

Chapter Outline

- 5.1** Substances That Exist as Gases
- 5.2** Pressure of a Gas
- 5.3** The Gas Laws
- 5.4** The Ideal Gas Equation
- 5.5** Gas Stoichiometry
- 5.6** Dalton's Law of Partial Pressures
- 5.7** The Kinetic Molecular Theory of Gases
- 5.8** Deviation from Ideal Behavior

A Look Ahead

We begin by examining the substances that exist as gases and their general properties. (5.1)

We learn units for expressing gas pressure and the characteristics of atmospheric pressure. (5.2)

Next, we study the relationship among pressure, volume, temperature, and amount of a gas in terms of various gas laws. We will see that these laws can be summarized by the ideal gas equation, which can be used to calculate the density or molar mass of a gas. (5.3 and 5.4)

We will see that the ideal gas equation can be used to study the stoichiometry involving gases. (5.5)

We learn that the behavior of a mixture of gases can be understood by Dalton's law of partial pressures, which is an extension of the ideal gas equation. (5.6)

We will see how the kinetic molecular theory of gases, which is based on the properties of individual molecules, can be used to describe macroscopic properties such as the pressure and temperature of a gas. We learn that this theory enables us to obtain an expression for the speed of molecules at a given temperature, and understand phenomena such as gas diffusion and effusion. (5.7)

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

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



Figure 5.1 Elements that exist as gases at 25°C and 1 atm. The noble gases (the Group 8A elements) are monatomic species; the other elements exist as diatomic molecules. Ozone (O₃) is also a gas.

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

Elements	Compounds
H ₂ (molecular hydrogen)	HF (hydrogen fluoride)
N ₂ (molecular nitrogen)	HCl (hydrogen chloride)
O ₂ (molecular oxygen)	HBr (hydrogen bromide)
O ₃ (ozone)	HI (hydrogen iodide)
F ₂ (molecular fluorine)	CO (carbon monoxide)
Cl ₂ (molecular chlorine)	CO ₂ (carbon dioxide)
He (helium)	NH ₃ (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO ₂ (nitrogen dioxide)
Kr (krypton)	N ₂ O (nitrous oxide)
Xe (xenon)	SO ₂ (sulfur dioxide)
Rn (radon)	H ₂ S (hydrogen sulfide)
	HCN (hydrogen cyanide)*

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

Of the gases listed in Table 5.1, only O₂ is essential for our survival. Hydrogen sulfide (H₂S) and hydrogen cyanide (HCN) are deadly poisons. Several others, such as CO, NO₂, O₃, and SO₂, are somewhat less toxic. The gases He, Ne, and Ar are chemically inert; that is, they do not react with any other substance. Most gases are colorless. Exceptions are F₂, Cl₂, and NO₂. The dark-brown color of NO₂ is sometimes visible in polluted air. All gases have the following physical characteristics:

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

5.2 Pressure of a Gas

Gases exert pressure on any surface with which they come in contact, because gas molecules are constantly in motion. We humans have adapted so well physiologically to the pressure of the air around us that we are usually unaware of it, perhaps as fish are not conscious of the water's pressure on them.

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

SI Units of Pressure

Pressure is one of the most readily measurable properties of a gas.

A gas is a substance that is normally in the gaseous state at ordinary temperatures and pressures; a vapor is the gaseous form of any substance that is a liquid or a solid at normal temperatures and pressures. Thus, at 25°C and 1 atm pressure, we speak of water vapor and oxygen gas.



NO₂ gas.

pressure as *force applied per unit area*:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

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

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

Atmospheric Pressure

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

Does atmospheric pressure act only downward, as you might infer from its definition? Imagine what would happen, then, if you were to hold a piece of paper tight (with both hands) above your head. You might expect the paper to bend due to the pressure of air acting on it, but this does not happen. The reason is that air, like water, is a fluid. The pressure exerted on an object in a fluid comes from all directions—downward and upward, as well as from the left and from the right. At the molecular level, air pressure results from collisions between the air molecules and any surface with which they come in contact. The magnitude of pressure depends on how often and how strongly the

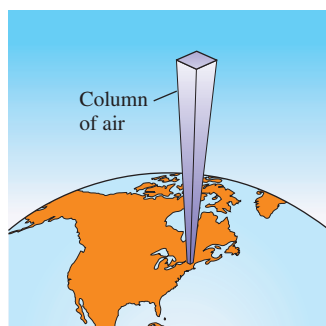


Figure 5.2 A column of air extending from sea level to the upper atmosphere.

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

[‡]Blaise Pascal (1623–1662). French mathematician and physicist. Pascal's work ranged widely in mathematics and physics, but his specialty was in the area of hydrodynamics (the study of the motion of fluids). He also invented a calculating machine.

molecules impact the surface. It turns out that there are just as many molecules hitting the paper from the top as there are from underneath, so the paper stays flat.

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

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

and

$$1 \text{ atm} = 760 \text{ mmHg} \quad (\text{exactly})$$

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

$$\begin{aligned} 1 \text{ atm} &= 101,325 \text{ Pa} \\ &= 1.01325 \times 10^5 \text{ Pa} \end{aligned}$$

and because $1000 \text{ Pa} = 1 \text{ kPa}$ (kilopascal)

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

Examples 5.1 and 5.2 show the conversion from mmHg to atm and kPa.

EXAMPLE 5.1

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

Strategy Because $1 \text{ atm} = 760 \text{ mmHg}$, the following conversion factor is needed to obtain the pressure in atmospheres

$$\frac{1 \text{ atm}}{760 \text{ mmHg}}$$

Solution The pressure in the cabin is given by

$$\begin{aligned} \text{pressure} &= 688 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \\ &= 0.905 \text{ atm} \end{aligned}$$

Practice Exercise Convert 749 mmHg to atmospheres.

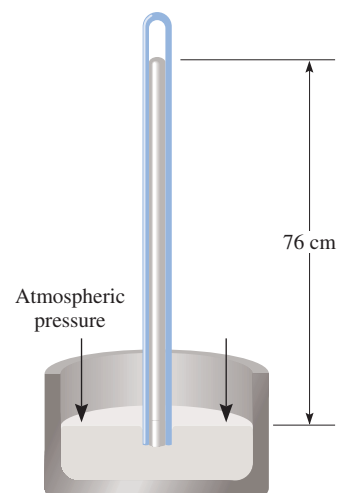


Figure 5.3 A barometer for measuring atmospheric pressure. Above the mercury in the tube is a vacuum. (The space actually contains a very small amount of mercury vapor.) The column of mercury is supported by the atmospheric pressure.

