5.4 The Mercury Barometer**
Average atmospheric pressure at sea level can support a column of mercury 760 mm in height.

As a convention, an SI unit that is derived from a proper name is capitalized. When the unit is spelled out in a sentence though, it begins with a lowercase letter.

TABLE 5.1 Common Units of Pressure

Pressure Measured in	Unit	Standard Pressure
bar	bar	1 bar
pascal	Pa	100 000 Pa
kilopascal	kPa	100 kPa
torr (mmHg)	Torr or mmHg	750.01 Torr
atmosphere	atm	0.98692 atm
pounds per square inch	psi	14.504 psi

The International Union of Pure and Applied Chemistry (IUPAC) has defined **standard pressure** as exactly 100 000 Pa for the purposes of specifying the properties of gaseous substances. The **bar** is a unit of pressure that is equal to 100 000 Pa, and 1 bar is standard pressure for gaseous components in a mixture. Some common units of pressure are displayed in Table 5.1, along with the standard pressure equivalent.

For example, car tires are typically inflated to about 2.5 bar, and the pressure at the top of Mount Everest is about one-third of a bar.

EXAMPLE 5.1 Converting Between Pressure Units

Aircraft tires operate at high pressures: 2.00×10^2 psi. What is this pressure in kPa and in bar?

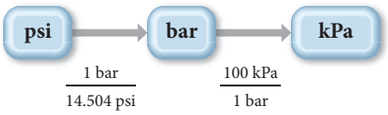
SORT The problem gives a pressure in psi and asks you to convert the units to kPa and bar.

GIVEN: 2.00×10^2 psi

FIND: the value in kPa and bar

STRATEGIZE Table 5.1 has a direct conversion factor between bar and psi, but not for kPa and psi. However, because there is a conversion between bar and kPa, once you convert to bar, you can convert to kPa.

CONCEPTUAL PLAN



RELATIONSHIPS USED

1 bar = 14.504 psi

100 kPa = 1 bar

SOLVE Follow the conceptual plan to solve the problem. Begin with 2.00×10^2 psi and use the conversion factors to arrive at the pressure in both bar and kPa.

SOLUTION

$$2.00 \times 10^2 \text{ psi} \times \frac{1 \text{ bar}}{14.504 \text{ psi}} = 13.8 \text{ bar}$$

$$13.8 \text{ bar} \times \frac{100 \text{ kPa}}{1 \text{ bar}} = 1.38 \times 10^3 \text{ kPa}$$

CHECK The units of the answers are correct. The magnitude of the pressure expressed in bar is smaller than the psi pressure, and the pressure in kPa is much larger, which is reasonable.

FOR PRACTICE 5.1

Barometric pressure is typically reported in hPa (h = hecto, 1 hPa = 0.1 kPa). Your local weather report says that the barometric pressure is 1005 hPa. What is the pressure in bar and in torr?

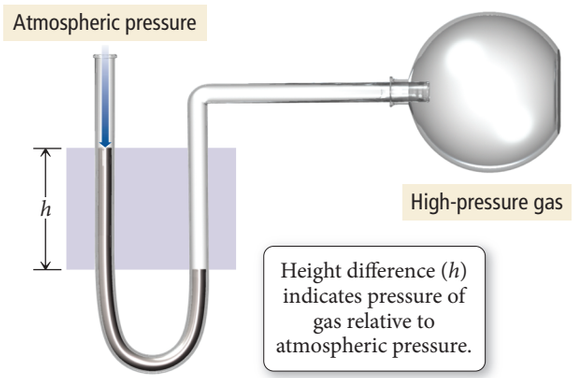
FOR MORE PRACTICE 5.1

In science labs, pressure gauges sometimes indicate pressures in vacuum chambers in **millibar (mbar)** or in Torr. A decent mechanical pump will produce a vacuum of about 1.0×10^{-2} Torr. Convert this pressure to mbar.

The Manometer: A Way to Measure Pressure in the Laboratory

We can measure the pressure of a gas sample in the laboratory with a **manometer**. A manometer is a U-shaped tube containing a dense liquid, usually mercury, as shown in Figure 5.5 ▶. In this manometer, one end of the tube is open to atmospheric pressure and the other is attached to a flask containing the gas sample. If the pressure of the gas sample is exactly equal to atmospheric pressure, then the mercury levels on both sides of the tube are the same. If the pressure of the sample is *greater than* atmospheric

pressure, the mercury level on the left side of the tube is *higher than* the level on the right. If the pressure of the sample is *less than* atmospheric pressure, the mercury level on the left side will be *lower than* the level on the right. This type of manometer always measures the pressure of the gas sample relative to atmospheric pressure. The difference in height between the two levels is equal to the difference between the sample's pressure and atmospheric pressure. The manometer is a "low-tech" way to read pressure, but it can be used to measure an accurate absolute pressure. To accurately obtain the absolute pressure of a sample, you also need a barometer to measure atmospheric pressure (which varies from day to day). In chemistry labs, pressures are usually measured with a number of "higher-tech" devices that always require calibration in order to obtain absolute pressures.



▲ **FIGURE 5.5 The Manometer** A manometer measures the pressure exerted by a sample of gas.

CHEMISTRY AND MEDICINE BLOOD PRESSURE



Blood pressure is the force within arteries that drives the circulation of blood throughout the body. Blood pressure in the body is analogous to water pressure in a plumbing system. Just as water pressure pushes water through the pipes to faucets and fixtures throughout a house, blood pressure pushes blood to muscles and other tissues throughout the body. However, unlike the water pressure in a plumbing system—which is typically nearly constant—our blood pressure varies with each heartbeat. When the heart muscle contracts, blood pressure increases; between contractions, it decreases. Systolic blood pressure is the peak pressure during a contraction, and diastolic blood pressure is the lowest pressure between contractions. Just as excessively high water pressure in a plumbing system can damage pipes, so too can high blood pressure in a circulatory system damage the heart and arteries, resulting in increased risk of stroke and heart attack.

Medical professionals usually measure blood pressure with an instrument called a sphygmomanometer—an inflatable cuff equipped with a pressure gauge—and a stethoscope. The cuff is wrapped around the patient's arm and inflated with air. As air is pumped into the cuff, the pressure in the cuff increases. The cuff tightens around the arm and compresses the artery, momentarily stopping blood flow. The person measuring the blood pressure listens to the artery through the stethoscope while slowly releasing the pressure in the cuff. When the pressure in the cuff equals the systolic blood pressure (the peak pressure), a pulse is heard through the stethoscope. The pulse is the sound of blood getting through the compressed artery during a contraction of the heart. The pressure reading at that exact moment is the systolic blood pressure. As the pressure in the cuff continues to decrease, the blood can flow through the compressed artery even between contractions, so the pulsing sound stops. The pressure reading when the pulsing sound stops is the diastolic blood pressure (the lowest pressure).

A blood pressure measurement is usually reported as two pressures, in mmHg, separated by a slash. For example, a blood pressure measurement of 122/84 indicates that the systolic blood pressure is 122 mmHg and the diastolic blood pressure is 84 mmHg. Although the value of blood pressure can vary throughout the day, a healthy (or normal) value is usually considered to be below 120 mmHg for systolic and below 80 mmHg for diastolic (Table 5.2). High blood pressure, also called hypertension, entails the health risks mentioned previously.



▲ A doctor or a nurse typically measures blood pressure with an inflatable cuff that compresses the main artery in the arm. A stethoscope is used to listen for blood flowing through the artery with each heartbeat.

Risk factors for hypertension include obesity, high salt (sodium) intake, high alcohol intake, lack of exercise, stress, a family history of high blood pressure, and age (blood pressure tends to increase as we get older). Mild hypertension can be managed with diet and exercise. Moderate to severe cases require doctor-prescribed medication.

TABLE 5.2 Blood Pressure Ranges

Blood Pressure	Systolic (mmHg)	Diastolic (mmHg)
Hypotension	<100	<60
Normal	100–119	60–79
Prehypertension	120–139	80–89
Hypertension Stage 1	140–159	90–99
Hypertension Stage 2	>160	>100

5.3 The Simple Gas Laws: Boyle's Law, Charles's Law, and Avogadro's Law

We have learned about pressure and its characteristics. We now broaden our discussion to include the four basic properties of a gas sample: pressure (P), volume (V), temperature (T), and amount in moles (n). These properties are interrelated—when one changes, it affects the others. The simple gas laws describe the relationships between pairs of these properties. For example, how does *volume* vary with *pressure* at constant temperature and amount of gas, or with *temperature* at constant pressure and amount of gas? We can elucidate these relationships by conducting experiments in which two of the four basic properties are held constant in order to determine the relationship between the other two. We can then express the results of the experiments as laws, called the simple gas laws.

Boyle's Law: Volume and Pressure

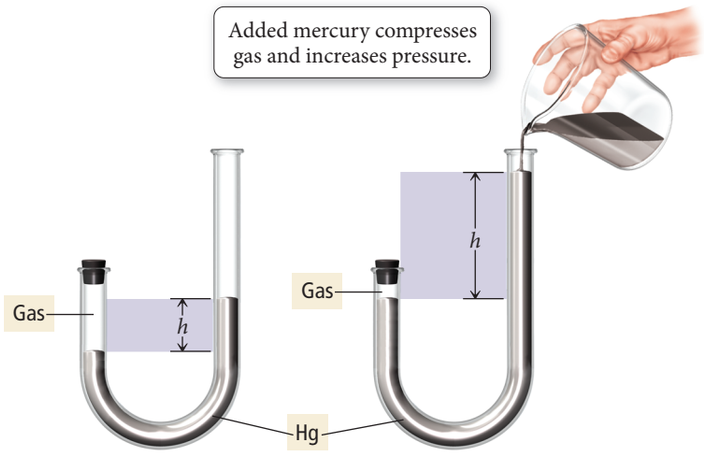
In the early 1660s, the pioneering English scientist Robert Boyle (1627–1691) and his assistant Robert Hooke (1635–1703) used a J-tube (Figure 5.6 ▼) to measure the volume of a sample of gas at different pressures. They trapped a sample of air in the J-tube and added mercury to increase the pressure on the gas. Boyle and Hooke observed an *inverse relationship* between volume and pressure—an increase in one results in a decrease in the other—as shown in Figure 5.7 ▼. This relationship is now known as **Boyle's law**.

Boyle's law assumes constant temperature and constant amount of gas.

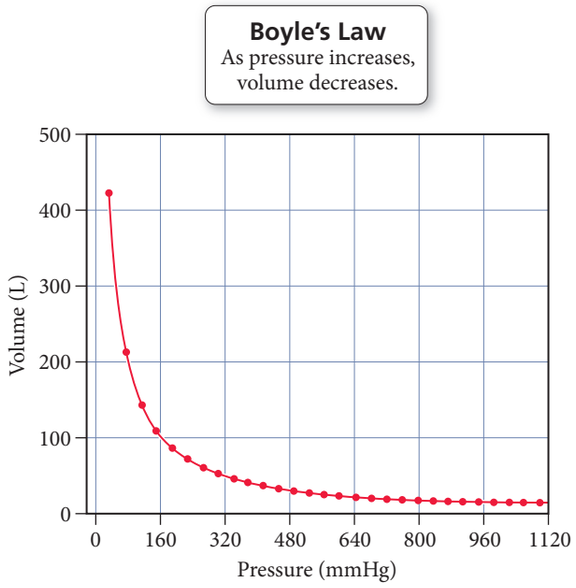
$$\text{Boyle's law:}\quad V \propto \frac{1}{P} \qquad (\text{constant } T \text{ and } n)$$

Boyle's law follows from the idea that pressure results from the collisions of the gas particles with the walls of their container. If the volume of a gas sample is decreased, the same number of gas particles is crowded into a smaller volume, resulting in more collisions with the walls and therefore an increase in the pressure (Figure 5.8 ▶).

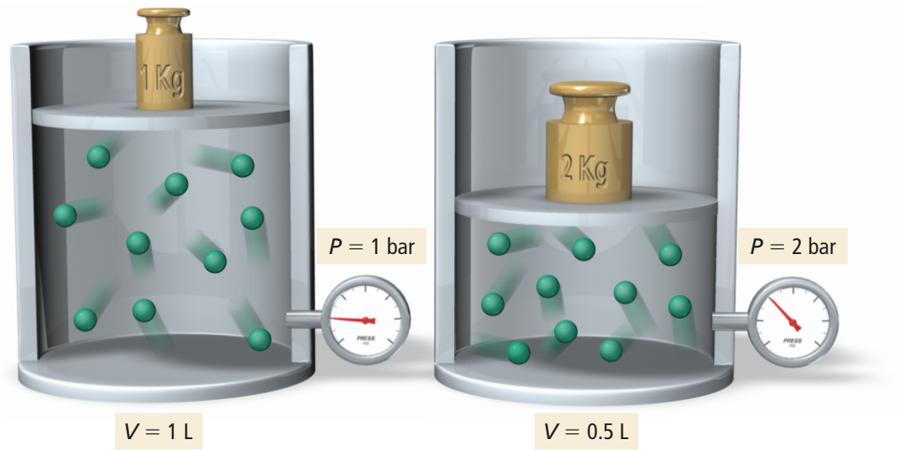
Scuba divers learn about Boyle's law during certification because it explains why they should not ascend toward the surface without continuous breathing. For every 10 m of depth that a diver descends in water, she experiences an additional 1 bar of pressure due to the weight of the water above her (Figure 5.9 ▶). The pressure regulator used in scuba diving delivers air into the diver's lungs at a pressure that matches the external pressure; otherwise, the diver could not inhale the air. For example, when a diver is 20 m



▲ **FIGURE 5.6 The J-Tube** In a J-tube, a column of mercury traps a sample of gas. The pressure on the gas can be increased by increasing the height (h) of mercury in the column.



▲ **FIGURE 5.7 Volume Versus Pressure** A plot of the volume of a gas sample—as measured in a J-tube—versus pressure. The plot shows that volume and pressure are inversely related.



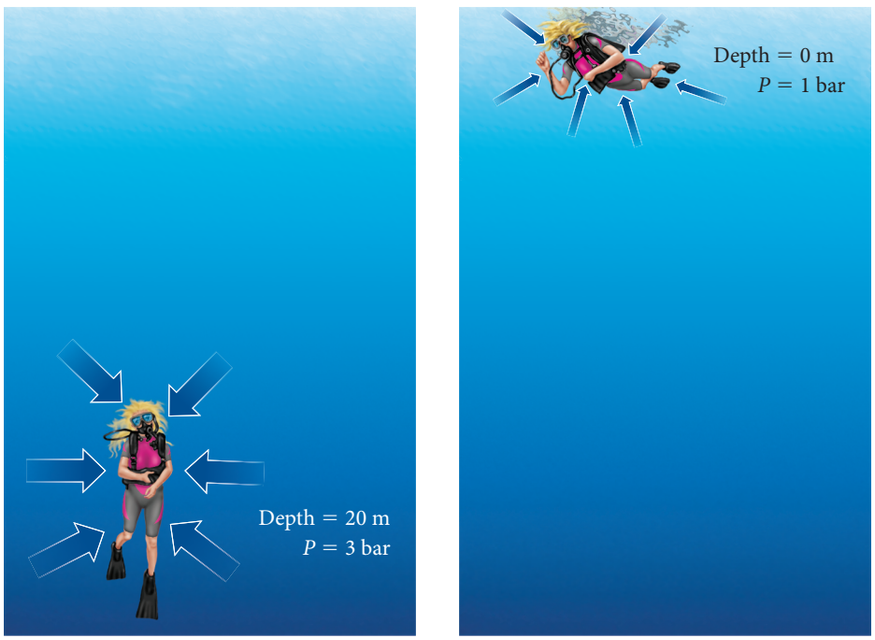
◀ **FIGURE 5.8 Molecular Interpretation of Boyle's Law** As the volume of a gas sample is decreased, gas molecules collide with surrounding surfaces more frequently, resulting in greater pressure.

below the surface, the regulator delivers air at a pressure of 3 bar to match the 3 bar of pressure around the diver (1 bar due to normal atmospheric pressure and 2 additional bar due to the weight of the water at 20 m). Suppose that a diver inhaled a lungful of air at a pressure of 3 bar and swam quickly to the surface (where the pressure is 1 bar) while holding her breath. What would happen to the volume of air in her lungs? Since the pressure decreases by a factor of 3, the volume of the air in her lungs would increase by a factor of 3—a dangerous situation. Of course, the volume increase in the diver's lungs would be so great that she would not be able to hold her breath all the way to the surface—the air would force itself out of her mouth but probably not before the expanded air severely damaged her lungs, possibly killing her. Consequently, the most important rule in diving is *never hold your breath*. To avoid such catastrophic results, divers must ascend slowly and breathe continuously, allowing the regulator to bring the air pressure in their lungs back to atmospheric pressure by the time they reach the surface.

We can use Boyle's law to calculate the volume of a gas following a pressure change or the pressure of a gas following a volume change *as long as the temperature and the amount of gas remain constant*. For these types of calculations, we write Boyle's law in a slightly different way:

$$\text{Since } V \propto \frac{1}{P}, \quad \text{then} \quad V = (\text{constant}) \times \frac{1}{P} \quad \text{or} \quad V = \frac{(\text{constant})}{P}$$

If two quantities are proportional, then one is equal to the other multiplied by a constant.



◀ **FIGURE 5.9 Increase in Pressure with Depth** For every 10 m of depth, a diver experiences approximately one additional bar of pressure due to the weight of the surrounding water. At 20 m, for example, the diver experiences approximately 3 bar of pressure (1 bar of normal atmospheric pressure plus an additional 2 bar due to the weight of the water).

If we multiply both sides by P, we get:

$$PV = \text{constant}$$

This relationship indicates that if the pressure increases, the volume decreases, but the product $P \times V$ always equals the same constant. For two different sets of conditions, we can say that:

$$P_1V_1 = \text{constant} = P_2V_2$$

or

$$P_1V_1 = P_2V_2 \qquad [5.2]$$

where P_1 and V_1 are the initial pressure and volume of the gas and P_2 and V_2 are the final volume and pressure, respectively.

EXAMPLE 5.2 Boyle's Law

A cylinder equipped with a movable piston has a volume of 7.25 L under an applied pressure of 657 mbar. What is the applied pressure, in bar, required to decrease the volume of the cylinder to 2.00 L?

To solve the problem, first solve Boyle's law (Equation 5.2) for P_2 and then substitute the given quantities to calculate P_2.

The question also asks to provide the answer in bar, so you must convert the answer you get from Boyle's law to the units requested.

SOLUTION

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2}$$

$$= \frac{657 \text{ mbar} \times 7.25 \cancel{\text{L}}}{2.00 \cancel{\text{L}}}$$

$$= 2380 \cancel{\text{mbar}} \times \frac{1 \text{ bar}}{1000 \cancel{\text{mbar}}}$$

$$= 2.38 \text{ bar}$$

CHECK The final volume is smaller than the initial volume by more than three times (almost four); therefore, the final pressure should be between three and four times larger, which it is.

FOR PRACTICE 5.2

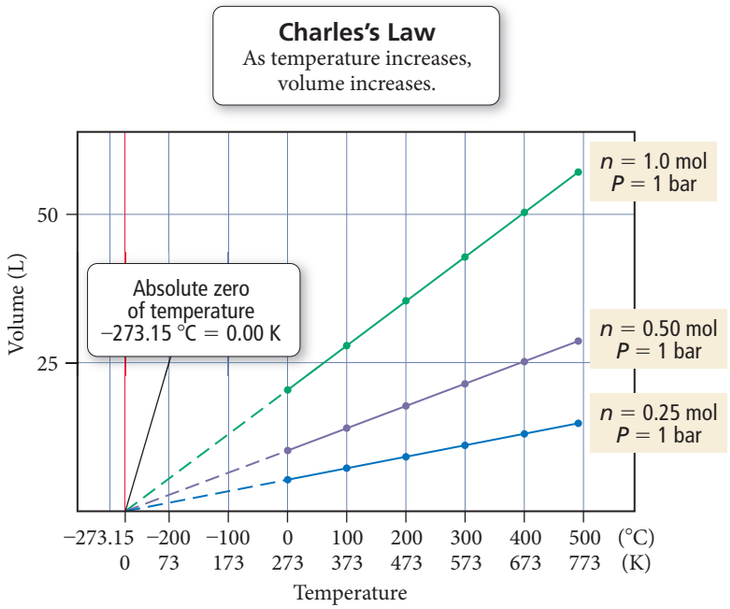
A snorkeller takes a syringe filled with 16 mL of air from the surface, in which the pressure is 1.0 bar, to an unknown depth. The volume of the air in the syringe at this depth is 7.5 mL. What is the pressure at this depth? If the pressure increases by 1 bar for every 10 m of depth, how deep is the snorkeller?

Charles's Law: Volume and Temperature

Suppose we keep the pressure of a gas sample constant and measure its volume at a number of different temperatures. Figure 5.10 ▶ shows the results of several such measurements. From the plot, we can see a relationship between volume and temperature: the volume of a gas increases with increasing temperature. Looking at the plot more closely, however, reveals more—volume and temperature are *linearly related*. If two variables are linearly related, then plotting one against the other produces a straight line.

Another interesting feature emerges if we extend or *extrapolate* the line in the plot backwards from the lowest measured temperature. The dashed extrapolated line shows that the gas should occupy zero volume at –273.15 °C. Recall from Chapter 1 that –273.15 °C corresponds to 0 K (zero on the Kelvin scale), the coldest possible temperature. The extrapolated line shows that below –273.15 °C, the gas would have a negative volume, which is physically impossible. For this reason, we refer to 0 K as *absolute zero*—colder temperatures do not exist.