Similar problem: 5.13.

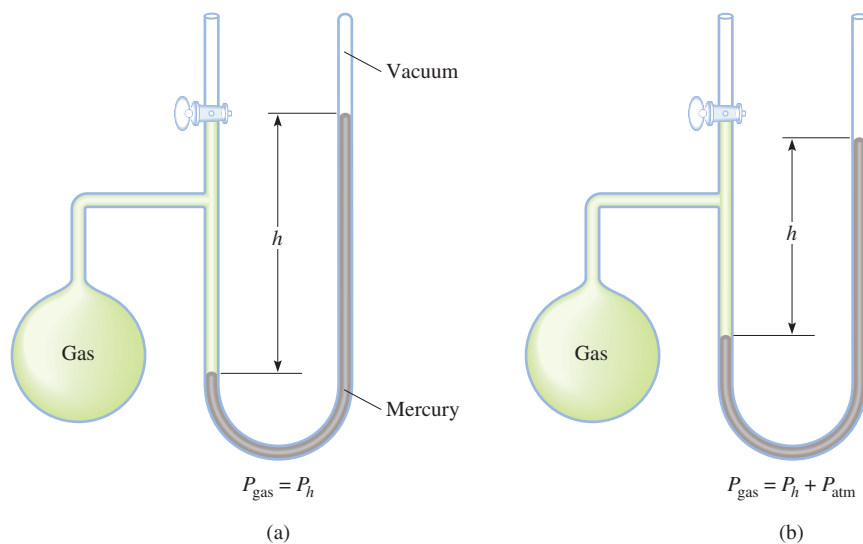


[†]Evangelista Torricelli (1608–1674). Italian mathematician. Torricelli was supposedly the first person to recognize the existence of atmospheric pressure.

A **manometer** is a device used to measure the pressure of gases other than the atmosphere. The principle of operation of a manometer is similar to that of a barometer. There are two types of manometers, shown in Figure 5.4. The *closed-tube manometer* is normally used to measure pressures below atmospheric pressure [Figure 5.4(a)], whereas the *open-tube manometer* is better suited for measuring pressures equal to or greater than atmospheric pressure [Figure 5.4(b)].

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

Figure 5.4 Two types of manometers used to measure gas pressures. (a) Gas pressure is less than atmospheric pressure. (b) Gas pressure is greater than atmospheric pressure.



5.3 The Gas Laws

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

The Pressure-Volume Relationship: Boyle's Law

In the seventeenth century, Robert Boyle[†] studied the behavior of gases systematically and quantitatively. In one series of studies, Boyle investigated the pressure-volume relationship of a gas sample. Typical data collected by Boyle are shown in Table 5.2. Note that as the pressure (P) is increased at constant temperature, the volume (V) occupied by a given amount of gas decreases. Compare the first data point with a pressure of 724 mmHg and a volume of 1.50 (in arbitrary unit) to the last data point with a pressure of 2250 mmHg and a volume of 0.58. Clearly there is an inverse relationship between pressure and volume of a gas at constant temperature. As the pressure is increased, the volume occupied by the gas decreases. Conversely, if the applied pressure is decreased, the volume the gas occupies increases. This relationship is now known as **Boyle's law**, which states that *the pressure of a fixed amount of gas at a constant temperature is inversely proportional to the volume of the gas*.

The apparatus used by Boyle in this experiment was very simple (Figure 5.5). In Figure 5.5(a), the pressure exerted on the gas is equal to atmospheric pressure and the volume of the gas is 100 mL. (Note that the tube is open at the top and is therefore exposed to atmospheric pressure.) In Figure 5.5(b), more mercury has been added to double the pressure on the gas, and the gas volume decreases to 50 mL. Tripling the pressure on the gas decreases its volume to a third of the original value [Figure 5.5(c)].

We can write a mathematical expression showing the inverse relationship between pressure and volume:

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

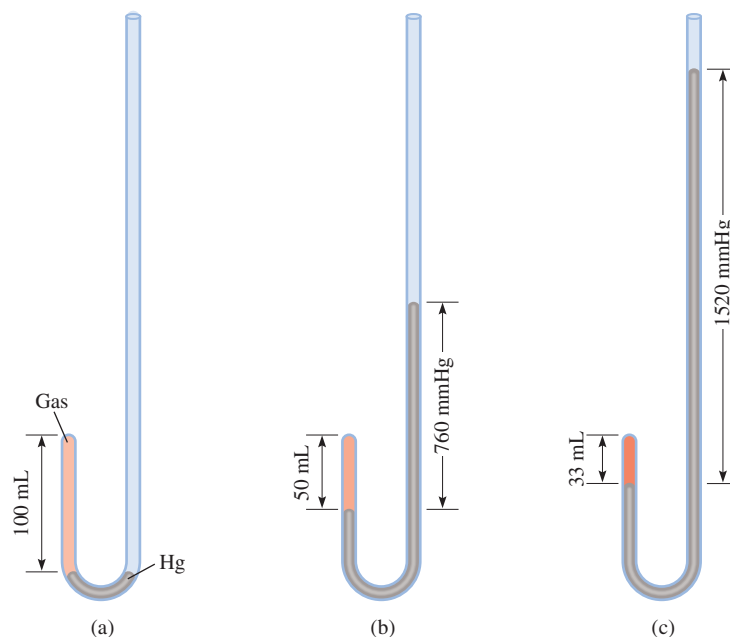
The pressure applied to a gas is equal to the gas pressure.

[†]Robert Boyle (1627–1691). British chemist and natural philosopher. Although Boyle is commonly associated with the gas law that bears his name, he made many other significant contributions in chemistry and physics. Despite the fact that Boyle was often at odds with scientists of his generation, his book *The Skeptical Chymist* (1661) influenced generations of chemists.

TABLE 5.2 Typical Pressure-Volume Relationship Obtained by Boyle

P (mmHg)	724	869	951	998	1230	1893	2250
V (arbitrary units)	1.50	1.33	1.22	1.18	0.94	0.61	0.58
PV	1.09×10^3	1.16×10^3	1.16×10^3	1.18×10^3	1.2×10^3	1.2×10^3	1.3×10^3

Figure 5.5 Apparatus for studying the relationship between pressure and volume of a gas. (a) The levels of mercury are equal and the pressure of the gas is equal to the atmospheric pressure (760 mmHg). The gas volume is 100 mL. (b) Doubling the pressure by adding more mercury reduces the gas volume to 50 mL. (c) Tripling the pressure decreases the gas volume to one-third of the original value. The temperature and amount of gas are kept constant.



where the symbol \propto means *proportional to*. We can change \propto to an equals sign and write

$$P = k_1 \times \frac{1}{V} \quad (5.1a)$$

where k_1 is a constant called the *proportionality constant*. Equation (5.1a) is the mathematical expression of Boyle's law. We can rearrange Equation (5.1a) and obtain

$$PV = k_1 \quad (5.1b)$$

This form of Boyle's law says that the product of the pressure and volume of a gas at constant temperature and amount of gas is a constant. The top diagram in Figure 5.6 is a schematic representation of Boyle's law. The quantity n is the number of moles of the gas and R is a constant to be defined in Section 5.4. We will see in Section 5.4 that the proportionality constant k_1 in Equations (5.1) is equal to nRT .

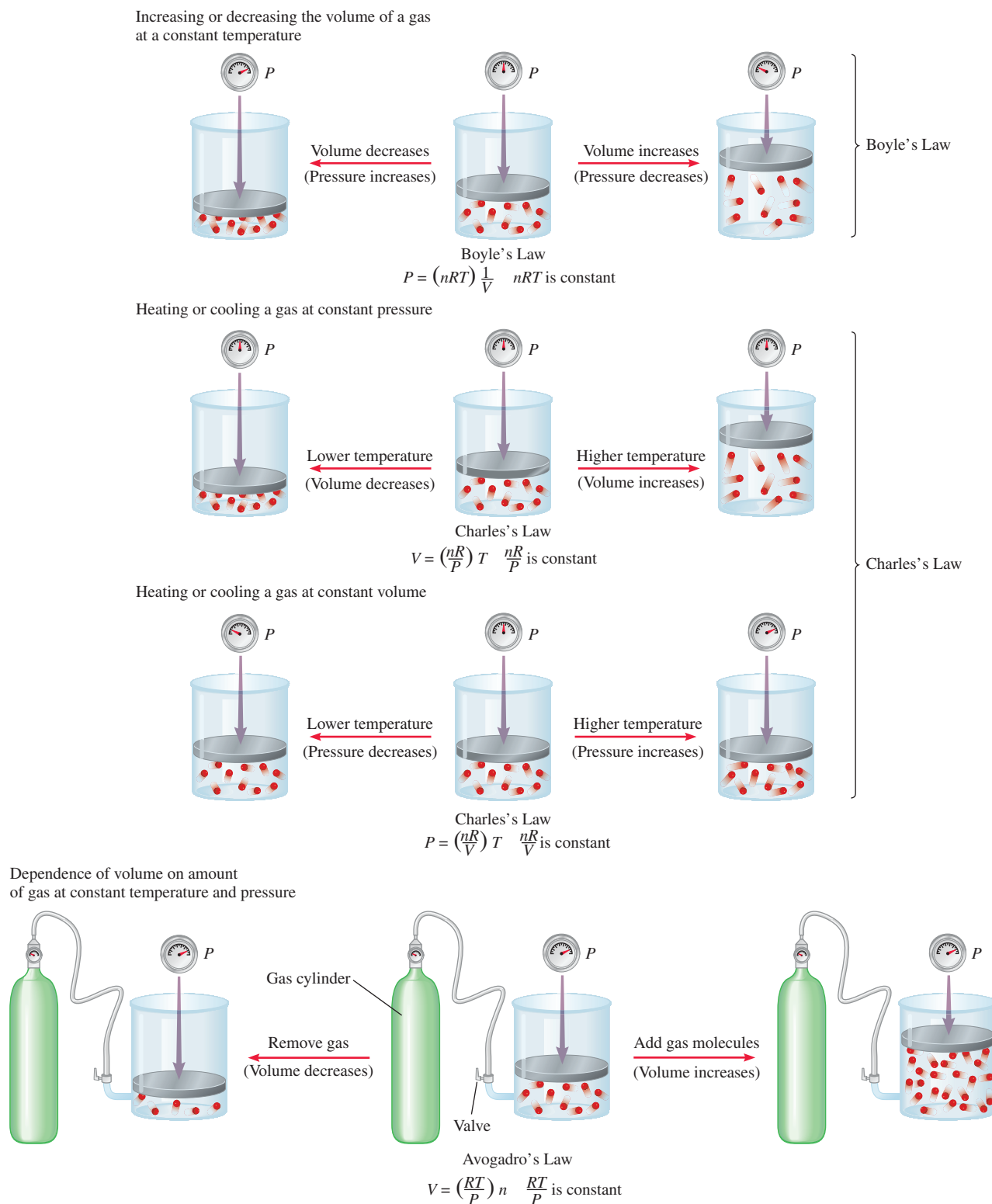


Figure 5.6 Schematic illustrations of Boyle's law, Charles's law, and Avogadro's law.

Figure 5.7 Graphs showing variation of the volume of a gas with the pressure exerted on the gas, at constant temperature. (a) P versus V . Note that the volume of the gas doubles as the pressure is halved. (b) P versus $1/V$. The slope of the line is equal to k_1 .