The first person to carefully quantify the relationship between the volume of a gas and its temperature was J. A. C. Charles (1746–1823), a French mathematician and physicist. Charles was interested in gases and was among the first people to ascend in a



◀ **FIGURE 5.10 Volume Versus Temperature** The volume of a fixed amount of gas at a constant pressure increases linearly with increasing temperature in kelvins. (The extrapolated lines could not be measured experimentally because all gases condense into liquids before –273.15 °C is reached.)

hydrogen-filled balloon. The direct proportionality between volume and temperature is named **Charles's law** after him.

Charles's law assumes constant pressure and constant amount of gas.

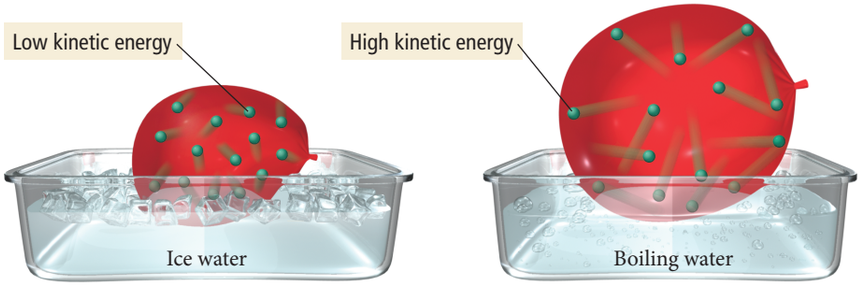
$$\text{Charles's law:} \quad V \propto T \qquad \text{(constant } P \text{ and } n\text{)}$$

When the temperature of a gas sample is increased, the gas particles move faster, collisions with the walls are more frequent, and the force exerted with each collision is greater. The only way for the pressure (the force per unit area) to remain constant is for the gas to occupy a larger volume, so that collisions become less frequent and occur over a larger area (Figure 5.11 ▼).

Charles's law explains why the second floor of a house is usually warmer than the ground floor. According to Charles's law, when air is heated, its volume increases, resulting in a lower density. The warm, less dense air tends to rise in a room filled with colder, denser air. Similarly, Charles's law explains why a hot-air balloon can take flight. The gas that fills a hot-air balloon is warmed with a burner, increasing its volume and lowering its density, and causing it to float in the colder, denser surrounding air.

You can experience Charles's law directly by holding a partially inflated balloon over a warm toaster. As the air in the balloon warms, you can feel the balloon expanding. Alternatively, you can a put an inflated balloon into liquid nitrogen and see that it becomes smaller as it cools.

We can use Charles's law to calculate the volume of a gas following a temperature change or the temperature of a gas following a volume change *as long as the pressure*



▲ **FIGURE 5.11 Molecular Interpretation of Charles's Law** If we move a balloon from an ice water bath to a boiling water bath, the temperature and therefore kinetic energy of the molecules increase, which causes the gas particles within the balloon to move faster. The end result of the temperature increase is that the volume of the gas expands.



▲ A hot-air balloon floats because the hot air is less dense than the surrounding cold air.



▲ If we place a balloon into liquid nitrogen (77 K), it shrivels up as the air within it cools and occupies less volume at the same external pressure.

and the amount of gas are constant. For these calculations, we rearrange Charles's law as follows:

$$\text{Since } V \propto T, \text{ then } V = \text{constant} \times T$$

If we divide both sides by T, we get:

$$V/T = \text{constant}$$

If the temperature increases, the volume increases in direct proportion so that the quotient, V/T, is always equal to the same constant. So, for two different measurements, we can say that:

$$V_1/T_1 = \text{constant} = V_2/T_2$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad [5.3]$$

where V_1 and T_1 are the initial volume and temperature of the gas and V_2 and T_2 are the final volume and temperature, respectively. *The temperatures must always be expressed in kelvins (K)*, because, as you can see in Figure 5.10, the volume of a gas is directly proportional to its absolute temperature, not its temperature in °C. For example, doubling the temperature of a gas sample from 1 °C to 2 °C does not double its volume, but doubling the temperature from 200 K to 400 K does double the volume of the gas.

Changing the temperature from 1 °C to 2 °C changes the temperature from 274 K to 275 K (an increase of 0.36%).

EXAMPLE 5.3 Charles's Law

A sample of gas has a volume of 2.80 L at an unknown temperature. When the sample is submerged in ice water at $T = 0.00$ °C, its volume decreases to 2.57 L. What was its initial temperature (in K and in °C)?

To solve the problem, first solve Charles's law for T_1.	**SOLUTION** $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ $T_1 = \frac{V_1}{V_2} T_2$
Before you substitute the numerical values to calculate T_1, you must convert the temperature to kelvins (K). *Remember, gas law problems must always be worked with Kelvin temperatures.*	$T_2\,(\text{K}) = 0.00 + 273.15 = 273.15\ \text{K}$
Substitute T_2 and the other given quantities to calculate T_1.	$T_1 = \frac{V_1}{V_2} T_2$ $= \frac{2.80\ \cancel{\text{L}}}{2.57\ \cancel{\text{L}}} \cdot 273.15\ \text{K}$ $= 297.6\ \text{K}$
Calculate T_1 in °C by subtracting 273.15 from the value in kelvins.	$T_1\,(°\text{C}) = 297.6 - 273.15 = 24\ °\text{C}$

FOR PRACTICE 5.3

A gas in a cylinder with a movable piston has an initial volume of 88.2 mL. If we heat the gas from 35 °C to 155 °C, what is its final volume (in mL)?

Avogadro's Law: Volume and Amount (in Moles)

So far, we have learned the relationships between volume and pressure, and volume and temperature, but we have considered only a constant amount of a gas. What happens when the amount of gas changes? The volume of a gas sample (at constant temperature and pressure) as a function of the amount of gas (in moles) in the sample is shown in Figure 5.12 ▶. We can see that the relationship between volume and amount is linear. As we might expect, extrapolation to zero moles shows zero volume. This relationship, first stated formally by Amedeo Avogadro, is called **Avogadro's law**:

Avogadro's law: $V \propto n$ (constant T and P)

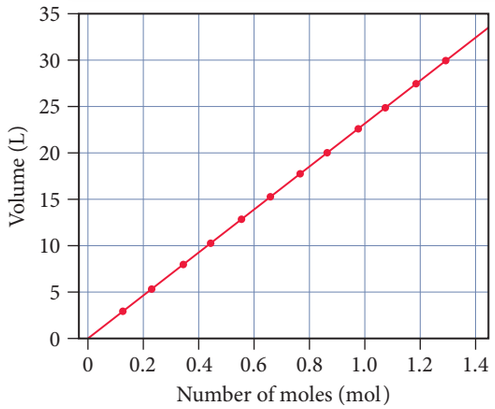
When the amount of gas in a sample increases at constant temperature and pressure, its volume increases in direct proportion because the greater number of gas particles fill more space.

You experience Avogadro's law when you inflate a balloon. With each exhaled breath, you add more gas particles to the inside of the balloon, increasing its volume. We can use Avogadro's law to calculate the volume of a gas following a change in the amount of the gas *as long as the pressure and temperature of the gas are constant*. For these types of calculations, we express Avogadro's law as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \qquad [5.4]$$

where V_1 and n_1 are the initial volume and number of moles of the gas and V_2 and n_2 are the final volume and number of moles, respectively. In calculations, we use Avogadro's law in a manner similar to the other gas laws, as demonstrated in the following example.

Avogadro's Law
As amount of gas increases, volume increases.



▲ **FIGURE 5.12 Volume Versus Number of Moles** The volume of a gas sample increases linearly with the number of moles of gas in the sample.

Avogadro's law assumes constant temperature and constant pressure and is independent of the identity of the gas.

EXAMPLE 5.4 **Avogadro's Law**

A 4.65-L sample of helium gas contains 0.225 mol of helium. How many additional moles of helium gas must we add to the sample to obtain a volume of 6.48 L? Assume constant temperature and pressure.

To solve the problem, first solve Avogadro's law for n_2. Then substitute the given quantities to calculate n_2.

Since the balloon already contains 0.225 mol of gas, calculate the amount of gas to add by subtracting 0.225 mol from the value you calculated for n_2.

SOLUTION

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$n_2 = \frac{V_2}{V_1} n_1$$

$$= \frac{6.48 \cancel{\text{L}}}{4.65 \cancel{\text{L}}} \cdot 0.225 \text{ mol}$$

$$= 0.314 \text{ mol}$$

$$\text{moles to add} = 0.314 \text{ mol} - 0.225 \text{ mol}$$

$$= 0.089 \text{ mol}$$

FOR PRACTICE 5.4

A chemical reaction occurring in a cylinder equipped with a movable piston produces 0.621 mol of a gaseous product. If the cylinder contained 0.120 mol of gas before the reaction and had an initial volume of 2.18 L, what was its volume after the reaction? (Assume constant pressure and temperature and that the initial amount of gas completely reacts.)

5.4 The Ideal Gas Law

The relationships that we have learned so far can be combined into a single law that encompasses all of them. So far, we know that:

$$V \propto \frac{1}{P} \qquad \text{(Boyle's law)}$$
$$V \propto T \qquad \text{(Charles's law)}$$
$$V \propto n \qquad \text{(Avogadro's law)}$$

Combining these three expressions, we get:

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

The volume of a gas is directly proportional to the number of moles of gas and to the temperature of the gas, but is inversely proportional to the pressure of the gas. We can replace the proportionality sign with an equal sign by incorporating R, a proportionality constant called the *ideal gas constant*:

$$V = \frac{RnT}{P}$$

Rearranging, we get:

$$PV = nRT \qquad [5.5]$$

This equation is the **ideal gas law**, and a hypothetical gas that exactly follows this law is an **ideal gas**. The value of R, the **ideal gas constant**, is the same for all gases and has the following value:

$$R = 0.08314 \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

L = litres
bar = pressure in bar
mol = moles
K = kelvins

The ideal gas law contains within it the simple gas laws that we have learned. For example, recall that Boyle's law states that $V \propto 1/P$ when the amount of gas (n) and the temperature of the gas (T) are kept constant. We can rearrange the ideal gas law as follows:

$$PV = nRT$$

First, divide both sides by P:

$$V = \frac{nRT}{P}$$

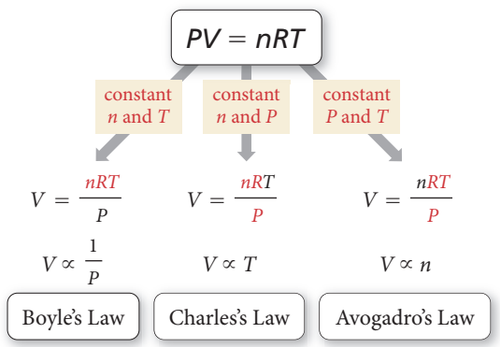
Then put the variables that are constant, along with R, in parentheses:

$$V = (nRT)\frac{1}{P}$$

Since n and T are constant in this case, and since R is always a constant, we can write:

$$V = (\text{constant}) \times \frac{1}{P}$$

which means that $V \propto 1/P$.



▲ The ideal gas law contains the simple gas laws within it.

The ideal gas law also shows how other pairs of variables are related. For example, from Charles's law we know that $V \propto T$ at constant pressure and constant number of moles. But what if we heat a sample of gas at constant *volume* and constant number of moles? This question applies to the warning labels on aerosol cans such as hair spray or deodorants. These labels warn against excessive heating or incineration of the can, even after the contents are used up. Why? An "empty" aerosol can is not really empty but contains a fixed amount of gas trapped in a fixed volume. What would happen if you were to heat the can? Let's rearrange the ideal gas law to clearly see the relationship between pressure and temperature at constant volume and constant number of moles:

$$PV = nRT$$

Divide both sides by V.

$$P = \frac{nRT}{V} = \left(\frac{nR}{V}\right)T$$

Since n and V are constant and since R is always a constant:

$$P = (\text{constant}) \times T$$

This relationship between pressure and temperature was first shown by Guillaume Amontons in the 17th century. As the temperature of a fixed amount of gas in a fixed volume increases, the pressure increases. In an aerosol can, this pressure increase can blow the can apart, which is why aerosol cans should not be heated or incinerated. They might explode.

The ideal gas law can also be used to determine the value of any one of the four variables (P, V, n, or T) given the other three. To do so, each of the quantities in the ideal gas law *must be expressed* in the units within R:

- pressure (P) in bar
- volume (V) in L
- moles (n) in mol
- temperature (T) in K



▲ The labels on most aerosol cans warn against incineration. Since the volume of the can is constant, an increase in temperature causes an increase in pressure and possibly an explosion.

EXAMPLE 5.5 Ideal Gas Law I

Calculate the volume occupied by 0.845 mol of nitrogen gas at a pressure of 1.37 bar and a temperature of 315 K. Assume that nitrogen is an ideal gas under these conditions.

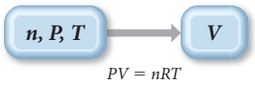
SORT The problem gives you the number of moles of nitrogen gas, the pressure, and the temperature. You are asked to find the volume.

GIVEN: $n = 0.845$ mol
$P = 1.37$ bar, $T = 315$ K

FIND: V

STRATEGIZE You are given three of the four variables (P, T, and n) in the ideal gas law and asked to find the fourth (V). The conceptual plan shows how the ideal gas law provides the relationship between the known quantities and the unknown quantity.

CONCEPTUAL PLAN



RELATIONSHIP USED $PV = nRT$

SOLVE To solve the problem, first solve the ideal gas law for V.

SOLUTION

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

Then substitute the given quantities to calculate V.

$$V = \frac{0.845\,\text{mol} \times 0.08314\,\frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \times 315\,\text{K}}{1.37\,\text{bar}}$$

$$= 16.2\,\text{L}$$

CHECK The units of the answer are correct. The magnitude of the answer (16.2 L) makes sense because, as you will see in the next section, one mole of an ideal gas under standard conditions (273.15 K and 1 bar) occupies 22.7 L. Although the present conditions are not standard, they are close enough for a ballpark check of the answer. Because this gas sample contains 0.845 mol, a volume of 16.2 L is reasonable.

FOR PRACTICE 5.5

An 8.50 L tire contains 0.552 mol of gas at a temperature of 305 K. What is the pressure (in bar and in psi) of the gas in the tire?

EXAMPLE 5.6 Ideal Gas Law II

Calculate the number of moles of gas in a 3.24 L basketball inflated to a *total pressure* of 24.3 psi at 25 °C. (Note: the *total pressure* is not the same as the pressure read on a pressure gauge, such as the kind used for checking a car or bicycle tire. That pressure, called the *gauge pressure*, is the *difference* between the total pressure and atmospheric pressure. In this case, if atmospheric pressure is 14.7 psi, the gauge pressure would be 9.6 psi. However, for calculations involving the ideal gas law, you must use the *total pressure* of 24.3 psi.)

SORT The problem gives you the pressure, the volume, and the temperature. You are asked to find the number of moles of gas.

GIVEN: $P = 24.3$ psi, $V = 3.24$ L, $T = 25$ °C

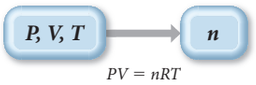
FIND: n

(*continued*)

EXAMPLE 5.6 (*continued*)

STRATEGIZE The conceptual plan shows how the ideal gas law provides the relationship between the given quantities and the quantity to be found.

CONCEPTUAL PLAN



RELATIONSHIP USED $PV = nRT$

SOLVE To solve the problem, first solve the ideal gas law for n.

SOLUTION

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

Before substituting into the equation, convert P and T into the correct units.

$$P = 24.3\,\text{psi} \times \frac{1\,\text{bar}}{14.504\,\text{psi}} = 1.6754\,\text{bar}$$

(Since rounding the intermediate answer would result in a slightly different final answer, we mark the least significant digit in the intermediate answer, but don't round until the end.)

$$T(\text{K}) = 25 + 273.15 = 298\,\text{K}$$

Finally, substitute into the equation and calculate n.

$$n = \frac{1.6754\,\text{bar} \times 3.24\,\text{L}}{0.08314\,\frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \times 298\,\text{K}} = 0.219\,\text{mol}$$

CHECK The units of the answer are correct. The magnitude of the answer (0.219 mol) makes sense because, as you will see in the next section, one mole of an ideal gas under standard conditions (273.15 K and 1 bar) occupies 22.7 L. At a pressure that is 65% higher than standard conditions, the volume of 1 mol of gas would be proportionally lower. Because this gas sample occupies 3.24 L, the answer of 0.219 mol is reasonable.

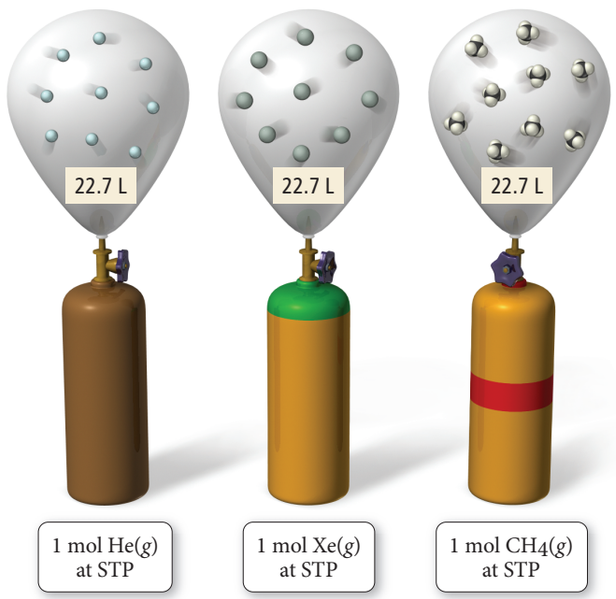
FOR PRACTICE 5.6

What volume does 0.556 mol of gas occupy at a pressure of 715 Torr and a temperature of 58 °C?

FOR MORE PRACTICE 5.6

Find the pressure in mbar of a 0.133 g sample of helium gas in a 648 mL container at a temperature of 32 °C.

The molar volume of 22.7 L only applies at conditions called STP.



▲ One mole of any gas occupies approximately 22.7 L at standard temperature (273.15 K) and pressure (1.00 bar).

5.5 Applications of the Ideal Gas Law: Molar Volume, Density, and Molar Mass of a Gas

We just examined how we can use the ideal gas law to calculate one of the variables (P, V, T, or n) given the other three. We now turn to three other applications of the ideal gas law: molar volume, density, and molar mass.

Molar Volume at Standard Temperature and Pressure

The volume occupied by one mole of a substance is its **molar volume**. For gases, we often specify the molar volume under conditions known as **standard temperature** ($T = 0\,°\text{C}$ or 273.15 K) **and pressure** ($P = 1.00$ bar), abbreviated as **STP**. Using the ideal gas law, we can determine that the molar volume of ideal gas at STP is:

$$V = \frac{nRT}{P}$$

$$V = \frac{1.00\,\text{mol} \times 0.08314\,\frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \times 273.15\,\text{K}}{1.00\,\text{bar}}$$

$$= 22.7\,\text{L}$$

The molar volume of an ideal gas at STP is useful because—as we saw in the *Check* sections of Examples 5.5 and 5.6—it gives us a way to approximate the volume of an ideal gas under conditions that are close to STP.



CONCEPTUAL CONNECTION 5.1

Molar Volume

Assuming ideal behaviour, which of the following gas samples will have the greatest volume at STP?

(a) 1 g of H_2 **(b)** 1 g of O_2 **(c)** 1 g of Ar

Density of a Gas

If we know the molar volume of an ideal gas under standard conditions, we can readily calculate the density of the gas under these conditions. Since density is mass/volume, and since the mass of one mole of a gas is simply its molar mass, the *density of a gas under standard conditions* is given by the following relationship:

$$\text{density} = \frac{\text{molar mass}}{\text{molar volume}}$$

For example, we calculate the densities of helium and nitrogen gas at STP as follows:

$$d_{He} = \frac{4.003 \text{ g } \cancel{\text{mol}^{-1}}}{22.7 \text{ L } \cancel{\text{mol}^{-1}}} = 0.176 \text{ g L}^{-1} \qquad d_{N_2} = \frac{28.02 \text{ g } \cancel{\text{mol}^{-1}}}{22.7 \text{ L } \cancel{\text{mol}^{-1}}} = 1.23 \text{ g L}^{-1}$$

Notice that *the density of a gas is directly proportional to its molar mass*. The greater the molar mass of a gas, the more dense the gas. For this reason, a gas with a molar mass lower than that of air tends to rise in air. For example, both helium and hydrogen gas (molar masses of 4.003 and 2.016 g mol^{-1}, respectively) have molar masses that are lower than the average molar mass of air (approximately 28.8 g mol^{-1}). Therefore, a balloon filled with either helium or hydrogen gas floats in air.

The detailed composition of air is covered in Section 5.6. The primary components of air are nitrogen (about four-fifths) and oxygen (about one-fifth).

We can calculate the density of a gas more generally (under any conditions) by using the ideal gas law. To do so, we can arrange the ideal gas law as follows:

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

Since the left-hand side of this equation has units of mol L^{-1}, it represents the *molar* density. We can obtain the density in g L^{-1} from the molar density by multiplying by the molar mass (M):

$$\frac{\cancel{\text{moles}}}{\text{litre}} \times \frac{\text{grams}}{\cancel{\text{mole}}} = \frac{\text{grams}}{\text{litre}}$$

Molar density × Molar mass = Density in g L^{-1}

Therefore,

$$d = \frac{PM}{RT} \qquad [5.6]$$

Density = $\frac{n}{V} \times M = \frac{PM}{RT}$

Molar density × Molar mass

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

Notice that, as expected, density increases with increasing molar mass. Notice also that as we learned in Section 5.3, density decreases with increasing temperature.