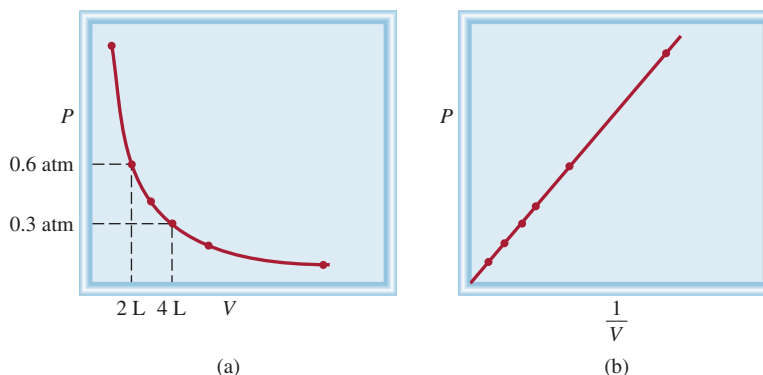


Figure 5.7 shows two conventional ways of expressing Boyle's findings graphically. Figure 5.7(a) is a graph of the equation $PV = k_1$; Figure 5.7(b) is a graph of the equivalent equation $P = k_1 \times 1/V$. Note that the latter is a linear equation of the form $y = mx + b$, where $b = 0$ and $m = k_1$.

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

$$P_1V_1 = k_1 = P_2V_2$$

or

$$P_1V_1 = P_2V_2 \quad (5.2)$$

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

The Temperature-Volume Relationship: Charles's and Gay-Lussac's Law

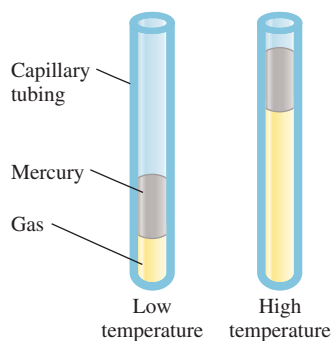


Figure 5.8 Variation of the volume of a gas sample with temperature, at constant pressure. The pressure exerted on the gas is the sum of the atmospheric pressure and the pressure due to the weight of the mercury.

Boyle's law depends on the temperature of the system remaining constant. But suppose the temperature changes: How does a change in temperature affect the volume and pressure of a gas? Let us first look at the effect of temperature on the volume of a gas. The earliest investigators of this relationship were French scientists, Jacques Charles[†] and Joseph Gay-Lussac.[‡] Their studies showed that, at constant pressure, the volume of a gas sample expands when heated and contracts when cooled (Figure 5.8). The quantitative relations involved in changes in gas temperature and volume turn out to be remarkably consistent. For example, we observe an interesting phenomenon when we study the temperature-volume relationship at various pressures. At any given pressure, the plot of volume versus temperature yields a straight line. By extending the line to zero volume, we find the intercept on the temperature axis to be -273.15°C . At any other pressure, we obtain a different straight line for the volume-temperature plot, but we get the *same* zero-volume temperature intercept

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

[‡]Joseph Louis Gay-Lussac (1778–1850). French chemist and physicist. Like Charles, Gay-Lussac was a balloon enthusiast. Once he ascended to an altitude of 20,000 ft to collect air samples for analysis.

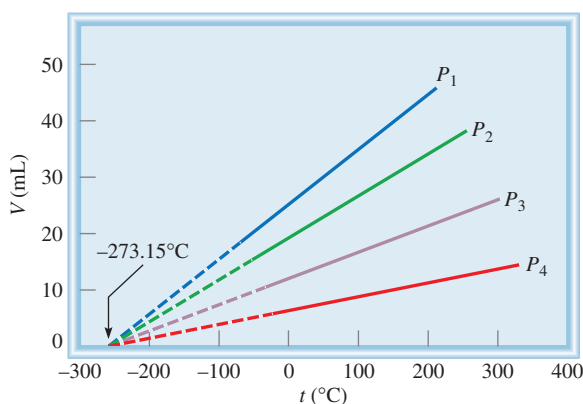


Figure 5.9 Variation of the volume of a gas sample with temperature, at constant pressure. Each line represents the variation at a certain pressure. The pressures increase from P_1 to P_4 . All gases ultimately condense (become liquids) if they are cooled to sufficiently low temperatures; the solid portions of the lines represent the temperature region above the condensation point. When these lines are extrapolated, or extended (the dashed portions), they all intersect at the point representing zero volume and a temperature of -273.15°C .

at -273.15°C (Figure 5.9). (In practice, we can measure the volume of a gas over only a limited temperature range, because all gases condense at low temperatures to form liquids.)

In 1848 Lord Kelvin[†] realized the significance of this phenomenon. He identified -273.15°C as **absolute zero**, *theoretically the lowest attainable temperature*. Then he set up an **absolute temperature scale**, now called the **Kelvin temperature scale**, with *absolute zero as the starting point*. (see Section 1.7). On the Kelvin scale, one kelvin (K) is equal *in magnitude* to one degree Celsius. The only difference between the absolute temperature scale and the Celsius scale is that the zero position is shifted. Important points on the two scales match up as follows:

	Kelvin Scale	Celsius Scale
Absolute zero	0 K	-273.15°C
Freezing point of water	273.15 K	0°C
Boiling point of water	373.15 K	100°C

Under special experimental conditions, scientists have succeeded in approaching absolute zero to within a small fraction of a kelvin.

The conversion between $^\circ\text{C}$ and K is given on p. 20. In most calculations we will use 273 instead of 273.15 as the term relating K and $^\circ\text{C}$. By convention, we use T to denote absolute (kelvin) temperature and t to indicate temperature on the Celsius scale.

Remember that temperature must be in kelvins in gas law calculations.

Charles's and Gay-Lussac's law, or simply **Charles's law**, which states that *the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas*. Charles's law is also illustrated in Figure 5.6. We see that the proportionality constant k_2 in Equation (5.3) is equal to nR/P .

[†]William Thomson, Lord Kelvin (1824–1907). Scottish mathematician and physicist. Kelvin did important work in many branches of physics.

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

$$\frac{V_1}{T_1} = k_2 = \frac{V_2}{T_2}$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (5.4)$$

where V_1 and V_2 are the volumes of the gas at temperatures T_1 and T_2 (both in kelvins), respectively.

or

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (5.6)$$

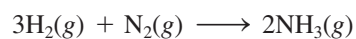
where P_1 and P_2 are the pressures of the gas at temperatures T_1 and T_2 , respectively.

The Volume-Amount Relationship: Avogadro's Law

The work of the Italian scientist Amedeo Avogadro complemented the studies of Boyle, Charles, and Gay-Lussac. In 1811 he published a hypothesis stating that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules (or atoms if the gas is monatomic).

Avogadro's law, which states that *at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.*

According to Avogadro's law we see that when two gases react with each other, their reacting volumes have a simple ratio to each other. If the product is a gas, its volume is related to the volume of the reactants by a simple ratio (a fact demonstrated earlier by Gay-Lussac). For example, consider the synthesis of ammonia from molecular hydrogen and molecular nitrogen:



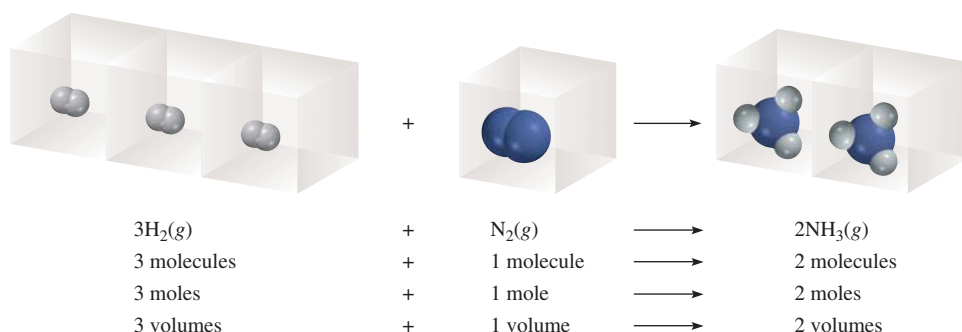
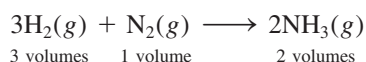


Figure 5.10 Volume relationship of gases in a chemical reaction. The ratio of the volumes of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to molecular hydrogen and molecular nitrogen combined (the reactants) is 2:4, or 1:2.

Because, at the same temperature and pressure, the volumes of gases are directly proportional to the number of moles of the gases present, we can now write



The volume ratio of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to the sum of the volumes of molecular hydrogen and molecular nitrogen (the reactants) is 2:4 or 1:2 (Figure 5.10).

Worked examples illustrating the gas laws are presented in Section 5.4.

5.4 The Ideal Gas Equation

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

$$\begin{array}{ll}
 \text{Boyle's law: } V \propto \frac{1}{P} & (\text{at constant } n \text{ and } T) \\
 \text{Charles's law: } V \propto T & (\text{at constant } n \text{ and } P) \\
 \text{Avogadro's law: } V \propto n & (\text{at constant } P \text{ and } T)
 \end{array}$$

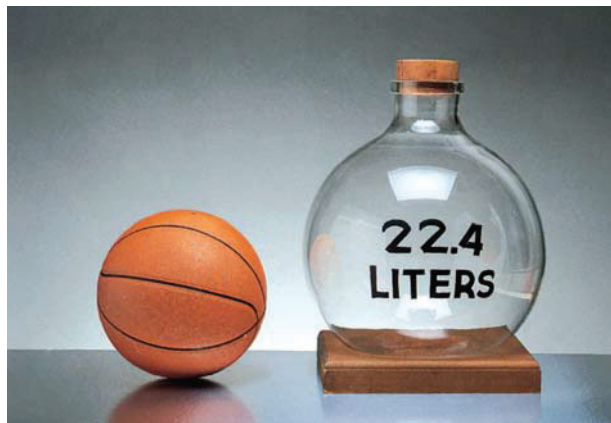
We can combine all three expressions to form a single master equation for the behavior of gases:

$$PV = nRT \quad (5.8)$$

where R , the proportionality constant, is called the **gas constant**. Equation (5.8), which is called the **ideal gas equation**, describes the relationship among the four variables P , V , T , and n . An **ideal gas** is a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation. The molecules of an ideal gas do not attract or repel one another, and their volume is negligible compared with the volume of the container. Although there is no such thing in nature as an ideal gas, the ideal gas approximation works rather well for most reasonable temperature and pressure ranges. Thus, we can safely use the ideal gas equation to solve many gas problems.

Keep in mind that the ideal gas equation, unlike the gas laws discussed in Section 5.3, applies to systems that do not undergo changes in pressure, volume, temperature, and amount of a gas.

Figure 5.11 A comparison of the molar volume at STP (which is approximately 22.4 L) with a basketball.



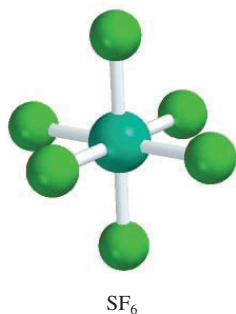
Before we can apply the ideal gas equation to a real system, we must evaluate the gas constant R . At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an ideal gas. Experiments show that under these conditions, 1 mole of an ideal gas occupies 22.414 L, which is somewhat greater than the volume of a basketball, as shown in Figure 5.11. The conditions 0°C and 1 atm are called **standard temperature and pressure**, often abbreviated **STP**. From Equation (5.8) we can write

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} \\ &= 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \\ &= 0.082057 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol} \end{aligned}$$

The gas constant can be expressed in different units (see Appendix 2).

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

Example 5.3 shows that if we know the quantity, volume, and temperature of a gas, we can calculate its pressure using the ideal gas equation. Unless otherwise stated, we assume that the temperatures given in $^{\circ}\text{C}$ in calculations are exact so that they do not affect the number of significant figures.



EXAMPLE 5.3

Sulfur hexafluoride (SF_6) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C .

Strategy The problem gives the amount of the gas and its volume and temperature. Is the gas undergoing a change in any of its properties? What equation should we use to solve for the pressure? What temperature unit should we use?

(Continued)

Solution Because no changes in gas properties occur, we can use the ideal gas equation to calculate the pressure. Rearranging Equation (5.8), we write

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(1.82 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(69.5 + 273) \text{ K}}{5.43 \text{ L}} \\ &= 9.42 \text{ atm} \end{aligned}$$

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

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

EXAMPLE 5.4

Calculate the volume (in liters) occupied by 7.40 g of NH_3 at STP.

Strategy What is the volume of one mole of an ideal gas at STP? How many moles are there in 7.40 g of NH_3 ?