EXAMPLE 5.7 Density

Calculate the density of nitrogen gas at 125 °C and a pressure of 925 mbar.

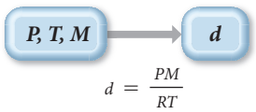
SORT The problem gives you the temperature and pressure of a gas and asks you to find its density. The problem also states that the gas is nitrogen.

GIVEN: $P = 925\,\text{mbar}$, $T = 125\,^\circ\text{C}$

FIND: d

STRATEGIZE Equation 5.6 provides the relationship between the density of a gas and its temperature, pressure, and molar mass. The temperature and pressure are given. You can calculate the molar mass from the formula of the gas, which we know is N_2.

CONCEPTUAL PLAN



RELATIONSHIPS USED

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

$$M_{N_2} = 28.02\ \text{g mol}^{-1}$$

SOLVE To solve the problem, gather each of the required quantities in the correct units. Convert the temperature to kelvin and the pressure to bar.

Now substitute the quantities into the equation to calculate density.

SOLUTION

$$T(\text{K}) = 125 + 273.15 = 398\,\text{K}$$

$$P = 925\,\text{mbar} \times \frac{1\,\text{bar}}{1000\,\text{mbar}} = 0.925\,\text{bar}$$

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

$$= \frac{0.925\,\text{bar} \times 28.02\,\frac{\text{g}}{\text{mol}}}{0.08314\,\frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \times 398\,\text{K}}$$

$$= 0.783\,\text{g L}^{-1}$$

CHECK The units of the answer are correct. The magnitude of the answer (0.783 g L^{-1}) makes sense because earlier we calculated the density of nitrogen gas at STP as 1.23 g L^{-1}. Because the temperature is higher than standard conditions, and the pressure is slightly lower, it follows that the density is lower.

FOR PRACTICE 5.7

Calculate the density of xenon gas at a pressure of 742 mmHg and a temperature of 45 °C.

FOR MORE PRACTICE 5.7

A gas has a density of 1.43 g L^{-1} at a temperature of 23 °C and a pressure of 0.789 bar. Calculate its molar mass.

Molar Mass of a Gas

We can use the ideal gas law in combination with mass measurements to calculate the molar mass of an unknown gas. First we measure the mass and volume of an unknown gas under conditions of known pressure and temperature. Then we determine the amount of the gas in moles from the ideal gas law. Finally, we calculate the molar mass by dividing the mass (in grams) by the amount (in moles) as shown in the following example.

EXAMPLE 5.8 Molar Mass of a Gas

A sample of gas has a mass of 0.311 g. Its volume is 0.225 L at a temperature of 55 °C and a pressure of 886 Torr. Find the molar mass of the gas.

SORT The problem gives you the mass of a gas sample, along with its volume, temperature, and pressure. You are asked to find the molar mass.

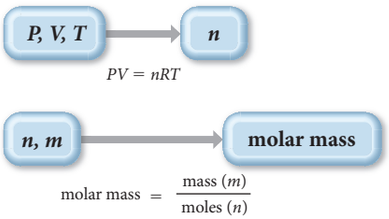
GIVEN: $m = 0.311$ g, $V = 0.225$ L, $T\,(^\circ\text{C}) = 55\,^\circ\text{C}$, $P = 886$ Torr

FIND: molar mass (g mol^{-1})

STRATEGIZE The conceptual plan has two parts. In the first part, use the ideal gas law to find the number of moles of gas.

In the second part, use the definition of molar mass to find the molar mass.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$PV = nRT$$

$$\text{Molar mass} = \frac{\text{mass } (m)}{\text{moles } (n)}$$

SOLVE To find the number of moles, first solve the ideal gas law for n.

Before substituting into the equation for n, convert the pressure to bar and the temperature to K.

Now, substitute into the equation and calculate n, the number of moles.

Finally, use the number of moles (n) and the given mass (m) to find the molar mass.

SOLUTION

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$P = 886\ \text{Torr} \times \frac{1\ \text{bar}}{750.01\ \text{Torr}} = 1.1813\ \text{bar}$$

$$T(\text{K}) = 55 + 273.15 = 328\ \text{K}$$

$$n = \frac{1.1813\ \text{bar} \times 0.225\ \text{L}}{0.08314 \dfrac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \times 328\ \text{K}}$$

$$= 9.7469 \times 10^{-3}\ \text{mol}$$

$$M = \frac{m}{n}$$

$$= \frac{0.311\ \text{g}}{9.7469 \times 10^{-3}\ \text{mol}}$$

$$= 31.9\ \text{g mol}^{-1}$$

CHECK The units of the answer are correct. The magnitude of the answer (31.9 g mol^{-1}) is a reasonable number for a molar mass. If you calculated some very small number (such as any number smaller than 1) or a very large number, you probably made some mistake. Most gases have molar masses between one and several hundred grams per mole.

FOR PRACTICE 5.8

A sample of gas has a mass of 827 mg. Its volume is 0.270 L at a temperature of 88 °C and a pressure of 1299 mbar. Find its molar mass.

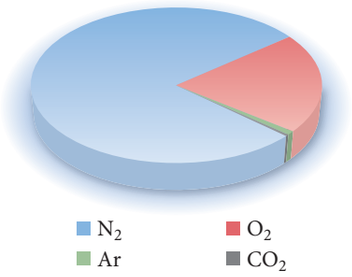
5.6 Mixtures of Gases and Partial Pressures

Many gas samples are not pure, but are mixtures of gases. Dry air, for example, is a mixture containing nitrogen, oxygen, argon, carbon dioxide, and a few other gases in trace amounts (Table 5.3).

Because the molecules in an ideal gas do not interact (as we will discuss further in Section 5.8), each of the components in an ideal gas mixture acts independently of the others. For example, the nitrogen molecules in air exert a certain pressure—78% of the total pressure—that is independent of the other gases in the mixture. Likewise, the oxygen molecules in air exert a certain pressure—21% of the total pressure—that is also independent of the other gases in the mixture. The pressure due to any individual component in a gas mixture is the **partial pressure** (P_n) of that component and can be calculated from the ideal gas law by assuming that each gas component acts independently. For a multicomponent gas mixture, we can calculate the partial

TABLE 5.3 Composition of Dry Air

Gas	Percent by Volume (%)
Nitrogen (N_2)	78
Oxygen (O_2)	21
Argon (Ar)	0.9
Carbon dioxide (CO_2)	0.04



pressure of each component from the ideal gas law and the number of moles of that component (n_n) as follows:

$$P_a = n_a \frac{RT}{V}; \quad P_b = n_b \frac{RT}{V}; \quad P_c = n_c \frac{RT}{V}; \cdots \qquad [5.7]$$

The sum of the partial pressures of the components in a gas mixture must equal the total pressure:

$$P_{total} = P_a + P_b + P_c + \cdots \qquad [5.8]$$

where P_{total} is the total pressure and P_a, P_b, P_c, . . . are the partial pressures of the components. This relationship is known as **Dalton's law of partial pressures**.

Combining Equations 5.7 and 5.8, we get:

$$\begin{aligned} P_{total} &= P_a + P_b + P_c + \cdots \\ &= n_a \frac{RT}{V} + n_b \frac{RT}{V} + n_c \frac{RT}{V} + \cdots \\ &= (n_a + n_b + n_c + \cdots) \frac{RT}{V} \\ &= (n_{total}) \frac{RT}{V} \end{aligned} \qquad [5.9]$$

The total number of moles in the mixture, when substituted into the ideal gas law, indicates the total pressure of the sample.

If we divide Equation 5.7 by Equation 5.9, we get the following result:

$$\frac{P_a}{P_{total}} = \frac{n_a \cancel{(RT/V)}}{n_{total} \cancel{(RT/V)}} = \frac{n_a}{n_{total}} \qquad [5.10]$$

The quantity n_a/n_{total}, the number of moles of a component in a mixture divided by the total number of moles in the mixture, is called the **mole fraction** (χ_a):

$$\chi_a = \frac{n_a}{n_{total}} \qquad [5.11]$$

Rearranging Equation 5.10 and substituting the definition of mole fraction gives the following:

$$\frac{P_a}{P_{total}} = \frac{n_a}{n_{total}}$$

$$P_a = \frac{n_a}{n_{total}} P_{total} = \chi_a P_{total}$$

or simply

$$P_a = \chi_a P_{total} \qquad [5.12]$$

The partial pressure of a component in a gaseous mixture is its mole fraction multiplied by the total pressure. For real gases, the mole fraction of a component is equivalent to its percent by volume divided by 100%. Therefore, based on Table 5.3, we calculate the partial pressure of nitrogen (P_{N_2}) in air at 1.00 bar as follows:

$$\begin{aligned} P_{N_2} &= 0.78 \times 1.00 \text{ bar} \\ &= 0.78 \text{ bar} \end{aligned}$$

Likewise, the partial pressure of oxygen in air at 1.00 bar is 0.21 bar and the partial pressure of Ar in air is 0.009 bar. Applying Dalton's law of partial pressures to air at 1.00 bar:

$$\begin{aligned} P_{total} &= P_{N_2} + P_{O_2} + P_{Ar} \\ P_{total} &= 0.78 \text{ bar} + 0.21 \text{ bar} + 0.009 \text{ bar} \\ &= 1.00 \text{ bar} \end{aligned}$$

For these purposes, we can ignore the contribution of the CO_2 and other trace gases because they are so small. However, they correspond to the 0.001 bar that is missing from the calculated sum, before rounding.

EXAMPLE 5.9 Total Pressure and Partial Pressures

A 1.00 L mixture of helium, neon, and argon has a total pressure of 662 Torr at 298 K. If the partial pressure of helium is 341 Torr and the partial pressure of neon is 112 Torr, what mass of argon is present in the mixture?

SORT The problem gives you the partial pressures of two of the three components in a gas mixture, along with the total pressure, the volume, and the temperature, and asks you to find the mass of the third component.

GIVEN: $P_{He} = 341$ Torr, $P_{Ne} = 112$ Torr, $P_{total} = 662$ Torr, $V = 1.00$ L, $T = 298$ K

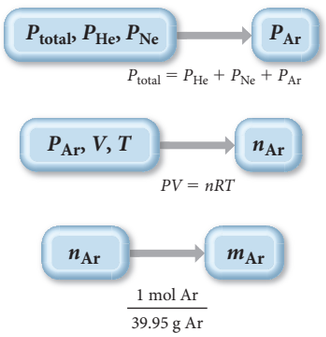
FIND: m_{Ar}

STRATEGIZE You can find the mass of argon from the number of moles of argon, which you can calculate from the partial pressure of argon and the ideal gas law. Begin by using Dalton's law to determine the partial pressure of argon.

Then use the partial pressure of argon together with the volume of the sample and the temperature to find the number of moles of argon.

Finally, use the molar mass of argon to calculate the mass of argon from the number of moles of argon.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$P_{total} = P_{He} + P_{Ne} + P_{Ar}$ (Dalton's law)
$PV = nRT$ (ideal gas law)
molar mass Ar $= 39.95$ g mol^{-1}

SOLVE Follow the conceptual plan. To find the partial pressure of argon, solve the equation for P_{Ar} and substitute the values of the other partial pressures to calculate P_{Ar}.

SOLUTION

$$P_{total} = P_{He} + P_{Ne} + P_{Ar}$$
$$P_{Ar} = P_{total} - P_{He} - P_{Ne}$$
$$= 662\,\text{Torr} - 341\,\text{Torr} - 112\,\text{Torr}$$
$$= 209\,\text{Torr}$$

Convert the partial pressure from Torr (mmHg) to bar and use it in the ideal gas law to calculate the amount of argon in moles.

$$209\,\text{Torr} \times \frac{1\,\text{bar}}{750.01\,\text{Torr}} = 0.27866\,\text{bar}$$

$$n = \frac{PV}{RT} = \frac{0.27866\,\text{bar} \times 1.00\,\text{L}}{0.08314\,\frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \times 298\,\text{K}} = 1.1247 \times 10^{-2}\,\text{mol}$$

Use the molar mass of argon to convert from amount of argon in moles to mass of argon.

$$m = nM = 1.1247 \times 10^{-2}\,\text{mol} \times 39.95\,\text{g mol}^{-1} = 0.449\,\text{g}$$

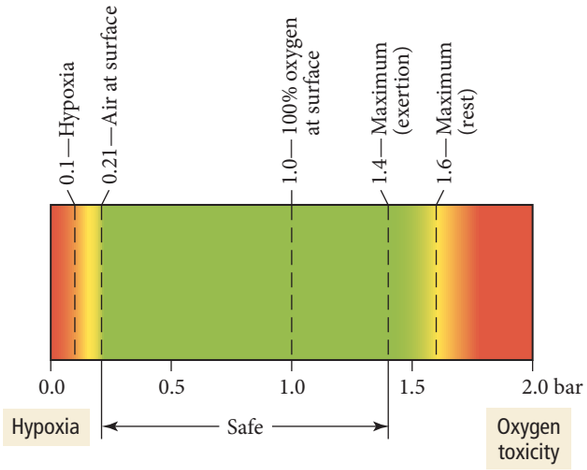
CHECK The units of the answer are correct. The magnitude of the answer makes sense because the volume is 1.0 L, which at STP would contain about 1/23 mol. Since the partial pressure of argon in the mixture is about 1/3 of the total pressure, we roughly estimate about 1/69 of one molar mass of argon, which is fairly close to the answer we got.

FOR PRACTICE 5.9

A sample of hydrogen gas is mixed with water vapour. The mixture has a total pressure of 1007 mbar and the water vapour has a partial pressure of 32 mbar. What amount (in moles) of hydrogen gas is contained in 1.55 L of this mixture at 298 K?

Deep-Sea Diving and Partial Pressures

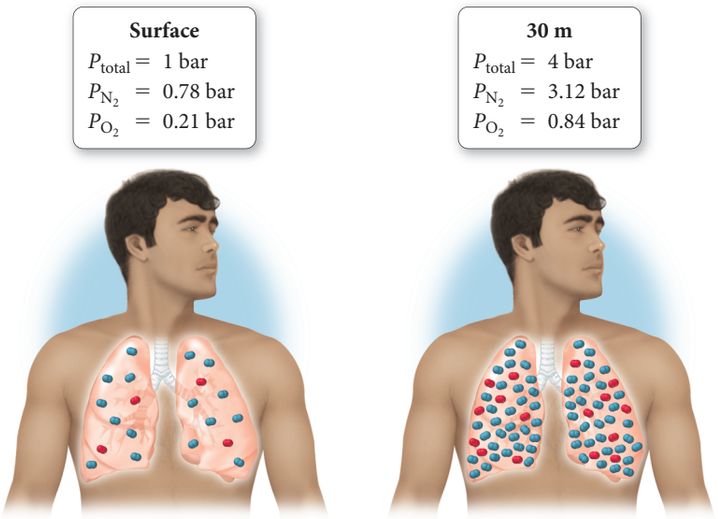
Our lungs have evolved to breathe oxygen at a partial pressure of $P_{O_2} = 0.21$ bar. If the total pressure decreases—when we climb a mountain, for example—the partial pressure of oxygen also decreases. On top of Mount Everest, where the total pressure is 0.311 bar, the partial pressure of oxygen is only 0.065 bar. Low oxygen levels produce a physiological condition called **hypoxia** or oxygen starvation (Figure 5.13 ▼). Mild hypoxia causes dizziness, headache, and shortness of breath. Severe hypoxia, which occurs when P_{O_2} drops below 0.1 bar, may result in unconsciousness or even death. For this reason, climbers hoping to make the summit of Mount Everest usually carry oxygen to breathe.



▲ **FIGURE 5.13 Oxygen Partial Pressure Limits** The partial pressure of oxygen in air at sea level is 0.21 bar. Partial pressures of oxygen below 0.1 bar and above 1.4 bar are dangerous to humans.

While not as dangerous as a lack of oxygen, too much oxygen can also cause physiological problems. Scuba divers, as we have learned, breathe pressurized air. At 30 m, a scuba diver breathes air at a total pressure of 4.0 bar, making P_{O_2} about 0.84 bar. This elevated partial pressure of oxygen raises the density of oxygen molecules in the lungs, resulting in a higher concentration of oxygen in body tissues. When P_{O_2} increases beyond 1.4 bar, the increased oxygen concentration in body tissues causes a condition called **oxygen toxicity**, which results in muscle twitching, tunnel vision, and convulsions. Divers who venture too deep without proper precautions have drowned because of oxygen toxicity. A second problem associated with breathing pressurized air is the increase of nitrogen in the lungs. At 30 m, a scuba diver breathes nitrogen at $P_{N_2} = 3.12$ bar, which increases the nitrogen concentration in body tissues and fluids. When P_{N_2} increases beyond about 4 bar, a condition called **nitrogen narcosis** or *rapture of the deep* results. Divers describe this condition as feeling inebriated or drunk. A diver breathing compressed air at 60 m feels as if he has consumed too much wine.

To avoid oxygen toxicity and nitrogen narcosis, deep-sea divers—those who descend beyond 50 m—breathe specialized mixtures of gases. One common mixture is called heliox, a mixture of helium and oxygen. These mixtures usually contain a smaller percentage of oxygen than would be found in air, thereby lowering the risk of oxygen toxicity. Heliox also contains helium instead of nitrogen, eliminating the risk of nitrogen narcosis.



▶ When a diver breathes compressed air, the abnormally high partial pressure of oxygen in the lungs leads to an elevated concentration of oxygen in body tissues.

EXAMPLE 5.10 Partial Pressures and Mole Fractions

A 12.5-L scuba diving tank contains a helium–oxygen (heliox) mixture made up of 24.2 g of He and 4.32 g of O_2 at 298 K. Calculate the mole fraction and partial pressure of each component in the mixture and the total pressure of the mixture.

SORT The problem gives the masses of two gases in a mixture and the volume and temperature of the mixture. You are to find the mole fraction and partial pressure of each component, as well as the total pressure.

GIVEN: $m_{He} = 24.2$ g, $m_{O_2} = 4.32$ g, $V = 12.5$ L, $T = 298$ K

FIND: χ_{He}, χ_{O_2}, P_{He}, P_{O_2}, P_{total}

STRATEGIZE The conceptual plan has several parts. To calculate the mole fraction of each component, you must first find the number of moles of each component. Therefore, in the first part of the conceptual plan, convert the masses to moles using the molar masses.

CONCEPTUAL PLAN

$m_{He} \rightarrow n_{He}$ $\left(\frac{1 \text{ mol He}}{4.003 \text{ g He}}\right)$ $\qquad$ $m_{O_2} \rightarrow n_{O_2}$ $\left(\frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2}\right)$

In the second part, calculate the mole fraction of each component using the mole fraction definition.

To calculate *partial pressures,* calculate the *total pressure* and then use the mole fractions from the previous part to calculate the partial pressures. Calculate the total pressure from the sum of the moles of both components. (Alternatively, you can calculate the partial pressures of the components individually, using the number of moles of each component. Then you can sum them to obtain the total pressure.)

Last, use the mole fractions of each component and the total pressure to calculate the partial pressure of each component.

$$\chi_{He} = \frac{n_{He}}{n_{He} + n_{O_2}}; \ \chi_{O_2} = \frac{n_{O_2}}{n_{He} + n_{O_2}}$$

$$P_{total} = \frac{(n_{He} + n_{O_2})RT}{V}$$

$$P_{He} = \chi_{He}P_{total}; \ P_{O_2} = \chi_{O_2}P_{total}$$

RELATIONSHIPS USED

$\chi_a = n_a/n_{total}$ (mole fraction definition)

$P_{total}V = n_{total}RT$ (ideal gas law)

$P_a = \chi_a P_{total}$

SOLVE Follow the plan to solve the problem. Begin by converting each of the masses to amounts in moles.

SOLUTION

$$24.2 \text{ g-}\cancel{\text{He}} \times \frac{1 \text{ mol He}}{4.003 \text{ g-}\cancel{\text{He}}} = 6.05 \text{ mol He}$$

$$4.32 \text{ g-}\cancel{O_2} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g-}\cancel{O_2}} = 0.135 \text{ mol } O_2$$

Calculate each of the mole fractions.

$$\chi_{He} = \frac{n_{He}}{n_{He} + n_{O_2}} = \frac{6.05}{6.05 + 0.135} = 0.97\underline{8}17$$

$$\chi_{O_2} = \frac{n_{O_2}}{n_{He} + n_{O_2}} = \frac{0.135}{6.05 + 0.135} = 0.021\underline{8}27$$

Calculate the total pressure.

$$P_{total} = \frac{(n_{He} + n_{O_2})RT}{V}$$

$$= \frac{(6.05 \cancel{\text{mol}} + 0.135 \cancel{\text{mol}})\left(0.08314 \frac{\cancel{\text{L}} \cdot \text{bar}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}}\right)(298 \cancel{\text{K}})}{12.5 \cancel{\text{L}}}$$

$$= 12.\underline{2}59 \text{ bar}$$

Finally, calculate the partial pressure of each component.

$$P_{He} = \chi_{He}P_{total} = 0.97\underline{8}17 \times 12.\underline{2}59 \text{ bar} = 12.0 \text{ bar}$$

$$P_{O_2} = \chi_{O_2}P_{total} = 0.021\underline{8}27 \times 12.\underline{2}59 \text{ bar} = 0.268 \text{ bar}$$

CHECK The units of the answers are correct and the magnitudes are reasonable.

FOR PRACTICE 5.10

A diver breathes a heliox mixture with an oxygen mole fraction of 0.050. What must the total pressure be for the partial pressure of oxygen to be 0.21 bar?