Solution Recognizing that 1 mole of an ideal gas occupies 22.41 L at STP and using the molar mass of NH_3 (17.03 g), we write the sequence of conversions as



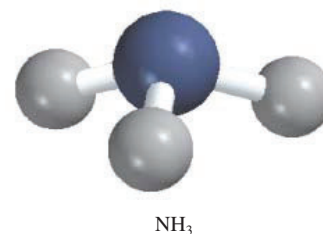
so the volume of NH_3 is given by

$$\begin{aligned} V &= 7.40 \text{ g-NH}_3 \times \frac{1 \text{ mol-NH}_3}{17.03 \text{ g-NH}_3} \times \frac{22.41 \text{ L}}{1 \text{ mol-NH}_3} \\ &= 9.74 \text{ L} \end{aligned}$$

It is often true in chemistry, particularly in gas-law calculations, that a problem can be solved in more than one way. Here the problem can also be solved by first converting 7.40 g of NH_3 to number of moles of NH_3 , and then applying the ideal gas equation ($V = nRT/P$). Try it.

Check Because 7.40 g of NH_3 is smaller than its molar mass, its volume at STP should be smaller than 22.41 L. Therefore, the answer is reasonable.

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



The ideal gas equation is useful for problems that do not involve changes in P , V , T , and n for a gas sample. Thus, if we know any three of the variables we can calculate the fourth one using the equation. At times, however, we need to deal with changes in pressure, volume, and temperature, or even in the amount of gas. When conditions change, we must employ a modified form of the ideal gas equation that takes into account the initial and final conditions. We derive the modified equation as follows.

The subscripts 1 and 2 denote the initial and final states of the gas, respectively.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (5.10)$$

Applications of Equation (5.9) are shown in Examples 5.5, 5.6, and 5.7.

EXAMPLE 5.5

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

Strategy The amount of gas inside the balloon and its temperature remain constant, but both the pressure and the volume change. What gas law do you need?

Solution We start with Equation (5.9)

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

Because $n_1 = n_2$ and $T_1 = T_2$,

$$P_1 V_1 = P_2 V_2$$

which is Boyle's law [see Equation (5.2)]. The given information is tabulated:

Initial Conditions	Final Conditions
$P_1 = 1.0 \text{ atm}$	$P_2 = 0.40 \text{ atm}$
$V_1 = 0.55 \text{ L}$	$V_2 = ?$

Therefore,

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \\ &= 0.55 \text{ L} \times \frac{1.0 \text{ atm}}{0.40 \text{ atm}} \\ &= 1.4 \text{ L} \end{aligned}$$

(Continued)



A scientific research helium balloon.

Check When pressure applied on the balloon is reduced (at constant temperature), the helium gas expands and the balloon's volume increases. The final volume is greater than the initial volume, so the answer is reasonable.

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

Similar problem: 5.19.



EXAMPLE 5.6

Argon is an inert gas used in lightbulbs to retard the vaporization of the tungsten filament. A certain lightbulb containing argon at 1.20 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure (in atm).

Strategy The temperature and pressure of argon change but the amount and volume of gas remain the same. What equation would you use to solve for the final pressure? What temperature unit should you use?

Solution Because $n_1 = n_2$ and $V_1 = V_2$, Equation (5.9) becomes

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

which is Charles's law [see Equation (5.6)]. Next we write

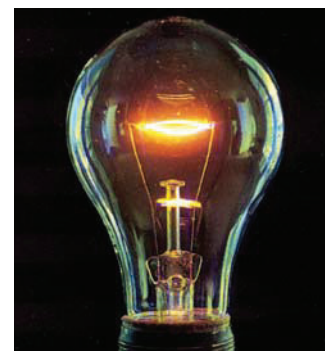
Initial Conditions	Final Conditions
$P_1 = 1.20 \text{ atm}$	$P_2 = ?$
$T_1 = (18 + 273) \text{ K} = 291 \text{ K}$	$T_2 = (85 + 273) \text{ K} = 358 \text{ K}$

The final pressure is given by

$$\begin{aligned} P_2 &= P_1 \times \frac{T_2}{T_1} \\ &= 1.20 \text{ atm} \times \frac{358 \text{ K}}{291 \text{ K}} \\ &= 1.48 \text{ atm} \end{aligned}$$

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

Practice Exercise A sample of oxygen gas initially at 0.97 atm is cooled from 21°C to -68°C at constant volume. What is its final pressure (in atm)?



Electric lightbulbs are usually filled with argon.

Remember to convert °C to K when solving gas-law problems.

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

Similar problem: 5.36.

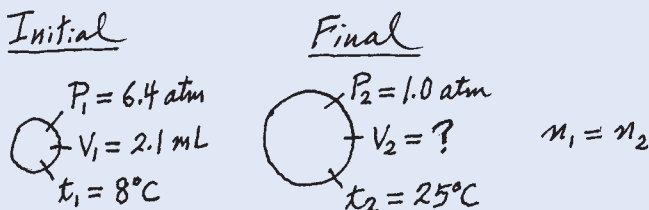


EXAMPLE 5.7

A small bubble rises from the bottom of a lake, where the temperature and pressure are 8°C and 6.4 atm, to the water's surface, where the temperature is 25°C and the pressure is 1.0 atm. Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL.

(Continued)

Strategy In solving this kind of problem, where a lot of information is given, it is sometimes helpful to make a sketch of the situation, as shown here:



What temperature unit should be used in the calculation?

Solution According to Equation (5.9)

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

We assume that the amount of air in the bubble remains constant, that is, $n_1 = n_2$ so that

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

which is Equation (5.10). The given information is summarized:

We can use any appropriate units for volume (or pressure) as long as we use the same units on both sides of the equation.

Initial Conditions	Final Conditions
$P_1 = 6.4 \text{ atm}$	$P_2 = 1.0 \text{ atm}$
$V_1 = 2.1 \text{ mL}$	$V_2 = ?$
$T_1 = (8 + 273) \text{ K} = 281 \text{ K}$	$T_2 = (25 + 273) \text{ K} = 298 \text{ K}$

Rearranging Equation (5.10) gives

$$\begin{aligned}
 V_2 &= V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \\
 &= 2.1 \text{ mL} \times \frac{6.4 \text{ atm}}{1.0 \text{ atm}} \times \frac{298 \text{ K}}{281 \text{ K}} \\
 &= 14 \text{ mL}
 \end{aligned}$$

Check We see that the final volume involves multiplying the initial volume by a ratio of pressures (P_1/P_2) and a ratio of temperatures (T_2/T_1). Recall that volume is inversely proportional to pressure, and volume is directly proportional to temperature. Because the pressure decreases and temperature increases as the bubble rises, we expect the bubble's volume to increase. In fact, here the change in pressure plays a greater role in the volume change.

Practice Exercise A gas initially at 4.0 L, 1.2 atm, and 66°C undergoes a change so that its final volume and temperature are 1.7 L and 42°C . What is its final pressure? Assume the number of moles remains unchanged.

Density Calculations

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

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

The number of moles of the gas, n , is given by

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

where m is the mass of the gas in grams and \mathcal{M} is its molar mass. Therefore

$$\frac{m}{\mathcal{M}V} = \frac{P}{RT}$$

Because density, d , is mass per unit volume, we can write

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT} \quad (5.11)$$

Unlike molecules in condensed matter (that is, in liquids and solids), gaseous molecules are separated by distances that are large compared with their size. Consequently, the density of gases is very low under atmospheric conditions. For this reason, gas densities are usually expressed in grams per liter (g/L) rather than grams per milliliter (g/mL), as Example 5.8 shows.

EXAMPLE 5.8

Calculate the density of carbon dioxide (CO_2) in grams per liter (g/L) at 0.990 atm and 55°C .

Strategy We need Equation (5.11) to calculate gas density. Is sufficient information provided in the problem? What temperature unit should be used?

Solution To use Equation (5.11), we convert temperature to kelvins ($T = 273 + 55 = 328 \text{ K}$) and use 44.01 g for the molar mass of CO_2 :

$$\begin{aligned} d &= \frac{P\mathcal{M}}{RT} \\ &= \frac{(0.990 \text{ atm})(44.01 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(328 \text{ K})} = 1.62 \text{ g/L} \end{aligned}$$

Alternatively, we can solve for the density by writing

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

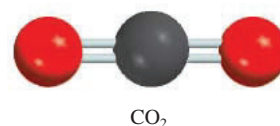
Assuming that we have 1 mole of CO_2 , the mass is 44.01 g. The volume of the gas can be obtained from the ideal gas equation

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(1 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(328 \text{ K})}{0.990 \text{ atm}} \\ &= 27.2 \text{ L} \end{aligned}$$

Therefore, the density of CO_2 is given by

$$d = \frac{44.01 \text{ g}}{27.2 \text{ L}} = 1.62 \text{ g/L}$$

(Continued)



Being an intensive property, density is independent of the amount of substance. Therefore, we can use any convenient amount to help us solve the problem.

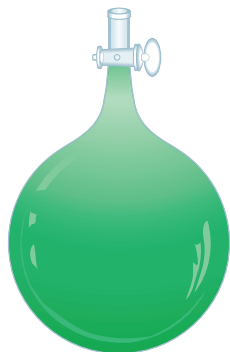


Figure 5.12 An apparatus for measuring the density of a gas. A bulb of known volume is filled with the gas under study at a certain temperature and pressure. First the bulb is weighed, and then it is emptied (evacuated) and weighed again. The difference in masses gives the mass of the gas. Knowing the volume of the bulb, we can calculate the density of the gas. Under atmospheric conditions, 100 mL of air weigh about 0.12 g, an easily measured quantity.

Comment In units of grams per milliliter, the gas density is 1.62×10^{-3} g/mL, which is a very small number. In comparison, the density of water is 1.0 g/mL and that of gold is 19.3 g/cm³.

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

The Molar Mass of a Gaseous Substance

From what we have seen so far, you may have the impression that the molar mass of a substance is found by examining its formula and summing the molar masses of its component atoms. However, this procedure works only if the actual formula of the substance is known. In practice, chemists often deal with substances of unknown or only partially defined composition. If the unknown substance is gaseous, its molar mass can nevertheless be found thanks to the ideal gas equation. All that is needed is an experimentally determined density value (or mass and volume data) for the gas at a known temperature and pressure. By rearranging Equation (5.11) we get

$$\mathcal{M} = \frac{dRT}{P} \quad (5.12)$$

In a typical experiment, a bulb of known volume is filled with the gaseous substance under study. The temperature and pressure of the gas sample are recorded, and the total mass of the bulb plus gas sample is determined (Figure 5.12). The bulb is then evacuated (emptied) and weighed again. The difference in mass is the mass of the gas. The density of the gas is equal to its mass divided by the volume of the bulb. Once we know the density of a gas, we can calculate the molar mass of the substance using Equation (5.12). Of course, a mass spectrometer would be the ideal instrument to determine the molar mass, but not every chemist can afford one.

Example 5.9 shows the density method for molar mass determination.

EXAMPLE 5.9

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

Strategy Because Equations (5.11) and (5.12) are rearrangements of each other, we can calculate the molar mass of a gas if we know its density, temperature, and pressure. The molecular formula of the compound must be consistent with its molar mass. What temperature unit should we use?

Solution From Equation (5.12)

$$\begin{aligned} \mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(7.71 \text{ g/L})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(36 + 273) \text{ K}}{2.88 \text{ atm}} \\ &= 67.9 \text{ g/mol} \end{aligned}$$

Note that we can determine the molar mass of a gaseous compound by this procedure without knowing its chemical formula.

(Continued)

Alternatively, we can solve for the molar mass by writing

$$\text{molar mass of compound} = \frac{\text{mass of compound}}{\text{moles of compound}}$$

From the given density we know there are 7.71 g of the gas in 1 L. The number of moles of the gas in this volume can be obtained from the ideal gas equation

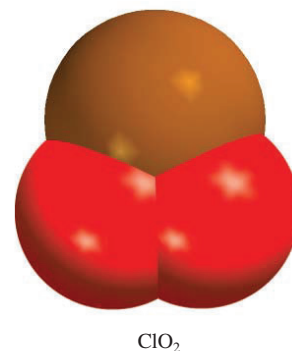
$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{(2.88 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(309 \text{ K})} \\ &= 0.1135 \text{ mol} \end{aligned}$$

Therefore, the molar mass is given by

$$\mathcal{M} = \frac{\text{mass}}{\text{number of moles}} = \frac{7.71 \text{ g}}{0.1135 \text{ mol}} = 67.9 \text{ g/mol}$$

We can determine the molecular formula of the compound by trial and error, using only the knowledge of the molar masses of chlorine (35.45 g) and oxygen (16.00 g). We know that a compound containing one Cl atom and one O atom would have a molar mass of 51.45 g, which is too low, while the molar mass of a compound made up of two Cl atoms and one O atom is 86.90 g, which is too high. Thus, the compound must contain one Cl atom and two O atoms and have the formula ClO_2 , which has a molar mass of 67.45 g.