Collecting Gases over Water

When the desired product of a chemical reaction is a gas, the gas is often collected by the displacement of water. For example, suppose the following reaction is used as a source of hydrogen gas:

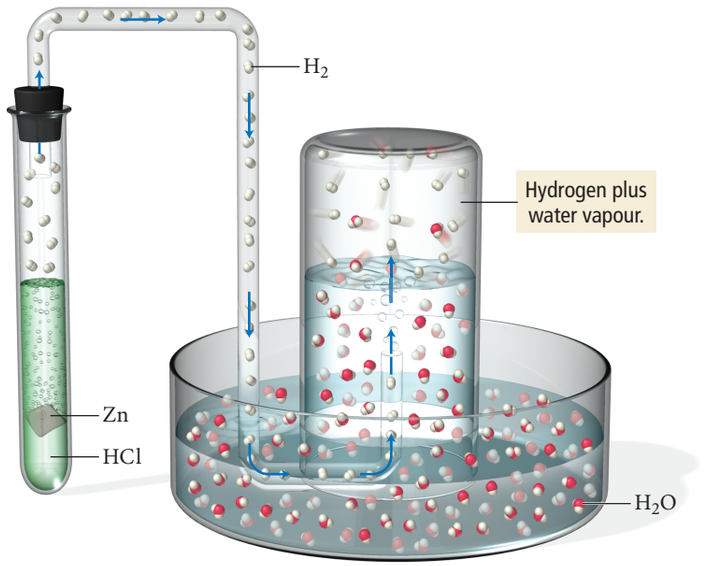
$$Zn(s) + 2 \text{ HCl}(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

As the hydrogen gas forms, it bubbles through the water and gathers in the collection flask (Figure 5.14 ▼). The hydrogen gas collected in this way is not pure, however, but mixed with water vapour because some water molecules evaporate and mix with the hydrogen molecules.

We cover vapour pressure in detail in Chapter 11.

The partial pressure of water in the mixture, called its **vapour pressure**, depends on temperature (Table 5.4). Vapour pressure increases with increasing temperature because higher temperatures cause more water molecules to evaporate.

Appendix IIE contains a more complete table of the vapour pressure of water versus temperature.



▶ FIGURE 5.14 Collecting a Gas over Water When the gaseous product of a chemical reaction is collected over water, the product molecules (in this case, H_2) become mixed with water molecules. The pressure of water in the final mixture is equal to the vapour pressure of water at the temperature at which the gas is collected. The partial pressure of the product is then the total pressure minus the partial pressure of water.

TABLE 5.4 Vapour Pressure of Water Versus Temperature

Temperature (°C)	Pressure (Torr)	Temperature (°C)	Pressure (Torr)
0	4.58	55	118.2
5	6.54	60	149.6
10	9.21	65	187.5
15	12.79	70	233.7
20	17.55	75	289.1
25	23.78	80	355.1
30	31.86	85	433.6
35	42.23	90	525.8
40	55.40	95	633.9
45	71.97	100	760.0
50	92.0		

Suppose we collect the hydrogen gas over water at a total pressure of 758.2 Torr and a temperature of 25 °C. What is the partial pressure of the hydrogen gas? We know that the total pressure is 758.2 Torr and we can see from Table 5.4 that the partial pressure of water is 23.78 Torr (its vapour pressure at 25 °C):

$$P_{\text{total}} = P_{H_2} + P_{H_2O}$$

$$758.2 \text{ Torr} = P_{H_2} + 23.78 \text{ Torr}$$

Therefore,

$$P_{H_2} = 758.2 \text{ Torr} - 23.78 \text{ Torr}$$

$$= 734.4 \text{ Torr}$$

The partial pressure of the hydrogen in the mixture will be 734.4 Torr.

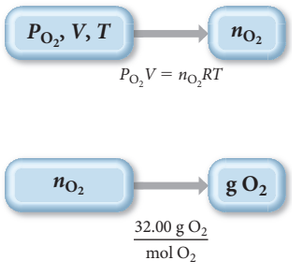
EXAMPLE 5.11 Collecting Gases over Water

In order to determine the rate of photosynthesis, the oxygen gas emitted by an aquatic plant was collected over water at a temperature of 293 K and a total pressure of 755.2 Torr. Over a specific time period, a total of 1.02 L of gas was collected. What mass of oxygen gas (in grams) was formed?

SORT The problem gives the volume of gas collected over water as well as the temperature and the pressure. You are to find the mass in grams of oxygen formed.	**GIVEN:** $V = 1.02$ L, $P_{\text{total}} = 755.2$ Torr, $T = 293$ K **FIND:** g O_2
STRATEGIZE You can determine the mass of oxygen from the amount of oxygen in moles, which you can calculate from the ideal gas law if you know the partial pressure of oxygen. Since the oxygen is mixed with water vapour, you can find the partial pressure of oxygen in the mixture by subtracting the partial pressure of water at 293 K (20 °C) from the total pressure.	**CONCEPTUAL PLAN** $P_{O_2} = P_{\text{total}} - P_{H_2O}$ (20 °C)

Next, use the ideal gas law to determine the number of moles of oxygen from its partial pressure, volume, and temperature.

Finally, use the molar mass of oxygen to convert the number of moles to grams.



RELATIONSHIPS USED

$P_{total} = P_a + P_b + P_c + \cdots$ (Dalton's law)

$PV = nRT$ (ideal gas law)

SOLVE Follow the conceptual plan to solve the problem. Begin by calculating the partial pressure of oxygen in the oxygen/water mixture. You can find the partial pressure of water at 20 °C in Table 5.4.

Next, solve the ideal gas law for number of moles. Before substituting into the ideal gas law, you must convert the partial pressure of oxygen from torr to bar.

Next, substitute into the ideal gas law to find the number of moles of oxygen.

Finally, use the molar mass of oxygen to convert to grams of oxygen.

SOLUTION

$$P_{O_2} = P_{total} - P_{H_2O}(\text{at } 20\ ^\circ\text{C})$$
$$= 755.2\ \text{Torr} - 17.55\ \text{Torr} = 737.65\ \text{Torr}$$
$$n_{O_2} = \frac{P_{O_2}V}{RT}$$
$$P_{O_2} = 737.65\ \text{Torr} \times \frac{1\ \text{bar}}{750.01\ \text{Torr}} = 0.98352\ \text{bar}$$
$$n_{O_2} = \frac{(0.98352\ \text{bar})(1.02\ \text{L})}{\left(0.08314\ \frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}\right)(293\ \text{K})}$$
$$= 4.1182 \times 10^{-2}\ \text{mol}$$
$$m = nM = (4.1182 \times 10^{-2}\ \text{mol})(32.00\ \text{g mol}^{-1}) = 1.32\ \text{g}$$

CHECK The answer is in the correct units. We can quickly check the magnitude of the answer by using molar volume. Under STP, one litre is about 1/23 of one mole. Therefore, the answer should be about 1/23 the molar mass of oxygen ($1/23 \times 32 = 1.39$). The magnitude of our answer seems reasonable.

FOR PRACTICE 5.11

A common way to make hydrogen gas in the laboratory is to place a metal such as zinc in hydrochloric acid. The hydrochloric acid reacts with the metal to produce hydrogen gas, which is then collected over water. Suppose a student carries out this reaction and collects a total of 154.4 mL of gas at a pressure of 742 Torr and a temperature of 25 °C. What mass of hydrogen gas (in mg) did the student collect?

5.7 Gases in Chemical Reactions: Stoichiometry Revisited

In Chapter 4, we learned how we can use the coefficients in chemical equations as conversion factors between number of moles of reactants and number of moles of products in a chemical reaction. We used these conversion factors to determine, for example, the mass of product obtained in a chemical reaction based on a given mass of reactant, or the mass of one reactant needed to react completely with a given mass of another reactant. The general conceptual plan for these kinds of calculations is:



where A and B are two different substances involved in the reaction and the conversion factor between amounts (in moles) of each comes from the stoichiometric coefficients in the balanced chemical equation.

In reactions involving *gaseous* reactants or products, we often specify the quantity of a gas in terms of its volume at a given temperature and pressure. As we have seen, stoichiometric relationships always express relative amounts in moles. However, we can

The pressures here could also be partial pressure.

use the ideal gas law to determine the amount in moles from the volume, or to determine the volume from the amount in moles:

$$n = \frac{PV}{RT} \qquad V = \frac{nRT}{P}$$

The general conceptual plan for these kinds of calculations is:



The following examples demonstrate this kind of calculation.

EXAMPLE 5.12 Gases in Chemical Reactions

Methanol (CH_3OH) can be synthesized by the following reaction:

$$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$$

What volume (in litres) of hydrogen gas, at a temperature of 355 K and a pressure of 984 mbar, is required to synthesize 35.7 g of methanol given an excess of CO gas?

SORT You are given the mass of methanol, the product of a chemical reaction. You are asked to find the required volume of one of the reactants (hydrogen gas) at a specified temperature and pressure.

GIVEN: 35.7 g CH_3OH, $T = 355$ K, $P = 984$ mbar

FIND: V_{H_2}

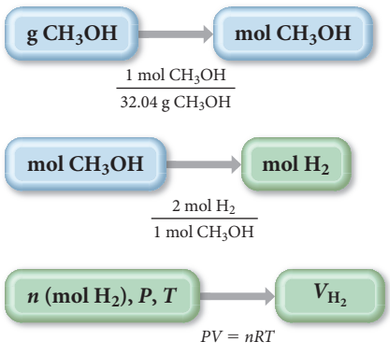
STRATEGIZE You can calculate the required volume of hydrogen gas from the number of moles of hydrogen gas, which you can obtain from the number of moles of methanol via the stoichiometry of the reaction.

First, find the number of moles of methanol from its mass by using the molar mass.

Then use the stoichiometric relationship from the balanced chemical equation to find the number of moles of hydrogen you need to form that quantity of methanol.

Finally, substitute the number of moles of hydrogen together with the pressure and temperature into the ideal gas law to find the volume of hydrogen.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$PV = nRT$ (ideal gas law)
2 mol H_2 : 1 mol CH_3OH (from balanced chemical equation)
molar mass $CH_3OH = 32.04$ g mol^{-1}

SOLVE Follow the conceptual plan to solve the problem. Begin by using the mass of methanol to determine the number of moles of methanol.

Next, convert the number of moles of methanol to moles of hydrogen.

Finally, use the ideal gas law to find the volume of hydrogen. Before substituting into the equation, you must convert the pressure to bar.

SOLUTION

$$35.7\ \text{g}\ CH_3OH \times \frac{1\ \text{mol}\ CH_3OH}{32.04\ \text{g}\ CH_3OH} = 1.1142\ \text{mol}\ CH_3OH$$

$$1.1142\ \text{mol}\ CH_3OH \times \frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ CH_3OH} = 2.2284\ \text{mol}\ H_2$$

$$V_{H_2} = \frac{n_{H_2} RT}{P}$$

$$P = 984\ \text{mbar} \times \frac{1\ \text{bar}}{1000\ \text{mbar}} = 0.984\ \text{bar}$$

$$V_{H_2} = \frac{(2.2284\ \text{mol})\left(0.08314\ \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}}\right)(355\ \text{K})}{(0.984\ \text{bar})}$$

$$= 66.8\ \text{L}$$

CHECK The units of the answer are correct. The magnitude of the answer (66.8 L) seems reasonable. You are given slightly more than one molar mass of methanol, which is therefore slightly more than one mole of methanol. From the equation, you can see that you need 2 mol hydrogen to make 1 mol methanol, so the answer must be slightly greater than 2 mol hydrogen. Under standard conditions, slightly more than 2 mol hydrogen occupies slightly more than $2 \times 22.7\ \text{L} = 45.4\ \text{L}$. At a temperature greater than standard temperature, the volume would be even greater; therefore, this answer is reasonable.

FOR PRACTICE 5.12

In the following reaction, 4.58 L of O_2 was formed at $P = 745$ Torr and $T = 308$ K. How many grams of Ag_2O must have decomposed?

$$2\ Ag_2O(s) \longrightarrow 4\ Ag(s) + O_2(g)$$

FOR MORE PRACTICE 5.12

In the above reaction, what mass of $Ag_2O(s)$ (in grams) is required to form 388 mL of oxygen gas at $P = 978.7$ mbar and 25.0 °C?

Molar Volume and Stoichiometry

In Section 5.5, we saw that, under standard conditions, 1 mol of an ideal gas occupies 22.7 L. Consequently, if a reaction is occurring at or near standard conditions, we can use 1 mol = 22.7 L as a conversion factor in stoichiometric calculations, as shown in the following example.

EXAMPLE 5.13 Using Molar Volume in Gas Stoichiometric Calculations

How many grams of water form when 1.24 L of H_2 gas at STP completely reacts with O_2?

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)$$

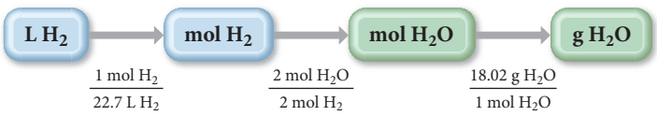
SORT You are given the volume of hydrogen gas (a reactant) at STP and asked to determine the mass of water that forms upon complete reaction.

GIVEN: 1.24 L H_2

FIND: g H_2O

STRATEGIZE Since the reaction occurs under standard conditions, you can convert directly from the volume (in L) of hydrogen gas to the amount in moles. Then use the stoichiometric relationship from the balanced equation to find the number of moles of water formed. Finally, use the molar mass of water to obtain the mass of water formed.

CONCEPTUAL PLAN



RELATIONSHIPS USED

1 mol = 22.7 L (at STP)
2 mol H_2 : 2 mol H_2O (from balanced equation)
molar mass $H_2O = 18.02\ \text{g mol}^{-1}$

SOLVE Follow the conceptual plan to solve the problem.

SOLUTION

$$1.24\ \cancel{\text{L H}_2} \times \frac{1\ \cancel{\text{mol H}_2}}{22.7\ \cancel{\text{L H}_2}} \times \frac{2\ \cancel{\text{mol H}_2\text{O}}}{2\ \cancel{\text{mol H}_2}} \times \frac{18.02\ \text{g H}_2\text{O}}{1\ \cancel{\text{mol H}_2\text{O}}} = 0.984\ \text{g H}_2\text{O}$$

CHECK The units of the answer are correct. The magnitude of the answer (0.984 g) is about 1/18 of the molar mass of water, roughly equivalent to the approximately 1/23 of a mole of hydrogen gas given, as expected for the 1:1 stoichiometric relationship between number of moles of hydrogen and number of moles of water.

FOR PRACTICE 5.13

How many litres of oxygen (at STP) are required to form 10.5 g of H_2O?

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)$$



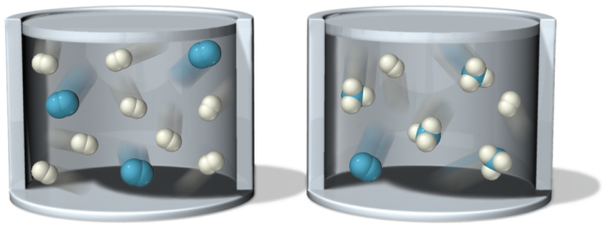
CONCEPTUAL CONNECTION 5.2

Pressure and Number of Moles

Nitrogen and hydrogen react to form ammonia according to the following equation:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

Consider the following representations of the initial mixture of reactants and the resulting mixture after the reaction has been allowed to react for some time:



If the volume is kept constant, and nothing is added to the reaction mixture, what happens to the total pressure during the course of the reaction?

(a) the pressure increases

(b) the pressure decreases

(c) the pressure does not change



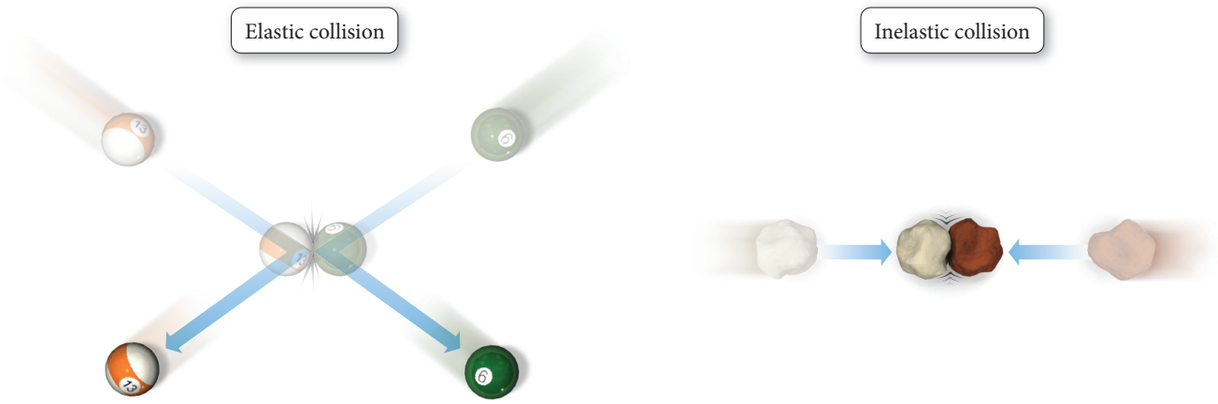
▲ **FIGURE 5.15 A Model for Gas Behaviour** In the kinetic molecular theory of gases, a gas sample is modelled as a collection of particles in constant straight-line motion. The size of the particles is negligibly small and their collisions are elastic.

5.8 Kinetic Molecular Theory: A Model for Gases

Applying the scientific method, one proceeds from observations to laws and eventually to theories. Laws summarize behaviour—for example, Charles's law summarizes *how* the volume of a gas depends on temperature—while theories give the underlying reasons for the behaviour. A theory of gas behaviour explains, for example, *why* the volume of a gas increases with increasing temperature.

The simplest model for the behaviour of gases is the **kinetic molecular theory**. In this theory, a gas is modelled as a collection of particles (either molecules or atoms, depending on the gas) in constant motion (Figure 5.15 ◂). A single particle moves in a straight line until it collides with another particle (or with the wall of the container). The basic postulates (or assumptions) of kinetic molecular theory are as follows:

1. **The size of each gas particle is negligibly small.** Kinetic molecular theory assumes that the particles themselves occupy no volume, even though they have mass. This postulate is justified because, under normal pressures, the space between atoms or molecules in a gas is very large compared to the size of an atom or molecule itself. For example, in a sample of argon gas at STP, only about 0.01% of the volume is occupied by atoms, and the average distance from one argon atom to another is 3.3 nm. In comparison, the atomic radius of argon is 97 pm. If an argon atom were the size of a golf ball, its nearest neighbour would be, on average, just over 1.3 m away at STP.
2. **The average kinetic energy of a particle is proportional to the temperature in kelvins.** The motion of atoms or molecules in a gas is due to thermal energy, which distributes itself among the particles in the gas. At any given moment, some particles are moving faster than others—there is a distribution of velocities—but the higher the temperature, the faster the overall motion, and the greater the average kinetic energy. Notice that *kinetic energy* ($\frac{1}{2}\,mv^2$)—not *velocity*—is proportional to temperature. The atoms in a sample of helium and a sample of argon at the same temperature have the same average *kinetic energy*, but not the same average *velocity*. Since the helium atoms are lighter, they must move faster to have the same kinetic energy as argon atoms.
3. **The collision of one particle with another (or with the walls of its container) is completely elastic.** This means that when two particles collide, they may



▲ **FIGURE 5.16 Elastic Versus Inelastic Collisions** When two billiard balls collide, the collision is elastic—the total kinetic energy of the colliding bodies is the same before and after the collision. When two lumps of clay collide, the collision is inelastic—the kinetic energy of the colliding bodies dissipates in the form of heat during the collision.

exchange energy, but there is no overall *loss of energy*. Any kinetic energy lost by one particle is completely gained by the other. In other words, the particles have no "stickiness," and they are not deformed by the collision. An encounter between two particles in kinetic molecular theory is more like the collision between two billiard balls than the collision between two lumps of clay (Figure 5.16 ▲). Between collisions, the particles do not exert any forces on one another.

If you start with the postulates of kinetic molecular theory, you can mathematically derive the ideal gas law (as we will show later). In other words, the ideal gas law follows directly from kinetic molecular theory, which gives us confidence that the assumptions of the theory are valid, at least under conditions where the ideal gas law applies. Let's see how the concept of pressure as well as each of the gas laws we have examined follow conceptually from kinetic molecular theory.

The Nature of Pressure In Section 5.2, we defined pressure as force divided by area:

$$P = \frac{F}{A}$$

According to kinetic molecular theory, a gas is a collection of particles in constant motion. The motion results in collisions between the particles and the surfaces around them. As each particle collides with a surface, it exerts a force upon that surface. The result of many particles in a gas sample exerting forces on the surfaces around them is a constant pressure.

The force (F) associated with an individual collision is given by $F = ma$, where m is the mass of the particle and a is its acceleration as it changes its direction of travel due to the collision.

Boyle's Law Boyle's law states that, for a constant number of particles at constant temperature, the volume of a gas is inversely proportional to its pressure. According to kinetic molecular theory, if you decrease the volume of a gas, you force the gas particles to occupy a smaller space. As long as the temperature remains the same, the number of collisions with the surrounding surfaces (per unit surface area) must necessarily increase, resulting in a greater pressure.

Charles's Law Charles's law states that, for a constant number of particles at constant pressure, the volume of a gas is proportional to its temperature. According to kinetic molecular theory, when you increase the temperature of a gas, the average kinetic energy—and thus the average speed—of the particles increases. Since this greater speed results in more frequent collisions and more force per collision, the pressure of the gas increases if its volume is held constant. The only way for the pressure to remain constant is for the volume to increase. The greater volume spreads the collisions out over a greater surface area, so that the pressure (defined as force per unit area) is unchanged.

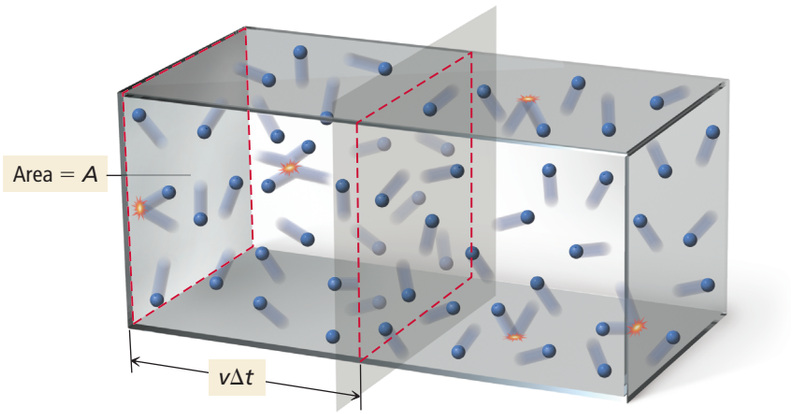
Avogadro's Law Avogadro's law states that, at constant temperature and pressure, the volume of a gas is proportional to the number of particles. According to kinetic molecular theory, when you increase the number of particles in a gas sample, the number of collisions with the surrounding surfaces increases. The greater number of collisions results in

a greater overall force on surrounding surfaces; the only way for the pressure to remain constant is for the volume to increase so that the number of particles per unit volume (and thus the number of collisions) remains constant.

Dalton's Law Dalton's law states that the total pressure of a gas mixture is the sum of the partial pressures of its components. In other words, according to Dalton's law, the components in a gas mixture act identically to, and independently of, one another. According to kinetic molecular theory, the particles have negligible size and they do not interact. Consequently, the only property that would distinguish one type of particle from another is its mass. However, even particles of different masses have the same average kinetic energy at a given temperature. Consequently, adding components to a gas mixture—even different *kinds* of gases—has the same effect as simply adding more particles. The partial pressures of all the components sum to the overall pressure.

Kinetic Molecular Theory and the Ideal Gas Law

We have just seen how each of the gas laws conceptually follows from kinetic molecular theory. We can also *derive* the ideal gas law from the postulates of kinetic molecular theory. In other words, the kinetic molecular theory is a quantitative model that *implies* $PV = nRT$. We now explore this derivation.



▲ **FIGURE 5.17 Pressure on the Wall of a Container** The pressure on the wall of a container can be calculated by determining the total force due to collisions of the particles with the wall.

The pressure on a wall of a container (Figure 5.17 ◂) occupied by particles in constant motion is the total force on the wall (due to the collisions) divided by the area of the wall:

$$P = \frac{F_{\text{total}}}{A} \qquad [5.13]$$

From Newton's second law, the force (F) associated with an individual collision is given by $F = ma$, where m is the mass of the particle and a is its acceleration as it changes its direction of travel due to the collision. The acceleration for each collision is the change in velocity (Δv) divided by the time interval (Δt), so the force imparted for each collision is:

$$F_{\text{collision}} = m\frac{\Delta v}{\Delta t} \qquad [5.14]$$

If a particle collides elastically with the wall, it bounces off the wall with no loss of energy. For a straight-line collision, the change in velocity is $2v$ (the particle's velocity was v before the collision and $-v$ after the collision; therefore, the change is $2v$). The force per collision is given by the following:

$$F_{\text{collision}} = m\frac{2v}{\Delta t} \qquad [5.15]$$

The total number of collisions in the time interval Δt on a wall of surface area A is proportional to the number of particles that can reach the wall in this time interval—in other words, all particles within a distance of $v\ \Delta t$ of the wall. These particles occupy a volume given by $v\ \Delta t \times A$, and their total number is equal to this volume multiplied by the density of particles in the container (n/V):

$$\text{Number of collisions} \propto \text{number of particles within } v\ \Delta t$$

$$\propto \underbrace{v\,\Delta t \times A}_{\text{Volume}} \times \underbrace{\frac{n}{V}}_{\text{Density of particles}} \qquad [5.16]$$

The *total force* on the wall is equal to the force per collision multiplied by the number of collisions:

$$\begin{aligned} F_{\text{total}} &= F_{\text{collision}} \times \text{number of collisions} \\ &\propto m\frac{2v}{\Delta t} \times v\,\Delta t \times \text{A} \times \frac{n}{V} \\ &\propto mv^2 \times A \times \frac{n}{V} \end{aligned} \qquad [5.17]$$

The pressure on the wall is equal to the total force divided by the surface area of the wall:

$$\begin{aligned} P &= \frac{F_{\text{total}}}{A} \\ P &\propto \frac{mv^2 \times A \times \frac{n}{V}}{A} \\ P &\propto mv^2 \times \frac{n}{V} \end{aligned} \qquad [5.18]$$

Notice that Equation 5.18 contains within it Boyle's law ($P \propto 1/V$) and Avogadro's law ($V \propto n$). We can get the complete ideal gas law from postulate 2 of the kinetic molecular theory, which states that the average kinetic energy ($\frac{1}{2}mv^2$) is proportional to the temperature in kelvins (T):

$$mv^2 \propto T \qquad [5.19]$$

By combining Equations 5.18 and 5.19, we get the following:

$$\begin{aligned} P &\propto \frac{T \times n}{V} \\ PV &\propto nT \end{aligned} \qquad [5.20]$$

The proportionality can be replaced by an equal sign if we provide the correct constant, R:

$$PV = nRT \qquad [5.21]$$

In other words, the kinetic molecular theory (a model for how gases behave) predicts behaviour that is consistent with our observations and measurements of gases—the theory agrees with the experiment. A scientific theory is the most powerful kind of scientific knowledge. In the kinetic molecular theory, we have a model for what a gas is like. Although the model is not perfect—indeed, it breaks down under certain conditions, as we shall see later in this chapter—it predicts a great deal about the behaviour of gases. Therefore, the model is a good approximation of what a gas is actually like. A careful examination of the conditions under which the model breaks down (see Section 5.10) gives us even more insight into the behaviour of gases.

Temperature and Molecular Velocities

According to kinetic molecular theory, particles of different masses have the same average kinetic energy at a given temperature. The kinetic energy of a particle depends on its mass and velocity according to the following equation:

$$\text{KE} = \tfrac{1}{2}mv^2$$

The only way for particles of different masses to have the same kinetic energy is if they are travelling at different velocities.

In a gas at a given temperature, lighter particles travel faster (on average) than heavier ones.

In kinetic molecular theory, we define the root mean square velocity (u_{rms}) of a particle as follows:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} \qquad [5.22]$$

where $\overline{u^2}$ is the average of the squares of the particle velocities. Even though the root mean square velocity of a collection of particles is not identical to the average velocity, the two are close in value and conceptually similar. Root mean square velocity is just a special *type* of average. The average kinetic energy of one mole of gas particles is then given by:

$$\mathrm{KE_{avg}} = \tfrac{1}{2} N_\mathrm{A}\, m\overline{u^2} \qquad [5.23]$$

where N_A is Avogadro's number.

Postulate 2 of the kinetic molecular theory states that the average kinetic energy is proportional to the temperature in kelvins. The constant of proportionality in this relationship is (3/2) R:

$$\mathrm{KE_{avg}} = (3/2)\, RT \qquad [5.24]$$

where R is the gas constant, but in different units ($R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$) than those we use in the ideal gas law. If we combine Equations 5.23 and 5.24, and solve for $\overline{u^2}$, we get the following:

$$(1/2)\, N_\mathrm{A} m\overline{u^2} = (3/2)\, RT$$

$$\overline{u^2} = \frac{(3/2)\, RT}{(1/2)\, N_\mathrm{A} m} = \frac{3RT}{N_\mathrm{A} m}$$

Briefly, the 3/2 R corresponds to 1/2 R for the velocity for each translational degree of freedom or dimension (i.e., x, y, z) but the derivation is beyond the scope of this book.

The joule (J) is a unit of energy, which we discuss in more detail in Section 6.1. $\left(1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}\right)$

Taking the square root of both sides, we get:

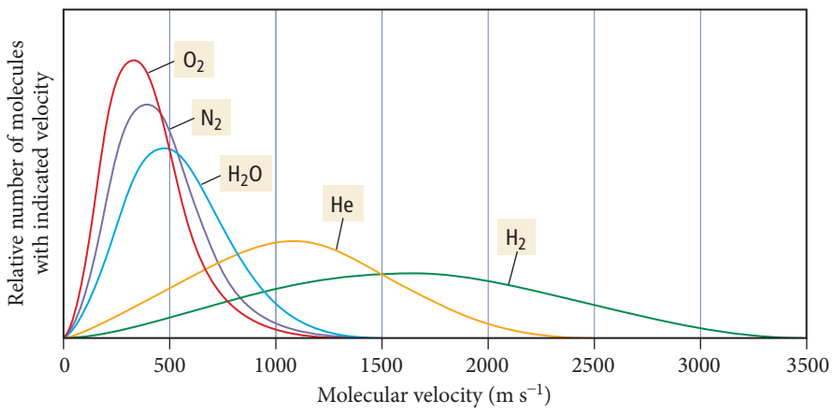
$$\sqrt{\overline{u^2}} = u_\mathrm{rms} = \sqrt{\frac{3RT}{N_\mathrm{A} m}} \qquad [5.25]$$

In Equation 5.25, m is the mass of a particle in kg and N_A is Avogadro's number. The product $N_\mathrm{A} m$, then, is the molar mass in kg $\mathrm{mol^{-1}}$. If we call this quantity $\mathcal{M}$, then the expression for the root mean square velocity as a function of temperature becomes the following important result:

$$u_\mathrm{rms} = \sqrt{\frac{3RT}{M}} \qquad [5.26]$$

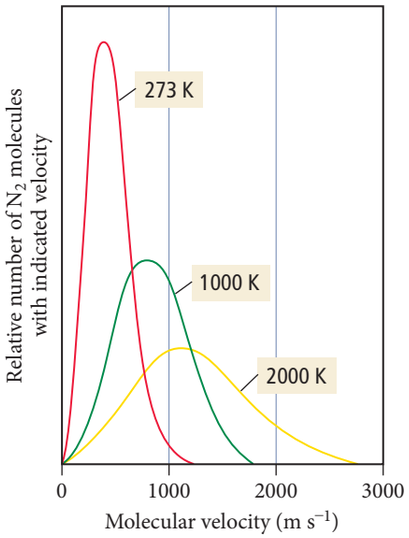
The root mean square velocity of a collection of gas particles is proportional to the square root of the temperature in kelvins and inversely proportional to the square root of the molar mass of the particles (because the units of M must be in kilograms per mole). The root mean square velocity of nitrogen molecules at 25 °C, for example, is 515 m $\mathrm{s^{-1}}$ (1854 km $\mathrm{h^{-1}}$). The root mean square velocity of hydrogen molecules at room temperature is 1920 m $\mathrm{s^{-1}}$ (6912 km $\mathrm{h^{-1}}$). Notice that the lighter molecules move much faster at a given temperature.

The root mean square velocity, as we have seen, is a kind of average velocity. Some particles are moving faster and some are moving slower than this average. The velocities of all the particles in a gas sample form distributions like those shown in Figure 5.18 ▼. We



▶ **FIGURE 5.18 Velocity Distribution for Several Gases at 25 °C** At a given temperature, there is a distribution of velocities among the particles in a sample of gas. The exact shape and peak of the distribution varies with the molar mass of the gas.

can see from these distributions that some particles are indeed travelling at the root mean square velocity. However, many particles are travelling faster and many slower than the root mean square velocity. For lighter particles, such as helium and hydrogen, the velocity distribution is shifted toward higher velocities and the curve becomes broader, indicating a wider range of velocities. The velocity distribution for nitrogen at different temperatures is shown in Figure 5.19 ▶. As the temperature increases, the root mean square velocity increases and the distribution becomes broader.



▶ **FIGURE 5.19 Velocity Distribution for Nitrogen at Several Temperatures**
As the temperature of a gas sample increases, the velocity distribution of the molecules shifts toward higher velocity and the breadth of the peak is increased.

EXAMPLE 5.14 Root Mean Square Velocity

Calculate the root mean square velocity of oxygen molecules at 25 °C.

SORT You are given the identity of the molecule and the temperature and asked to find the root mean square velocity.

GIVEN: O_2, $T = 25\ °C$

FIND: u_{rms}

STRATEGIZE The conceptual plan for this problem shows how the molar mass of oxygen and the temperature (in kelvins) can be used with the equation that defines the root mean square velocity to calculate root mean square velocity.

CONCEPTUAL PLAN

$M, T \rightarrow u_{rms}$

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

RELATIONSHIP USED

$u_{rms} = \sqrt{\frac{3RT}{M}}$ (Equation 5.26)

SOLVE First gather the required quantities in the correct units. Note that molar mass must be in kg mol^{-1}.

SOLUTION

$T = 25 + 273.15 = 298\ K$

$$M = \frac{32.00\ \text{g}\ O_2}{1\ \text{mol}\ O_2} \times \frac{1\ \text{kg}}{1000\ \text{g}} = \frac{32.00 \times 10^{-3}\ \text{kg}\ O_2}{1\ \text{mol}\ O_2}$$

Substitute the quantities into the equation to calculate root mean square velocity. Note that 1 J = 1 kg m^2 s^{-2}.

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

$$= \sqrt{\frac{3\left(8.314\ \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(298\ \text{K})}{\frac{32.00 \times 10^{-3}\ \text{kg}\ O_2}{1\ \text{mol}\ O_2}}}$$

$$= \sqrt{2.32 \times 10^5\ \frac{\text{J}}{\text{kg}}}$$

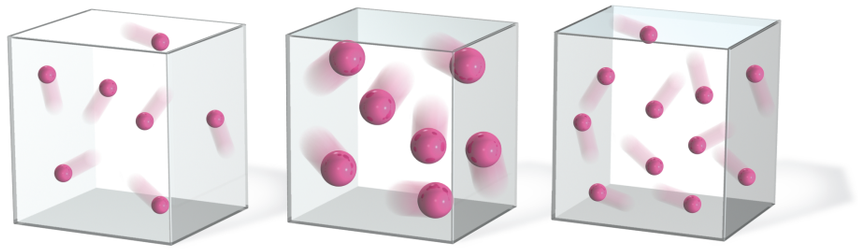
$$= \sqrt{2.32 \times 10^5\ \frac{\frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}{\text{kg}}} = 482\ \text{m}\ \text{s}^{-1}$$

CHECK The units of the answer (m s^{-1}) are correct. The magnitude of the answer seems reasonable because oxygen is slightly heavier than nitrogen and should therefore have a slightly lower root mean square velocity at the same temperature. Recall that earlier we stated that the root mean square velocity of nitrogen is 515 m s^{-1} at 25 °C.

FOR PRACTICE 5.14
Calculate the root mean square velocity of gaseous xenon atoms at 25 °C.

CONCEPTUAL CONNECTION 5.3
Kinetic Molecular Theory

Which sample of an ideal gas has the greatest pressure? Assume that the mass of each particle is proportional to its size and that all the gas samples are at the same temperature.

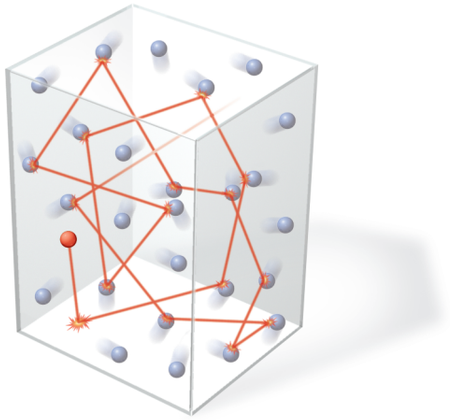


5.9 Mean Free Path, Diffusion, and Effusion of Gases

In a ventilated room, air currents also enhance the transport of gas molecules.

We have just learned that the root mean square velocity of gas molecules at room temperature is measured in hundreds of metres per second. However, suppose that your roommate just put on too much perfume in the bathroom only 2 m away. Why does it take a minute or two before you can smell the fragrance? Although most molecules in a perfume bottle have higher molar masses than nitrogen, their velocities are still hundreds of metres per second, so why the delay? The answer is that, even though gaseous particles travel at tremendous speeds, they also travel in haphazard paths (Figure 5.20 ◂). To a perfume molecule, the path from the perfume bottle in the bathroom to your nose 2 m away is much like a bargain hunter's path through a busy shopping mall during a clearance sale. The molecule travels only a short distance before it collides with another molecule, changes direction, only to collide again, and so on. In fact, at room temperature and atmospheric pressure, a molecule in the air experiences several billion collisions per second. The average distance that a molecule travels between collisions is called its **mean free path**. At room temperature and atmospheric pressure, the mean free path of a nitrogen molecule with a molecular diameter of 300 pm (four times the covalent radius) is 93 nm, or about 310 molecular diameters. If the nitrogen molecule were the size of a golf ball, it would travel about 12 m between collisions. Mean free path increases with *decreasing* pressure. Under conditions of ultrahigh vacuum (10^{-10} Torr), the mean free path of a nitrogen molecule is hundreds of kilometres.

The average distance between collisions is the mean free path.



▲ **FIGURE 5.20 Mean Free Path**
A molecule in a volume of gas follows a haphazard path, involving many collisions with other molecules.

The process by which gas molecules spread out in response to a concentration gradient is called **diffusion**, and even though the particles undergo many collisions, the root mean square velocity still influences the rate of diffusion. Heavier molecules diffuse more slowly than lighter ones, so the first molecules you would smell from a perfume mixture (in a room with no air currents) are the lighter ones.

A process related to diffusion is **effusion**, the process by which a gas escapes from a container into a vacuum through a small hole (Figure 5.21 ▸). The rate of effusion is also related to root mean square velocity—heavier molecules effuse more slowly than lighter ones. The rate of effusion—the amount of gas that effuses in a given time—is inversely proportional to the square root of the molar mass of the gas as follows:

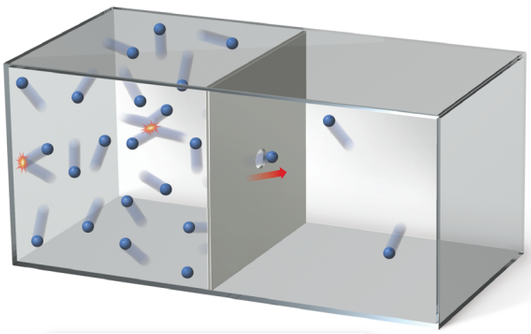
$$\text{rate} \propto \frac{1}{\sqrt{M}}$$

The ratio of effusion rates of two different gases is given by **Graham's law of effusion**, named after Thomas Graham (1805–1869):

$$\frac{\text{rate}_A}{\text{rate}_B} = \sqrt{\frac{M_B}{M_A}} \qquad [5.27]$$

In this expression, rate_A and rate_B are the effusion rates of gases A and B and M_A and M_B are the molar masses, respectively.

Graham's law explains, in part, why helium balloons only float for a day or so. Since helium has a such a low molar mass, it escapes from the balloon quite quickly. A balloon filled with air, by contrast, remains inflated longer.



Gas escapes from container into a vacuum through a small hole.

▲ **FIGURE 5.21 Effusion** Effusion is the escape of a gas from a container into a vacuum through a small hole.

EXAMPLE 5.15 **Graham's Law of Effusion**

An unknown atomic gas effuses at a rate that is 0.462 times that of nitrogen gas (at the same temperature). Calculate the molar mass of the unknown gas in g mol^{-1}.

SORT You are given the ratio of effusion rates for the unknown gas and nitrogen and asked to find the molar mass of the unknown gas.

GIVEN: $\frac{\text{Rate}_{unk}}{\text{Rate}_{N_2}} = 0.462$

FIND: M_{unk}

STRATEGIZE The conceptual plan uses Graham's law of effusion. You are given the ratio of rates and you know the molar mass of nitrogen. You can use Graham's law to find the molar mass of the unknown gas.

CONCEPTUAL PLAN

$\frac{\text{Rate}_{unk}}{\text{Rate}_{N_2}}, M_{N_2} \rightarrow M_{unk}$

$$\frac{\text{Rate}_{unk}}{\text{Rate}_{N_2}} = \sqrt{\frac{M_{N_2}}{M_{unk}}}$$

RELATIONSHIP USED

$$\frac{\text{rate}_A}{\text{rate}_B} = \sqrt{\frac{M_B}{M_A}} \text{ (Graham's law)}$$

SOLVE Solve the equation for M_{unk} and substitute the correct values to calculate it.

SOLUTION

$$\frac{\text{rate}_{unk}}{\text{rate}_{N_2}} = \sqrt{\frac{M_{N_2}}{M_{unk}}}$$

$$M_{unk} = \frac{M_{N_2}}{\left(\frac{\text{rate}_{unk}}{\text{rate}_{N_2}}\right)^2}$$

$$= \frac{28.02 \text{ g mol}^{-1}}{(0.462)^2}$$

$$= 131 \text{ g mol}^{-1}$$

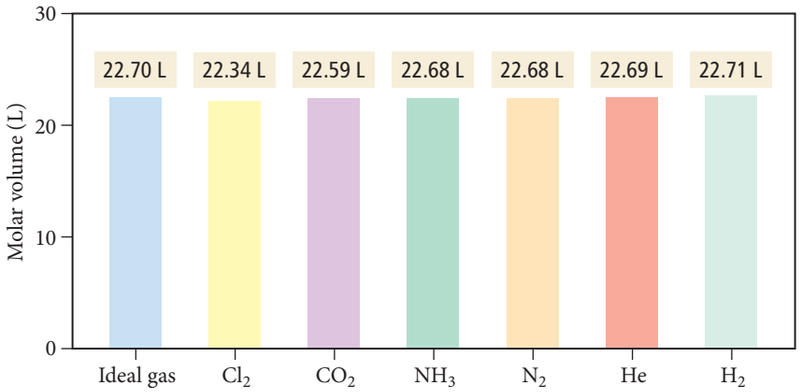
CHECK The units of the answer are correct. The magnitude of the answer seems reasonable for the molar mass of a gas. In fact, from the answer, we can even conclude that the gas is probably xenon, which has a molar mass of 131.29 g mol^{-1}.

FOR PRACTICE 5.15

Find the ratio of effusion rates of hydrogen gas and krypton gas.

5.10 Real Gases: The Effects of Size and Intermolecular Forces

One mole of an ideal gas has a volume of 22.7 L at STP. Figure 5.22 ▼ shows the molar volume of several real gases at STP. As you can see, most of these gases have a volume that is very close to 22.7 L, meaning that they are acting very nearly as



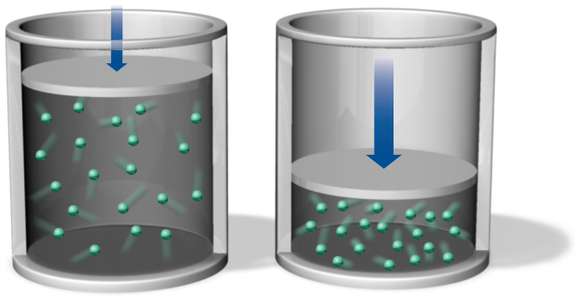
▶ **FIGURE 5.22 Molar Volumes of Real Gases** The molar volumes of several gases at STP are all close to 22.7 L, indicating that their departures from ideal behaviour are small.

ideal gases. Gases behave ideally when both of the following are true: (a) the volume of the gas particles is small compared to the space between them, and (b) the forces between the gas particles are not significant. At STP, these assumptions are valid for most common gases. However, these assumptions break down at higher pressures or lower temperatures.

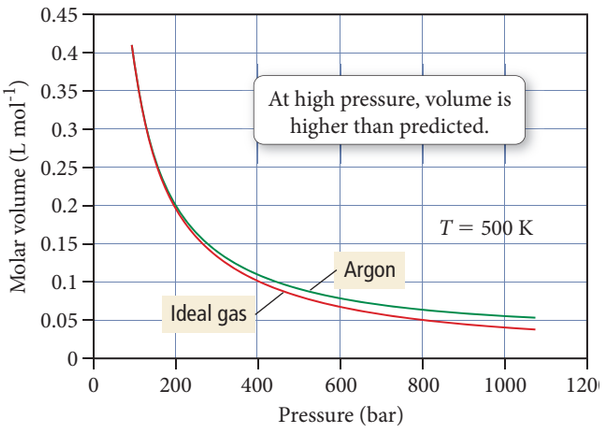
The Effect of the Finite Volume of Gas Particles

The finite volume of gas particles—that is, their actual *size*—becomes important at high pressure because the volume of the particles themselves occupies a significant portion of the total gas volume (Figure 5.23 ▼). We can see the effect of particle volume by comparing the molar volume of argon to the molar volume of an ideal gas as a function of pressure at 500 K as shown in Figure 5.24 ▼. At low pressures, the molar volume of argon is nearly identical to that of an ideal gas. But as the pressure increases, the molar volume of argon becomes *greater than* that of an ideal gas. At the higher pressures, the argon atoms themselves occupy a significant portion of the gas volume, making the actual volume greater than that predicted by the ideal gas law.

In 1873, Johannes van der Waals (1837–1923) modified the ideal gas equation to fit the behaviour of real gases. From the graph for argon in Figure 5.24, we can see that the



▲ **FIGURE 5.23 Particle Volume and Ideal Behaviour** As a gas is compressed, the gas particles themselves begin to occupy a significant portion of the total gas volume, leading to deviations from ideal behaviour.



▲ **FIGURE 5.24 The Effect of Particle Volume** At high pressures, 1 mol of argon occupies a larger volume than 1 mol of an ideal gas because of the volume of the argon atoms themselves. (This example was chosen to minimize the effects of intermolecular forces, which are very small in argon at 500 K, thereby isolating the effect of particle volume.)

ideal gas law predicts a volume that is too small. Van der Waals suggested a small correction factor that accounts for the volume of the gas particles themselves:

Ideal behaviour $$V = \frac{nRT}{P}$$

Corrected for volume of gas particles $$V = \frac{nRT}{P} + nb \qquad [5.28]$$

The correction adds the quantity nb to the volume, where n is the number of moles and b is a constant that depends on the gas (see Table 5.5). We can rearrange the corrected equation as follows:

$$(V - nb) = \frac{nRT}{P} \qquad [5.29]$$

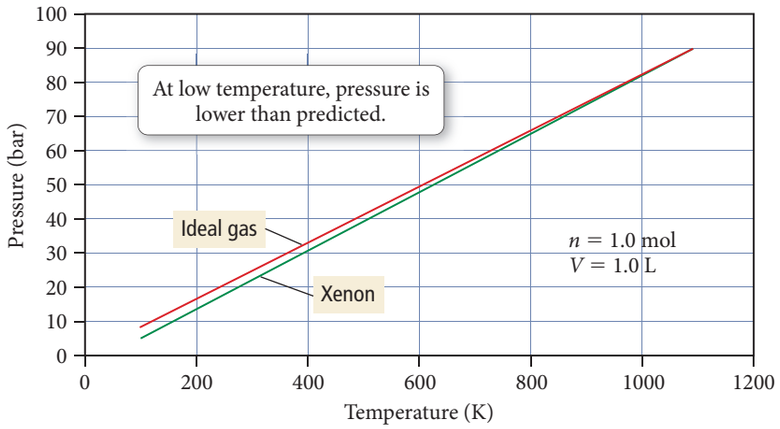
TABLE 5.5 Van der Waals Constants for Common Gases

Gas	a (L^2 bar mol^{-2})	b (L mol^{-1})
He	0.03475	0.0237
Ne	0.2135	0.0171
Ar	1.363	0.0322
Kr	2.349	0.0398
Xe	4.250	0.0511
H_2	0.2476	0.0266
N_2	1.408	0.0391
O_2	6.579	0.0562
Cl_2	6.579	0.0562
H_2O	5.536	0.0305
CH_4	2.283	0.0428
CO_2	3.640	0.0427
CCl_4	19.75	0.1383

The Effect of Intermolecular Forces

Intermolecular forces, covered in more detail in Chapter 11, are attractions between the atoms or molecules that compose any substance. These attractions are typically negligible in gases because the kinetic energy of the molecules is enough to overcome the intermolecular forces of attraction. Therefore, at high temperatures and low pressures, the weak attractions, compared with the relatively large kinetic energy between them, do not significantly affect their collisions. At lower temperatures, however, the collisions occur with less kinetic energy, and weak attractions can affect the molecular collisions and even the direction of their motion. We can understand this difference with an analogy to billiard balls. Imagine two billiard balls that are coated with a substance that makes them slightly sticky. If they collide when moving at high velocities, the stickiness will not have much of an effect—the balls bounce off one another as if the sticky substance was not even there. However, if the two billiard balls collide when moving very slowly (say, barely rolling), the sticky substance would have an effect—the billiard balls might even stick together and not bounce off one another.

The effect of these weak attractions between particles is a lower number of collisions with the surfaces of the container, thereby lowering the pressure compared to that of an ideal gas. We can see the effect of intermolecular forces by comparing the pressure of 1.0 mol of xenon gas to the pressure of 1.0 mol of an ideal gas as a function of temperature and at a fixed volume of 1.0 L, as shown in Figure 5.25 ▼. At high temperature, the pressure of the xenon gas is nearly identical to that of an ideal gas. But at lower temperatures, the pressure of xenon is *less than* that of an ideal gas. At the lower temperatures, the xenon atoms interact significantly with one another. These interactions reduce the number of collisions with the wall of the container, making the pressure less than that of an ideal gas where there are no forces of attraction between the gas molecules.



◀ **FIGURE 5.25 The Effect of Intermolecular Forces** At low temperatures, the pressure of xenon is less than an ideal gas exerts because interactions among xenon atoms reduce the number of collisions with the walls of the container.

From the graph for xenon shown in Figure 5.25, we can see that the ideal gas law predicts a pressure that is too large at low temperatures. Van der Waals suggested a small correction factor that accounts for the intermolecular forces between gas particles:

Ideal behaviour $$P = \frac{nRT}{V}$$

Corrected for intermolecular forces $$P = \frac{nRT}{V} - a\left(\frac{n}{V}\right)^2 \qquad [5.30]$$

The correction subtracts the quantity $a(n/V)^2$ from the pressure, where n is the number of moles, V is the volume, and a is a constant that depends on the gas (see Table 5.5). Notice that the correction factor increases as n/V (the number of moles of particles per unit volume) increases because a greater concentration of particles makes it more likely that they will interact with one another. We can rearrange the corrected equation as follows:

$$P + a\left(\frac{n}{V}\right)^2 = \frac{nRT}{V} \qquad [5.31]$$

Van der Waals Equation

We can now combine the effects of particle volume (Equation 5.29) and particle intermolecular forces (Equation 5.31) into one equation that describes nonideal gas behaviour:

$$\left[P + a\left(\frac{n}{V}\right)^2\right] \times [V - nb] = nRT \qquad [5.32]$$

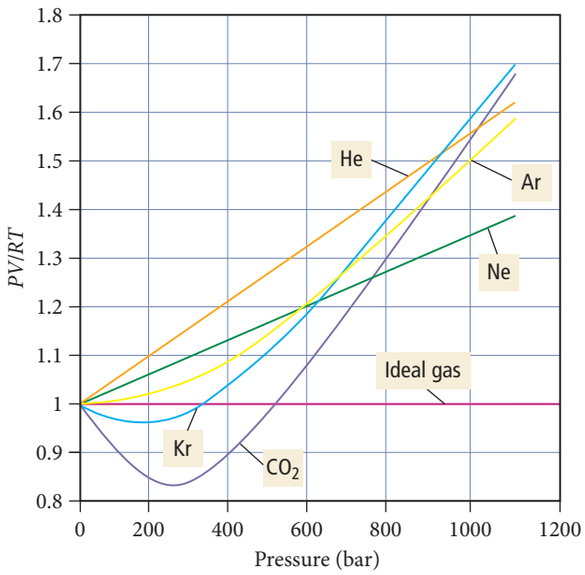
Correction for intermolecular forces

Correction for particle volume

The above equation is called the **van der Waals equation** and can be used to calculate the properties of a gas under nonideal conditions. A nonideal gas—one that does not obey the assumptions that define an ideal gas—is called a **real gas**.

Real Gases

We can see the combined effects of particle volume and intermolecular forces by examining a plot of PV/RT versus P for 1 mol of a number of real gases (Figure 5.26 ▼). For an ideal gas, $PV/RT = n$, the number of moles of gas. Therefore, for 1 mol of an ideal gas, PV/RT is equal to 1, as shown in the plot. For real gases, PV/RT deviates from 1, but the deviations are not uniform. For example, water displays a large negative deviation from



▶ **FIGURE 5.26 Real Versus Ideal Behaviour** For 1 mol of an ideal gas, PV/RT would be equal to 1. The combined effects of the volume of gas particles and the interactions among them cause each real gas to deviate from ideal behaviour in a slightly different way. These curves were calculated at a temperature of 273.15 K.

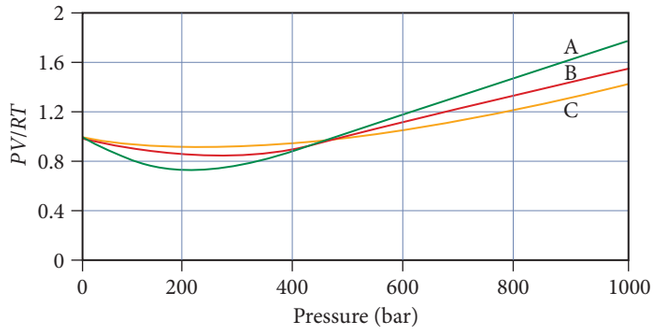
PV/RT because, for water, the effect of intermolecular forces on lowering the pressure (relative to an ideal gas) is far greater than the effect of particle size on increasing the volume. Notice from Table 5.5 that water has a high value of a, the constant that corrects for intermolecular forces, but a moderate value of b, the constant that corrects for particle size. Therefore, PV/RT is lower than predicted from the ideal gas law for water.

By contrast, consider the behaviour of helium, which displays a positive deviation from the ideal behaviour. This is because helium has very weak intermolecular forces and their effect on lowering the pressure (relative to ideal gas) is small compared to the effect of particle size on increasing the volume. Therefore, PV/RT is greater than predicted from the ideal gas law for helium.



CONCEPTUAL CONNECTION 5.4
Real Gases

The graph below shows PV/RT for carbon dioxide at three different temperatures. Rank the curves in order of increasing temperature.



CHEMISTRY IN YOUR DAY Pressure in Outer Space



The Earth's atmospheric pressure drops from 1.01 bar at sea level to about 300 mbar at typical cruising altitudes of planes (~9 km, almost at the top of the troposphere), which is also about the altitude of the summit of Mount Everest. At high altitudes where atmospheric pressure is so low that humans cannot acclimatize to the low oxygen levels, their bodies begin to deteriorate. Most climbers must use oxygen tanks above 8 km.

At about 30 km above the Earth's surface, the middle of the stratosphere and the approximate altitude of the ozone layer (see Figure 5.27 ▼), the pressure drops to about 10 mbar. More than 99.9 percent of the Earth's atmosphere lies in the troposphere and stratosphere. You might wonder where the Earth's atmosphere ends and "outer space" begins. Scientists have also puzzled over this very question. In 2009, scientists at the University of Calgary designed an instrument that measures the direction and speed of ions (the Supra-Thermal Ion Imager), which allowed them to determine that space begins at 118 km above the Earth. There is a gradual transition over many tens of kilometres from the gentle winds of Earth's atmosphere to the quite violent flows of charged particles outside the atmosphere, and the midpoint of this transition is 118 km. The pressure at 118 km is about 0.001 mbar. At these small pressures, scientists usually talk about number densities rather than gas pressure. The number density is the number of molecules per unit volume—which is simply another unit of a concentration. We can solve the ideal gas law, as we did before, for concentration:

$$\frac{n}{V} = \frac{P}{RT}$$

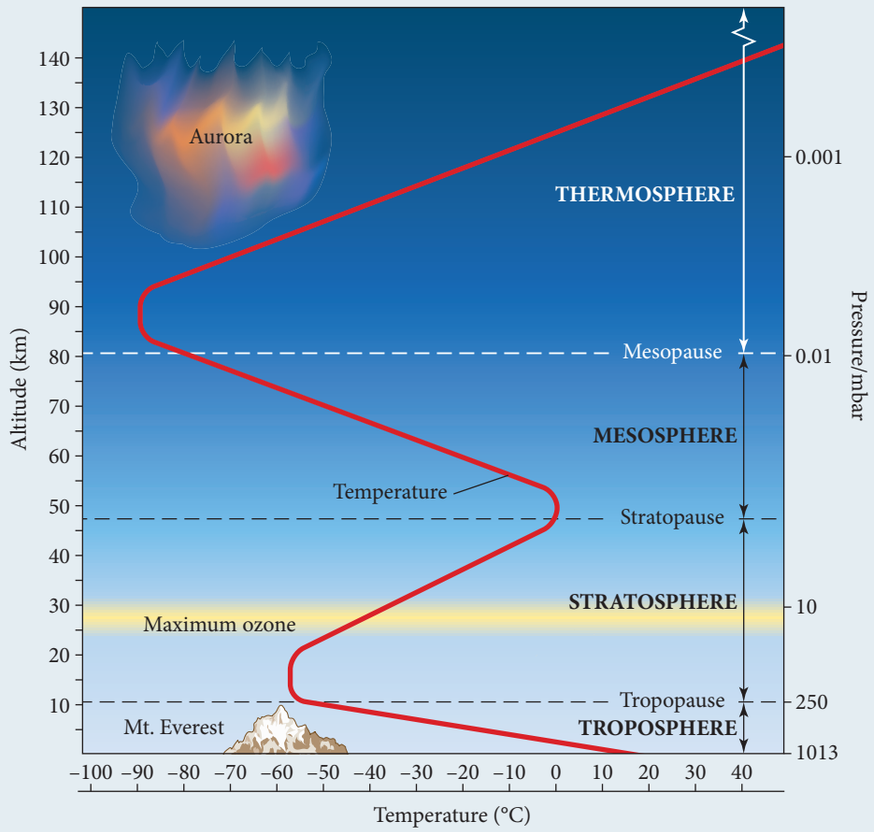
Under standard conditions, the molar concentration (n/V) is 4.4×10^{-2} mol L^{-1}. To convert to number density, simply multiply by Avogadro's number to yield 2.7×10^{22} molecules L^{-1}. Scientists typically express number density in molecules cm^{-3}, so under standard conditions, the number density is 2.7×10^{19} molecules cm^{-3}; and at 118 km above sea level, where the temperature and pressure are about –10 °C and 0.001 mbar, respectively, the number density is 2.8×10^{13} molecules cm^{-3}.

In outer space, the number density can get very small. For example, there are regions of interstellar space (the space between star systems within a galaxy) with number densities as low as 1 atom dm^{-3}. Much of the matter is a plasma

(*continued*)

On October 5, 1982, Laurie Skreslet, born in Calgary, Alberta, became the first Canadian to reach the summit of Mount Everest.

CHEMISTRY IN YOUR DAY (Continued)



▶ **FIGURE 5.27 The Structure of the Atmosphere** Earth's atmosphere contains several different regions, including the troposphere and stratosphere.

composed of ionized hydrogen atoms. At these very low pressures, in one cubic centimetre of space, there is fewer than one collision every few hundred thousand years. In enormous molecular clouds where stars form (see Figure 5.28 ▶), the number densities are between 10^2 and 10^6 atoms and molecules cm^{-3}, and collisions occur between once every 100 years and once every hour. As chemists, we typically measure reaction rates in mol L^{-1} s^{-1}; that is, moles of product formed per litre of reaction mixture per second. At the very small molecular densities and small collision rates of interstellar space, one product molecule is formed between every hour and every 100 years for each cubic centimetre of space. That scientists have observed molecules in interstellar space is testament to both the age of our galaxy (and universe) as well as the vastness of it.



▲ **FIGURE 5.28 Molecular Cloud** This small molecular cloud, about two light years across, has broken off part of the Carina Nebula, a star-forming region about 8000 light years from Earth.

Imagine on a clear day, looking miles into the horizon and being able to see a distant mountain or hill, even though you are looking through miles of atmosphere containing more than 10^{19} molecules cm^{-3}. The small molecular cloud in Figure 5.28 has a number density of about 10^4 molecules cm^{-3}. That it is visible to telescopes at such a low number density is due to the fact that the image is about two light years across. Assuming that the composition of the cloud is molecular hydrogen, can you determine the mass that is contained in a molecular cloud that is two light years across, assuming a cubic molecular cloud? Can you determine the pressure in mbar of the molecular cloud, assuming a temperature of 30 K?

(Answer: $m = 4 \times 10^{17}$ kg, $P = 4 \times 10^{-14}$ mbar)

CHAPTER IN REVIEW

Key Terms

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bar (148)
millibar (mbar) (148)
manometer (148)

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Key Concepts

Pressure (5.1, 5.2)

Gas pressure is the force per unit area that results from gas particles colliding with the surfaces around them. Pressure is measured in a number of units, including bar, mbar, mmHg, torr, Pa, psi, and atm.

The Simple Gas Laws (5.3)

The simple gas laws express relationships between pairs of variables when the other variables are held constant. Boyle's law states that the volume of a gas is inversely proportional to its pressure. Charles's law states that the volume of a gas is directly proportional to its temperature. Avogadro's law states that the volume of a gas is directly proportional to the amount (in moles).

The Ideal Gas Law and Its Applications (5.4, 5.5)

The ideal gas law, $PV = nRT$, gives the relationship among all four gas variables and contains the simple gas laws within it. We can use the ideal gas law to find one of the four variables given the other three. We can use it to calculate the molar volume of an ideal gas, which is 22.7 L at STP, and to calculate the density and molar mass of a gas.

Mixtures of Gases and Partial Pressures (5.6)

In a mixture of gases, each gas acts independently of the others so that any overall property of the mixture is the sum of the properties of the individual components. The pressure of any individual component is its partial pressure.

Gas Stoichiometry (5.7)

In reactions involving gaseous reactants and products, quantities are often reported in volumes at specified pressures and temperatures. We can convert these quantities to amounts (in moles) using the ideal gas law. Then we can use the stoichiometric coefficients from the balanced equation to determine the stoichiometric amounts of other reactants or products. The general form for these types of calculations is often as follows: volume A $\rightarrow$ amount A (in moles) $\rightarrow$ amount B (in moles) $\rightarrow$ quantity of B (in desired units). In cases where the reaction is carried out at STP, the molar volume at STP (22.7 L = 1 mol) can be used to convert between volume in litres and amount in moles.

Kinetic Molecular Theory and Its Applications (5.8, 5.9)

Kinetic molecular theory is a quantitative model for gases. The theory has three main assumptions: (1) the gas particles are negligibly small, (2) the average kinetic energy of a gas particle is proportional to the temperature in kelvin, and (3) the collision of one gas particle with another is completely elastic (the particles do not stick together). The gas laws all follow from the kinetic molecular theory.

We can also use the theory to derive the expression for the root mean square velocity of gas particles. This velocity is inversely proportional to the molar mass of the gas, and therefore—at a given temperature—smaller gas particles are (on average) moving more quickly than larger ones. The kinetic molecular theory also allows us to predict the mean free path of a gas particle (the distance it travels between collisions) and relative rates of diffusion or effusion.

Real Gases (5.10)

Real gases differ from ideal gases to the extent that they do not always fit the assumptions of kinetic molecular theory. These assumptions tend to break down at high pressures, where the volume is higher than predicted for an ideal gas because the particles are no longer negligibly small compared to the space between them. The assumptions also break down at low temperatures where the pressure is lower than predicted because the attraction between molecules combined with low kinetic energies causes partially inelastic collisions. The van der Waals equation predicts gas properties under nonideal conditions.

Key Equations and Relationships

Relationship Between Pressure (P), Force (F), and Area (A) (5.2)

$$P = \frac{F}{A}$$

Boyle's Law: Relationship Between Pressure (P) and Volume (V) (5.3)

$$V \propto \frac{1}{P}$$

$$P_1V_1 = P_2V_2$$

Charles's Law: Relationship Between Volume (V) and Temperature (T) (5.3)

$$V \propto T \quad \text{(in K)}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Avogadro's Law: Relationship Between Volume (V) and Amount in Moles (n) (5.3)

$$V \propto n$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Ideal Gas Law: Relationship Between Volume (V), Pressure (P), Temperature (T), and Amount (n) (5.4)

$$PV = nRT$$

Dalton's Law: Relationship Between Partial Pressures (P_n) in Mixture of Gases and Total Pressure (P_{total}) (5.6)

$$P_{total} = P_a + P_b + P_c + \cdots$$

$$P_a = \frac{n_aRT}{V} \qquad P_b = \frac{n_bRT}{V} \qquad P_c = \frac{n_cRT}{V}$$

Mole Fraction (χ_a) (5.6)

$$\chi_a = \frac{n_a}{n_{total}}$$

$$P_a = \chi_a P_{total}$$

Average Kinetic Energy (KE_{avg}) (5.8)

$$KE_{avg} = \frac{3}{2}RT$$

Relationship Between Root Mean Square Velocity (u_{rms}) and Temperature (T) (5.8)

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

Relationship of Effusion Rates of Two Different Gases (5.9)

$$\frac{\text{rate A}}{\text{rate B}} = \sqrt{\frac{M_B}{M_A}}$$

Van der Waals Equation: The Effects of Volume and Intermolecular Forces on Nonideal Gas Behaviour (5.10)

$$[P + a(n/V)^2] \times (V - nb) = nRT$$

Key Skills

Converting Between Pressure Units (5.2)

• Example 5.1 • For Practice 5.1 • For More Practice 5.1 • Exercises 25–30

Relating Volume and Pressure: Boyle's Law (5.3)

• Example 5.2 • For Practice 5.2 • Exercises 31, 32

Relating Volume and Temperature: Charles's Law (5.3)
• Example 5.3 • For Practice 5.3 • Exercises 33, 34

Relating Volume and Moles: Avogadro's Law (5.3)
• Example 5.4 • For Practice 5.4 • Exercises 35, 36

Determining *P*, *V*, *n*, or *T* using the Ideal Gas Law (5.4)
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Calculating the Molar Mass of a Gas with the Ideal Gas Law (5.5)
• Example 5.8 • For Practice 5.8 • Exercises 57–60

Calculating Total Pressure, Partial Pressures, and Mole Fractions of Gases in a Mixture (5.6)
• Examples 5.9, 5.10, 5.11 • For Practice 5.9, 5.10, 5.11 • Exercises 61–70

Relating the Amounts of Reactants and Products in Gaseous Reactions: Stoichiometry (5.7)
• Examples 5.12, 5.13 • For Practice 5.12, 5.13 • For More Practice 5.12 • Exercises 71–78

Calculating the Root Mean Square Velocity of a Gas (5.8)
• Example 5.14 • For Practice 5.14 • Exercises 81, 82

Calculating the Effusion Rate or the Ratio of Effusion Rates of Two Gases (5.9)
• Example 5.15 • For Practice 5.15 • Exercises 83–90

EXERCISES

Review Questions

1. What is pressure? What causes pressure?
2. Explain what happens when you inhale. What forces air into your lungs?
3. Explain what happens when you exhale. What forces air out of your lungs?
4. What are some common units of pressure? List these in order of smallest to largest unit.
5. What is a manometer? How does it measure the pressure of a sample of gas?
6. Summarize each of the simple gas laws (Boyle's law, Charles's law, and Avogadro's law). For each law, explain the relationship between the two variables and also state which variables must be kept constant.
7. Explain why scuba divers should never hold their breath as they ascend to the surface.
8. Why is it impossible to breathe air through an extra-long snorkel (greater than a couple of metres) while swimming underwater?
9. Explain why hot-air balloons float above the ground, and why the second storey of a two-storey home is often warmer than the ground storey.
10. What is the ideal gas law? Why is it useful?
11. Explain how the ideal gas law contains within it the simple gas laws (show an example).
12. Define molar volume and give its value for a gas at STP.
13. How does the density of a gas depend on temperature? Pressure? How does it depend on the molar mass of the gas?
14. What is partial pressure? What is the relationship between the partial pressures of each gas in a sample and the total pressure of gas in the sample?
15. Why do deep-sea divers breathe a mixture of helium and oxygen?
16. When a gas is collected over water, is the gas pure? Why or why not? How can the partial pressure of the collected gas be determined?
17. If a reaction occurs in the gas phase at STP, the mass of a product can be determined from the volumes of reactants. Explain.
18. What are the basic postulates of kinetic molecular theory? How does the concept of pressure follow from kinetic molecular theory?
19. Explain how Boyle's law, Charles's law, Avogadro's law, and Dalton's law all follow from kinetic molecular theory.
20. How is the kinetic energy of a gas related to temperature? How is the root mean square velocity of a gas related to its molar mass?
21. Describe how the molecules in a perfume bottle travel from the bottle to your nose. What is mean free path?
22. Explain the difference between diffusion and effusion. How is the effusion rate of a gas related to its molar mass?
23. Deviations from the ideal gas law are often observed at high pressure and low temperature. Explain why, in light of kinetic molecular theory.
24. If a gas were composed entirely of positive ions (this can actually be accomplished in an ion trapping mass spectrometer), and you could measure the pressure of this gas, would it be greater or less than that of an ideal gas? Explain.

Problems by Topic

Converting Between Pressure Units

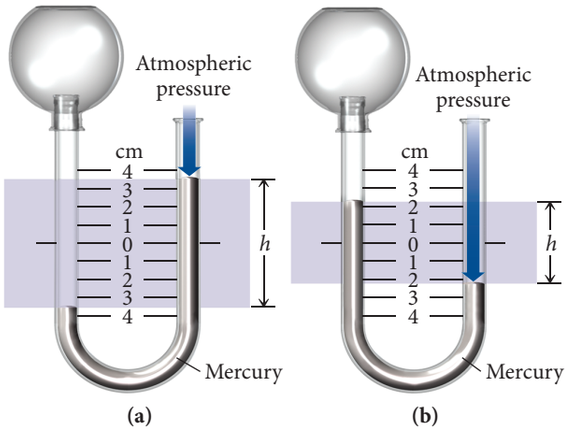
25. The pressure in Lake Louise (elevation 1600 m) is about 875 mbar. Convert this pressure to:
a. atm **b.** psi **c.** Pa **d.** torr **e.** bar

26. The pressure on top of Mount Everest averages about 235 Torr. Convert this pressure to:
a. atm **b.** psi **c.** Pa **d.** mbar **e.** bar

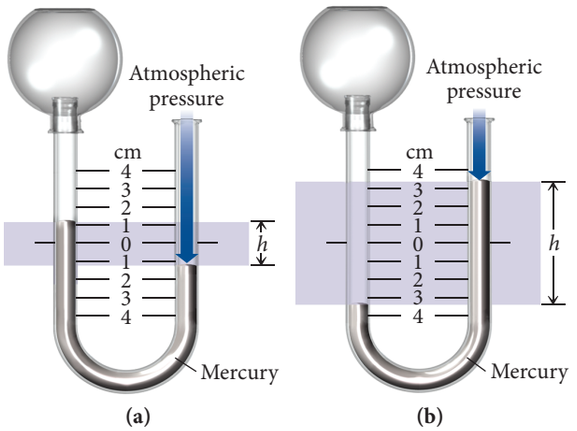
27. The North American record for highest recorded barometric pressure is 1078 hPa set in 1989 in Northway, Alaska. Convert this pressure to:
a. atm **b.** torr **c.** kPa **d.** mbar **e.** bar

28. The world record for lowest pressure (at sea level) was 652.5 mmHg recorded inside Typhoon Tip on October 12, 1979, in the Western Pacific Ocean. Convert this pressure to:
a. torr **b.** kPa **c.** bar **d.** psi

29. Given a barometric pressure of 762.4 mmHg, calculate the pressure of each gas sample as indicated by the manometer.



30. Given a barometric pressure of 751.5 mmHg, calculate the pressure of each gas sample as indicated by the manometer.



Simple Gas Laws

31. A sample of gas has an initial volume of 5.6 L at a pressure of 735 Torr. If the volume of the gas is increased to 9.4 L, what will the pressure be?

32. A sample of gas has an initial volume of 13.9 L at a pressure of 1.22 bar. If the sample is compressed to a volume of 10.3 L, what will its pressure be?

33. A 48.3 mL sample of gas in a cylinder is warmed from 22 °C to 87 °C. What is its volume at the final temperature?

34. A syringe containing 1.55 mL of oxygen gas is cooled from 95.3 °C to 0.0 °C. What is the final volume of oxygen gas?

35. A balloon contains 0.158 mol of gas and has a volume of 2.46 L. If an additional 0.113 mol of gas is added to the balloon (at the same temperature and pressure), what will its final volume be?

36. A cylinder with a movable piston contains 0.553 mol of gas and has a volume of 253 mL. What will its volume be if an additional 0.365 mol of gas is added to the cylinder? (Assume constant temperature and pressure.)

Ideal Gas Law

37. What is the volume occupied by 0.118 mol of helium gas at a pressure of 0.97 bar and a temperature of 305 K? Would the volume be different if the gas was argon (under the same conditions)?

38. What is the volume occupied by 12.5 g of argon gas at a pressure of 1.05 bar and a temperature of 322 K? Would the volume be different if the sample were 12.5 g of helium (under identical conditions)?

39. What is the pressure in a 10.0 L cylinder filled with 0.448 mol of nitrogen gas at a temperature of 315 K?

40. What is the pressure in a 15.0 L cylinder filled with 32.7 g of oxygen gas at a temperature of 302 K?

41. A cylinder contains 28.5 L of oxygen gas at a pressure of 1.8 bar and a temperature of 298 K. How much gas (in moles) is in the cylinder?

42. What is the temperature of 0.52 mol of gas at a pressure of 1.3 bar and a volume of 11.8 L?

43. An automobile tire has a maximum rating of 38.0 psi (gauge pressure). The tire is inflated (while cold) to a volume of 11.8 L and a gauge pressure of 36.0 psi at a temperature of 12.0 °C. Driving on a hot day, the tire warms to 65.0 °C and its volume expands to 12.2 L. Does the pressure in the tire exceed its maximum rating? (Note: the *gauge pressure* is the *difference* between the total pressure and atmospheric pressure. In this case, assume that atmospheric pressure is 14.7 psi.)

44. A weather balloon is inflated to a volume of 28.5 L at a pressure of 748 Torr and a temperature of 28.0 °C. The balloon rises in the atmosphere to an altitude of approximately 7600 m, where the pressure is 385 Torr and the temperature is –15.0 °C. Assuming the balloon can freely expand, calculate the volume of the balloon at this altitude.

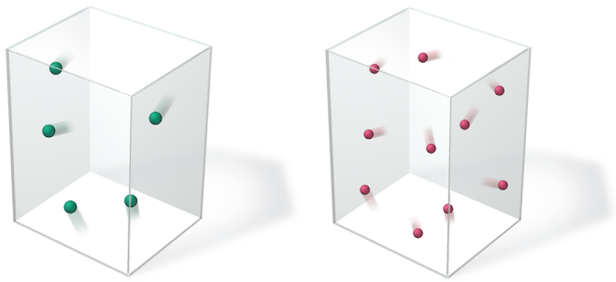
45. A piece of dry ice (solid carbon dioxide) with a mass of 28.8 g sublimes (converts from solid to gas) into a large balloon. Assuming that all of the carbon dioxide ends up in the balloon, what is the volume of the balloon at a temperature of 22 °C and a pressure of 989 mbar?

46. A 1.0 L container of liquid nitrogen is kept in a closet measuring 1.0 m by 1.0 m by 2.0 m. Assuming that the container is completely full, that the temperature is 25.0 °C, and that the atmospheric pressure is 1.0 bar, calculate the percent (by volume) of air that is displaced if all of the liquid nitrogen evaporates. (Liquid nitrogen has a density of 0.807 g mL^{-1}.)

47. A wine-dispensing system uses argon canisters to pressurize and preserve wine in the bottle. An argon canister for the system has a volume of 55.0 mL and contains 26.0 g of argon. Assuming ideal gas behaviour, what is the pressure in the canister at 295 K? When the argon is released from the canister, it expands to fill the wine bottle. How many 750.0-mL wine bottles can be purged with the argon in the canister at a pressure of 1.20 bar and a temperature of 295 K?

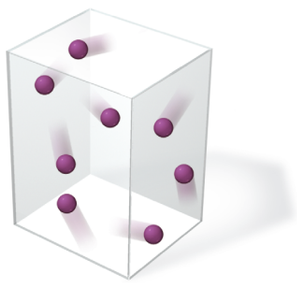
48. Pressurized carbon dioxide inflators can be used to inflate a bicycle tire in the event of a flat. These inflators use metal cartridges that contain 16.0 g of carbon dioxide. At 298 K, to what pressure (in psi) can the carbon dioxide in the cartridge inflate a 3.45 L mountain bike tire? (Note: the *gauge pressure* is the *difference* between the total pressure and atmospheric pressure. In this case, assume that atmospheric pressure is 14.7 psi.)

49. Which gas sample representation has the greatest pressure? Explain. Assume that all the samples are at the same temperature.



(a)

(b)



(c)

50. This picture represents a sample of gas at a pressure of 1 bar, a volume of 1 L, and a temperature of 25 °C. Draw a similar picture showing what would happen to the sample if the volume were reduced to 0.5 L and the temperature increased to 250 °C. What would happen to the pressure?



51. Aerosol cans carry clear warnings against incineration because of the high pressures that can develop upon heating. Suppose that a can contains a residual amount of gas at a pressure of 755 Torr and a temperature of 25 °C. What would the pressure be if the can were heated to 1155 °C?

52. A sample of nitrogen gas in a 1.75 L container exerts a pressure of 1.35 bar at 25 °C. What is the pressure if the volume of the container is maintained constant and the temperature is raised to 355 °C?

Molar Volume, Density, and Molar Mass of a Gas

53. Use the molar volume of a gas at STP to determine the volume (in L) occupied by 33.6 g of neon at STP.

54. Use the molar volume of a gas at STP to calculate the density (in g L^{-1}) of nitrogen gas at STP.

55. What is the density (in g L^{-1}) of hydrogen gas at 20.0 °C and a pressure of 1655 psi?

56. A sample of N_2O gas has a density of 2.85 g L^{-1} at 298 K. What is the pressure of the gas (in mbar)?

57. An experiment shows that a 248 mL gas sample has a mass of 0.433 g at a pressure of 745 Torr and a temperature of 28 °C. What is the molar mass of the gas?

58. An experiment shows that a 113 mL gas sample has a mass of 0.171 g at a pressure of 721 Torr and a temperature of 32 °C. What is the molar mass of the gas?

59. A sample of gas has a mass of 38.8 mg. Its volume is 224 mL at a temperature of 55 °C and a pressure of 886 mbar. Find the molar mass of the gas.

60. A sample of gas has a mass of 0.555 g. Its volume is 117 mL at a temperature of 85 °C and a pressure of 753 Torr. Find the molar mass of the gas.

Partial Pressure

61. A gas mixture contains each of the following gases at the indicated partial pressures: N_2, 215 Torr; O_2, 102 Torr; and He, 117 Torr. What is the total pressure of the mixture? What mass of each gas is present in a 1.35 L sample of this mixture at 25.0 °C?

62. A gas mixture with a total pressure of 745 mbar contains each of the following gases at the indicated partial pressures: CO_2, 125 mbar; Ar, 214 mbar; and O_2, 187 mbar. The mixture also contains helium gas. What is the partial pressure of the helium gas? What mass of helium gas is present in a 12.0 L sample of this mixture at 273 K?

63. A 1.20 g sample of dry ice is added to a 755 mL flask containing nitrogen gas at a temperature of 25.0 °C and a pressure of 725 Torr. The dry ice sublimes (converts from solid to gas) and the mixture returns to 25.0 °C. What is the total pressure in the flask?

64. A 275 mL flask contains pure helium at a pressure of 752 Torr. A second flask with a volume of 475 mL contains pure argon at a pressure of 722 Torr. If the two flasks are connected through a stopcock and the stopcock is opened, what are the partial pressures of each gas and the total pressure?

65. A gas mixture contains 1.25 g N_2 and 0.85 g O_2 in a 1.55 L container at 18 °C. Calculate the mole fraction and partial pressure of each component in the gas mixture.

66. What is the mole fraction of oxygen gas in air (see Table 5.3)? What volume of air contains 10.0 g of oxygen gas at 273 K and 1.00 bar?

67. The hydrogen gas formed in a chemical reaction is collected over water at 30.0 °C at a total pressure of 732 Torr. What is the partial pressure of the hydrogen gas collected in this way? If the total volume of gas collected is 722 mL, what mass of hydrogen gas is collected?

68. The air in a bicycle tire is bubbled through water and collected at 25 °C. If the total volume of gas collected is 5.45 L at a temperature of 25 °C and a pressure of 745 Torr, how many moles of gas were in the bicycle tire?

69. The zinc within a copper-plated penny will dissolve in hydrochloric acid if the copper coating is filed down in several spots (so that the hydrochloric acid can get to the zinc). The reaction

between the acid and the zinc is $2\,H^+(aq) + Zn(s) \longrightarrow H_2(g) + Zn^{2+}(aq)$. When the zinc in a certain penny dissolves, the total volume of gas collected over water at 25 °C was 0.951 L at a total pressure of 0.990 bar. What mass of hydrogen gas was collected?

70. A heliox deep-sea diving mixture contains 2.0 g of oxygen to every 98.0 g of helium. What is the partial pressure of oxygen when this mixture is delivered at a total pressure of 8.5 bar?

Reaction Stoichiometry Involving Gases

71. Consider the chemical reaction:

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

How many litres of hydrogen gas are formed from the complete reaction of 15.7 g C? Assume that the hydrogen gas is collected at a pressure of 1.0 bar and a temperature of 355 K.

72. Consider the chemical reaction:

$$2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g)$$

What mass of H_2O is required to form 1.4 L of O_2 at a temperature of 315 K and a pressure of 0.957 bar?

73. CH_3OH can be synthesized by the reaction:

$$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$$

What volume of H_2 gas (in L), at 748 Torr and 86 °C, is required to synthesize 25.8 g CH_3OH? How many litres of CO gas, measured under the same conditions, are required?

74. Oxygen gas reacts with powdered aluminum according to the reaction:

$$4\,Al(s) + 3\,O_2(g) \longrightarrow 2\,Al_2O_3(s)$$

What volume of O_2 gas (in L), measured at 782 Torr and 25 °C, completely reacts with 53.2 g Al?

75. Automobile air bags inflate following a serious impact. The impact triggers the chemical reaction:

$$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g)$$

If an automobile air bag has a volume of 11.8 L, what mass of NaN_3 (in g) is required to fully inflate the air bag upon impact? Assume STP conditions.

76. Lithium reacts with nitrogen gas according to the reaction:

$$6\,Li(s) + N_2(g) \longrightarrow 2\,Li_3N(s)$$

What mass of lithium (in g) reacts completely with 58.5 mL of N_2 gas at STP?

77. Hydrogen gas (a potential future fuel) can be formed by the reaction of methane with water according to the equation:

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3\,H_2(g)$$

In a particular reaction, 25.5 L of methane gas (measured at a pressure of 732 Torr and a temperature of 25 °C) mixes with 22.8 L of water vapour (measured at a pressure of 702 Torr and a temperature of 125 °C). The reaction produces 26.2 L of hydrogen gas at STP. What is the percent yield of the reaction?

78. Ozone is depleted in the stratosphere by chlorine from CF_3Cl according to the set of equations:

$$CF_3Cl + \text{UV light} \longrightarrow CF_3 + Cl$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$O_3 + \text{UV light} \longrightarrow O_2 + O$$
$$ClO + O \longrightarrow Cl + O_2$$

What total volume of ozone at a pressure of 25.0 Torr and a temperature of 225 K is destroyed when all of the chlorine from 15.0 g of CF_3Cl goes through ten cycles of the above reactions?

Kinetic Molecular Theory

79. Consider a 1.0 L sample of helium gas and a 1.0 L sample of argon gas, both at room temperature and atmospheric pressure.
- **a.** Do the atoms in the helium sample have the same *average kinetic energy* as the atoms in the argon sample?
- **b.** Do the atoms in the helium sample have the same *average velocity* as the atoms in the argon sample?
- **c.** Do the argon atoms, because they are more massive, exert a greater pressure on the walls of the container? Explain.
- **d.** Which gas sample would have the faster rate of effusion?

80. A flask at room temperature contains exactly equal amounts (in moles) of nitrogen and xenon.
- **a.** Which of the two gases exerts the greater partial pressure?
- **b.** The molecules or atoms of which gas have the greater average velocity?
- **c.** The molecules of which gas have the greater average kinetic energy?
- **d.** If a small hole were opened in the flask, which gas would effuse more quickly?

81. Calculate the root mean square velocity and kinetic energy of F_2, Cl_2, and Br_2 at 298 K. Rank these three halogens with respect to their rates of effusion.

82. Calculate the root mean square velocity and kinetic energy of CO, CO_2, and SO_3 at 298 K. Which gas has the greatest velocity? The greatest kinetic energy? The greatest effusion rate?

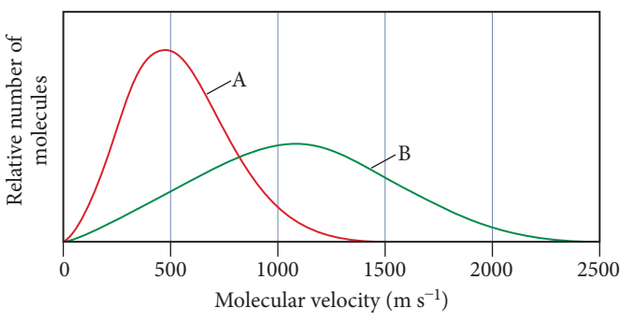
83. We obtain uranium-235 from U-238 by fluorinating the uranium to form UF_6 (which is a gas) and then taking advantage of the different rates of effusion and diffusion for compounds containing the two isotopes. Calculate the ratio of effusion rates for $^{238}UF_6$ and $^{235}UF_6$. The atomic mass of U-235 is 235.054 amu and that of U-238 is 238.051 amu.

84. Calculate the ratio of effusion rates for Ar and Kr.

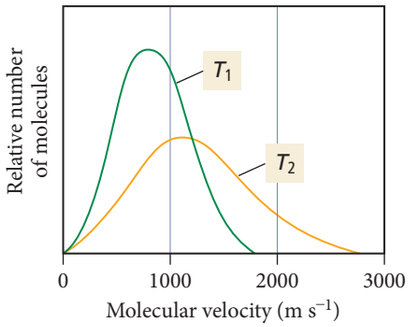
85. A sample of neon effuses from a container in 76 seconds. The same amount of an unknown noble gas requires 155 seconds. Identify the gas.

86. A sample of N_2O effuses from a container in 42 seconds. How long would it take the same amount of gaseous I_2 to effuse from the same container under identical conditions?

87. The graph shows the distribution of molecular velocities for two different molecules (A and B) at the same temperature. Which molecule has the higher molar mass? Which molecule would have the higher rate of effusion?



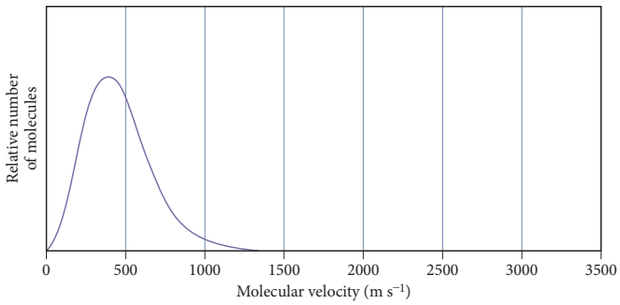
88. The graph shows the distribution of molecular velocities for the same molecule at two different temperatures (T_1 and T_2). Which temperature is greater? Explain.



89. Oxygen (O_2) and chlorine (Cl_2) have molar masses of 32.00 and 70.90 g mol^{-1}, respectively. In one hour, 0.315 mol of chlorine effuses through a tiny hole. How much oxygen effuses through the same hole in the same amount of time?

90. The following is a plot of the distribution of molecular speeds for N_2 at 298 K. Sketch the distribution of molecular speeds for:

a. N_2 at 150 K **b.** N_2 at 500 K **c.** He at 298 K



Real Gases

91. Which postulate of the kinetic molecular theory breaks down under conditions of high pressure? Explain.

92. Which postulate of the kinetic molecular theory breaks down under conditions of low temperature? Explain.

93. Use the van der Waals equation and the ideal gas equation to calculate the volume of 1.000 mol of neon at a pressure of 500.0 bar and a temperature of 355.0 K. Explain why the two values are different. (*Hint:* One way to solve the van der Waals equation for V is to use successive approximations. Use the ideal gas law to get a preliminary estimate for V.)

94. Use the van der Waals equation and the ideal gas equation to calculate the pressure exerted by 1.000 mol of Cl_2 in a volume of 5.000 L at a temperature of 273.0 K. Explain why the two values are different.

Cumulative Problems

95. Modern American pennies are composed of zinc coated with copper. A student determines the mass of a penny to be 2.482 g and then makes several scratches in the copper coating (to expose the underlying zinc). The student puts the scratched penny in hydrochloric acid, where the following reaction occurs between the zinc and the HCl (the copper remains undissolved):

$$Zn(s) + 2\,HCl(aq) \longrightarrow H_2(g) + ZnCl_2(aq)$$

The student collects the hydrogen produced over water at 25 °C. The collected gas occupies a volume of 0.899 L at a total pressure of 791 mmHg. Assuming that all the Zn in the penny dissolves, calculate the percent zinc by mass in the penny.

96. A 2.85 g sample of an unknown chlorofluorocarbon decomposes and produces 564 mL of chlorine gas at a pressure of 752 Torr and a temperature of 298 K. What is the percent chlorine (by mass) in the unknown chlorofluorocarbon?

97. The mass of an evacuated 255-mL flask is 143.187 g. The mass of the flask filled with 356 mbar of an unknown gas at 25 °C is 143.289 g. Calculate the molar mass of the unknown gas.

98. A 118 mL flask is evacuated and found to have a mass of 97.129 g. When the flask is filled with 1024 mbar of helium gas at 35 °C, it has a mass of 97.171 g. Was the helium gas pure?

99. A gaseous hydrogen and carbon–containing compound is decomposed and found to contain 82.66% carbon and 17.34% hydrogen by mass. The mass of 158 mL of the gas, measured at 556 Torr and 25 °C, was 0.275 g. What is the molecular formula of the compound?

100. A gaseous hydrogen and carbon–containing compound is decomposed and found to contain 85.63% C and 14.37% H by mass. The mass of 258 mL of the gas, measured at STP, was 0.646 g. What is the molecular formula of the compound?

101. Consider the reaction:

$$2\,NiO(s) \longrightarrow 2\,Ni(s) + O_2(g)$$

If O_2 is collected over water at 40.0 °C and a total pressure of 745 mmHg, what volume of gas will be collected for the complete reaction of 24.78 g of NiO?

102. Consider the reaction:

$$2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$$

If this reaction produces 15.8 g of Ag(s), what total volume of gas can be collected over water at a temperature of 25 °C and a total pressure of 752 Torr?

103. When hydrochloric acid is poured over potassium sulfide, 42.9 mL of hydrogen sulfide gas is produced at a pressure of 752 Torr and 25.8 °C. Write an equation for the gas-evolution reaction and determine how much potassium sulfide (in grams) reacted.

104. Consider the reaction:

$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$$

a. If 285.5 mL of SO_2 reacts with 158.9 mL of O_2 (both measured at 315 K and 67 mbar), what is the limiting reactant and the theoretical yield of SO_3?

b. If 187.2 mL of SO_3 is collected (measured at 315 K and 67 mbar), what is the percent yield for the reaction?

105. Ammonium carbonate decomposes upon heating according to the balanced equation:

$$(NH_4)_2CO_3(s) \longrightarrow 2\,NH_3(g) + CO_2(g) + H_2O(g)$$

Calculate the total volume of gas produced at 22 °C and 1.02 bar by the complete decomposition of 11.83 g of ammonium carbonate.

106. Ammonium nitrate decomposes explosively upon heating according to the balanced equation:

$$2\ NH_4NO_3(s) \longrightarrow 2\ N_2(g) + O_2(g) + 4\ H_2O(g)$$

Calculate the total volume of gas (at 125 °C and 748 Torr) produced by the complete decomposition of 1.55 kg of ammonium nitrate.

107. Olympic cyclists fill their tires with helium to make them lighter. Calculate the mass of air in an air-filled tire and the mass of helium in a helium-filled tire. What is the mass difference between the two? Assume that the volume of the tire is 855 mL, that it is filled to a total pressure of 125 psi, and that the temperature is 25 °C. Also, assume an average molar mass for air of 28.8 g mol^{-1}.

108. In a common classroom demonstration, a balloon is filled with air and submerged in liquid nitrogen. The balloon contracts as the gases within the balloon cool. Suppose the balloon initially contains 2.95 L of air at a temperature of 25.0 °C and a pressure of 0.998 bar. Calculate the expected volume of the balloon upon cooling to −195.8 °C (the boiling point of liquid nitrogen). When the demonstration is carried out, the actual volume of the balloon decreases to 0.61 L. How does the observed volume of the balloon compare to your calculated value? Can you explain the difference?




109. Gaseous ammonia can be injected into the exhaust stream of a coal-burning power plant to reduce the pollutant NO to N_2 according to the reaction:

$$4\ NH_3(g) + 4\ NO(g) + O_2(g) \longrightarrow 4\ N_2(g) + 6\ H_2O(g)$$

Suppose that the exhaust stream of a power plant has a flow rate of 335 L s^{-1} at a temperature of 955 K, and that the exhaust contains a partial pressure of NO of 22.4 Torr. What should be the flow rate of ammonia delivered at 1.007 bar and 298 K into the stream to react completely with the NO if the ammonia is 65.2% pure (by volume)?

110. The emission of NO_2 by fossil fuel combustion can be prevented by injecting gaseous urea into the combustion mixture. The urea reduces NO (which oxidizes in air to form NO_2) according to the reaction:

$$2\ CO(NH_2)_2(g) + 4\ NO(g) + O_2(g) \longrightarrow 4\ N_2(g) + 2\ CO_2(g) + 4\ H_2O(g)$$

Suppose that the exhaust stream of an automobile has a flow rate of 2.55 L s^{-1} at 655 K and contains a partial pressure of NO of 16.5 mbar. What total mass of urea is necessary to react completely with the NO formed during 8.0 hours of driving?

111. An ordinary gasoline can measuring 30.0 cm by 20.0 cm by 15.0 cm is evacuated with a vacuum pump. Assuming that virtually all of the air can be removed from inside the can, and that atmospheric pressure is 1.01 bar, what is the total force (in Newtons) on the surface of the can? Do you think that the can could withstand the force?

112. Twenty-five millilitres of liquid nitrogen (density = 0.807 g mL^{-1}) is poured into a cylindrical container with a radius of 10.0 cm and a length of 20.0 cm. The container initially contains only air at a pressure of 1.01 bar and a temperature of 298 K. If the liquid nitrogen completely vapourizes, what is the total force (in N) on the interior of the container at 298 K?

113. A 160.0 L helium tank contains pure helium at a pressure of 1855 psi and a temperature of 298 K. How many 3.5-L helium balloons will the helium in the tank fill? (Assume an atmospheric pressure of 1.01 bar and a temperature of 298 K.)

114. An 11.5 mL sample of liquid butane (density = 0.573 g mL^{-1}) is evaporated in an otherwise empty container at a temperature of 28.5 °C. The pressure in the container following evaporation is 892 Torr. What is the volume of the container?

115. A scuba diver creates a spherical bubble with a radius of 2.5 cm at a depth of 30.0 m where the total pressure (including atmospheric pressure) is 4.00 atm. What is the radius of the bubble when it reaches the surface of the water? (Assume that the atmospheric pressure is 1.01 bar and the temperature is 298 K.)

116. A particular balloon can be stretched to a maximum surface area of 1257 cm^2. The balloon is filled with 3.0 L of helium gas at a pressure of 1.007 bar and a temperature of 298 K. The balloon is then allowed to rise in the atmosphere. If the atmospheric temperature is 273 K, at what pressure will the balloon burst? (Assume the balloon to be in the shape of a sphere.)

117. A catalytic converter in an automobile uses a palladium or platinum catalyst (a substance that increases the rate of a reaction without being consumed by the reaction) to convert carbon monoxide gas to carbon dioxide according to the reaction:

$$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$$

A chemist researching the effectiveness of a new catalyst combines a 2.0 : 1.0 mole ratio mixture of carbon monoxide and oxygen gas (respectively) over the catalyst in a 2.45 L flask at a total pressure of 993 mbar and a temperature of 552 °C. When the reaction is complete, the pressure in the flask has dropped to 552 Torr. What percentage of the carbon monoxide was converted to carbon dioxide?

118. A quantity of N_2 occupies a volume of 1.0 L at 300 K and 1.0 bar. The gas expands to a volume of 3.0 L as the result of a change in both temperature and pressure. Find the density of the gas at these new conditions.

119. A mixture of $CO(g)$ and $O_2(g)$ in a 1.0 L container at 1.0×10^3 K has a total pressure of 2.2 bar. After some time, the total pressure falls to 1.9 bar as the result of the formation of CO_2. Find the mass (in grams) of CO_2 that forms.

120. The radius of a xenon atom is 1.3×10^{-8} cm. A 100 mL flask is filled with Xe at a pressure of 1.0 bar and a temperature of 273 K. Calculate the fraction of the volume that is occupied by Xe atoms. (*Hint:* The atoms are spheres.)

121. A natural gas storage tank is a cylinder with a movable top whose volume can change only as its height changes. Its radius remains fixed. The height of the cylinder is 22.6 m on a day when the temperature is 22 °C. The next day, the height of the cylinder increases to 23.8 m when the gas expands because of a heat wave. Find the temperature on the second day, assuming that the pressure and amount of gas in the storage tank have not changed.

122. A mixture of 8.0 g CH_4 and 8.0 g Xe is placed in a container and the total pressure is found to be 0.44 bar. Find the partial pressure of CH_4.

123. A steel container of volume 0.35 L can withstand pressures up to 88 bar before exploding. What mass of helium can be stored in this container at 299 K?

124. Binary compounds of alkali metals and hydrogen react with water to liberate $H_2(g)$. The H_2 from the reaction of a sample of NaH with an excess of water fills a volume of 0.490 L above the water. The temperature of the gas is 35 °C and the total pressure is 758 Torr. Determine the mass of H_2 liberated and the mass of NaH that reacted.

125. In a given diffusion apparatus, 15.0 mL of HBr gas diffused in 1.0 min. In the same apparatus and under the same conditions, 20.3 mL of an unknown gas diffused in 1.0 min. The unknown gas is a hydrocarbon. Find its molecular formula.

126. A sample of $N_2O_3(g)$ has a pressure of 0.017 bar. The temperature (in K) is then doubled and the N_2O_3 undergoes complete decomposition to $NO_2(g)$ and $NO(g)$. Find the total pressure of the mixture of gases assuming constant volume and no additional temperature change.

127. When 0.583 g of neon is added to an 800 cm^3 bulb containing a sample of argon, the total pressure of the gases is found to be 1.17 bar at a temperature of 295 K. Find the mass of the argon in the bulb.

128. A gas mixture composed of helium and argon has a density of 0.670 g L^{-1} at 1.01 bar and 298 K. What is the composition of the mixture by volume?

129. A gas mixture contains 75.2% nitrogen and 24.8% krypton by mass. What is the partial pressure of krypton in the mixture if the total pressure is 993 mbar?

130. Lightning McQueen's tires have a maximum rating of 270 kPa. When a tire is cold (12.0 °C), it is inflated to a volume of 11.8 L and a pressure of 250 kPa. While racing on a hot day, the tire warms to 65.0 °C and its volume expands slightly to 12.1 L. Does the pressure in the tire exceed the maximum rating?

131. a. A liquid hydrocarbon (containing only C and H) is analyzed by combustion analysis. 1.75 g of the substance was found to produce 3.17 L of CO_2 at 1.0 bar, 298 K, and 1.92 g H_2O (molar mass = 18.015 g mol^{-1}). What is the empirical formula of the compound?

b. To obtain the actual molecular formula, the liquid was analyzed by the Dumas method to determine the molar mass. The following data was obtained:

volume of flask = 247 mL temperature = 100 °C
mass of empty flask = 71.814 g pressure = 813 Torr
mass of flask and compound vapour = 72.523 g

What is the molar mass and the molecular formula of the compound?

Challenge Problems

132. A 10-litre container is filled with 0.10 mol of $H_2(g)$ and heated to 3000 K, causing some of the $H_2(g)$ to decompose into $H(g)$. The pressure is found to be 3.0 bar. Find the partial pressure of the $H(g)$ that forms from H_2 at this temperature. (Assume two significant figures for the temperature.)

133. A mixture of $NH_3(g)$ and $N_2H_4(g)$ is placed in a sealed container at 300 K. The total pressure is 0.50 bar. The container is heated to 1200 K at which time both substances decompose completely according to the equations $2\ NH_3(g) \longrightarrow N_2(g) + 3\ H_2(g)$; and $N_2H_4(g) \longrightarrow N_2(g) + 2\ H_2(g)$. After decomposition is complete, the total pressure at 1200 K is found to be 4.5 bar. Find the percent of $N_2H_4(g)$ in the original mixture. (Assume two significant figures for the temperature.)

134. A quantity of CO gas occupies a volume of 0.48 L at 1.0 atm and 275 K. The pressure of the gas is lowered and its temperature is raised until its volume is 1.3 L. Find the density of the CO under the new conditions.

135. When $CO_2(g)$ is put in a sealed container at 701 K and a pressure of 10.0 bar and is heated to 1401 K, the pressure rises to 22.5 bar. Some of the CO_2 decomposes to CO and O_2. Calculate the mole percent of CO_2 that decomposes.

136. The world burns approximately 9.0×10^{12} kg of fossil fuel per year. Use the combustion of octane as the representative reaction and determine the mass of carbon dioxide (the most significant greenhouse gas) formed per year. The current concentration of carbon dioxide in the atmosphere is approximately 387 ppm (by volume). By what percentage does the concentration increase each year due to fossil fuel combustion? Approximate the average properties of the entire atmosphere by assuming that the atmosphere extends from sea level to 15 km and that it has an average pressure of 381 Torr and average temperature of 275 K. Assume Earth is a perfect sphere with a radius of 6371 km.

137. The atmosphere slowly oxidizes hydrocarbons in a number of steps that eventually convert the hydrocarbon into carbon dioxide and water. The overall reaction of a number of such steps for methane gas is:

$$CH_4(g) + 5\ O_2(g) + 5\ NO(g) \longrightarrow CO_2(g) + H_2O(g) + 5\ NO_2(g) + 2\ OH(g)$$

Suppose that an atmospheric chemist combines 155 mL of methane at STP, 885 mL of oxygen at STP, and 55.5 mL of NO at STP in a 2.0 L flask. The flask is allowed to stand for several weeks at 275 K. If the reaction reaches 90.0% of completion (90.0% of the limiting reactant is consumed), what is the partial pressure of each of the reactants and products in the flask at 275 K? What is the total pressure in the flask?

138. Two identical balloons are filled to the same volume, one with air and one with helium. The next day, the volume of the air-filled balloon has decreased by 5.0%. By what percent has the volume of the helium-filled balloon decreased? (Assume that the air is four-fifths nitrogen and one-fifth oxygen, and that the temperature did not change.)

139. A mixture of $CH_4(g)$ and $C_2H_6(g)$ has a total pressure of 0.53 bar. Just enough $O_2(g)$ is added to the mixture to bring about its complete combustion to $CO_2(g)$ and $H_2O(g)$. The total pressure of the two product gases is found to be 2.2 bar. Assuming constant volume and temperature, find the mole fraction of CH_4 in the mixture.

140. A sample of $C_2H_2(g)$ has a pressure of 7.8 kPa. After some time, a portion of it reacts to form $C_6H_6(g)$. The total pressure of the mixture of gases is then 3.9 kPa. Assume that the volume and temperature do not change. What fraction of $C_2H_2(g)$ has undergone reaction?

Conceptual Problems

141. When the driver of an automobile applies the brakes, the passengers are pushed toward the front of the car, but a helium balloon inside the car is pushed toward the back of the car. Upon forward acceleration, the passengers are pushed toward the back of the car, but the helium balloon is pushed toward the front of the car. Why?

142. Suppose that a liquid is 10 times more dense than water. If you were to sip this liquid at sea level using a straw, what would be the maximum length of the straw?

143. This reaction occurs in a closed container:

$$A(g) + 2\,B(g) \longrightarrow 2\,C(g)$$

A reaction mixture initially contains 1.5 L of A and 2.0 L of B. Assuming that the volume and temperature of the reaction mixture remain constant, what is the percent change in pressure if the reaction goes to completion?

144. One mole of nitrogen and one mole of neon are combined in a closed container at STP. How big is the container?

145. Exactly equal amounts (in moles) of gas A and gas B are combined in a 1 L container at room temperature. Gas B has a molar mass that is twice that of gas A. Which statement is true for the mixture of gases and why?

a. The molecules of gas B have greater kinetic energy than those of gas A.

b. Gas B has a greater partial pressure than gas A.

c. The molecules of gas B have a greater average velocity than those of gas A.

d. Gas B makes a greater contribution to the average density of the mixture than gas A.

146. Which gas would you expect to deviate most from ideal behaviour under conditions of low temperature: F_2, Cl_2, or Br_2? Explain.