Practice Exercise The density of a gaseous organic compound is 3.38 g/L at 40°C and 1.97 atm. What is its molar mass?



Similar problems: 5.43, 5.47.



Because Equation (5.12) is derived from the ideal gas equation, we can also calculate the molar mass of a gaseous substance using the ideal gas equation, as shown in Example 5.10.

EXAMPLE 5.10

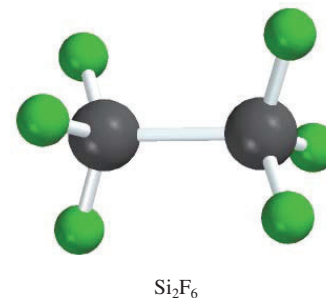
Chemical analysis of a gaseous compound showed that it contained 33.0 percent silicon (Si) and 67.0 percent fluorine (F) by mass. At 35°C, 0.210 L of the compound exerted a pressure of 1.70 atm. If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

Strategy This problem can be divided into two parts. First, it asks for the empirical formula of the compound from the percent by mass of Si and F. Second, the information provided enables us to calculate the molar mass of the compound and hence determine its molecular formula. What is the relationship between empirical molar mass and molar mass calculated from the molecular formula?

Solution We follow the procedure in Example 3.9 (p. 90) to calculate the empirical formula by assuming that we have 100 g of the compound, so the percentages are converted to grams. The number of moles of Si and F are given by

$$\begin{aligned} n_{\text{Si}} &= 33.0 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 1.17 \text{ mol Si} \\ n_{\text{F}} &= 67.0 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 3.53 \text{ mol F} \end{aligned}$$

(Continued)



Therefore, the empirical formula is $\text{Si}_{1.17}\text{F}_{3.53}$, or, dividing by the smaller subscript (1.17), we obtain SiF_3 .

To calculate the molar mass of the compound, we need first to calculate the number of moles contained in 2.38 g of the compound. From the ideal gas equation

$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{(1.70 \text{ atm})(0.210 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(308 \text{ K})} = 0.0141 \text{ mol} \end{aligned}$$

Because there are 2.38 g in 0.0141 mole of the compound, the mass in 1 mole, or the molar mass, is given by

$$\mathcal{M} = \frac{2.38 \text{ g}}{0.0141 \text{ mol}} = 169 \text{ g/mol}$$

The molar mass of the empirical formula SiF_3 is 85.09 g. Recall that the ratio (molar mass/empirical molar mass) is always an integer ($169/85.09 \approx 2$). Therefore, the molecular formula of the compound must be $(\text{SiF}_3)_2$ or Si_2F_6 .

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

5.5 Gas Stoichiometry

The key to solving stoichiometry problems is mole ratio, regardless of the physical state of the reactants and products.

In Chapter 3 we used relationships between amounts (in moles) and masses (in grams) of reactants and products to solve stoichiometry problems. When the reactants and/or products are gases, we can also use the relationships between amounts (moles, n) and volume (V) to solve such problems (Figure 5.13). Examples 5.11, 5.12, and 5.13 show how the gas laws are used in these calculations.

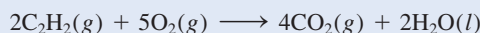


The reaction of calcium carbide (CaC_2) with water produces acetylene (C_2H_2), a flammable gas.

Similar problem: 5.26.

EXAMPLE 5.11

Calculate the volume of O_2 (in liters) required for the complete combustion of 7.64 L of acetylene (C_2H_2) measured at the same temperature and pressure.



Strategy Note that the temperature and pressure of O_2 and C_2H_2 are the same. Which gas law do we need to relate the volume of the gases to the moles of gases?

Solution According to Avogadro's law, at the same temperature and pressure, the number of moles of gases are directly related to their volumes. From the equation, we have $5 \text{ mol } \text{O}_2 \approx 2 \text{ mol } \text{C}_2\text{H}_2$; therefore, we can also write $5 \text{ L } \text{O}_2 \approx 2 \text{ L } \text{C}_2\text{H}_2$. The volume of O_2 that will react with 7.64 L C_2H_2 is given by

$$\begin{aligned} \text{volume of } \text{O}_2 &= 7.64 \text{ L } \text{C}_2\text{H}_2 \times \frac{5 \text{ L } \text{O}_2}{2 \text{ L } \text{C}_2\text{H}_2} \\ &= 19.1 \text{ L} \end{aligned}$$

(Continued)

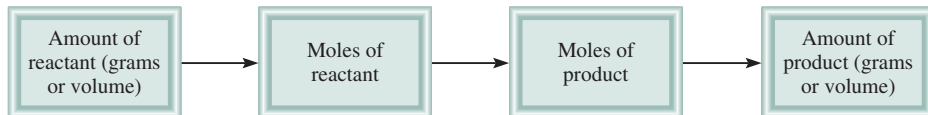


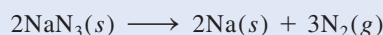
Figure 5.13 Stoichiometric calculations involving gases.

Practice Exercise Assuming no change in temperature and pressure, calculate the volume of O_2 (in liters) required for the complete combustion of 14.9 L of butane (C_4H_{10}):



EXAMPLE 5.12

Sodium azide (NaN_3) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN_3 as follows:



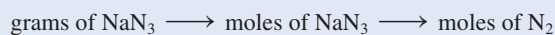
The nitrogen gas produced quickly inflates the bag between the driver and the windshield and dashboard. Calculate the volume of N_2 generated at $80^\circ C$ and 823 mmHg by the decomposition of 60.0 g of NaN_3 .

Strategy From the balanced equation we see that 2 mol $NaN_3 \rightleftharpoons 3$ mol N_2 so the conversion factor between NaN_3 and N_2 is

$$\frac{3 \text{ mol } N_2}{2 \text{ mol } NaN_3}$$

Because the mass of NaN_3 is given, we can calculate the number of moles of NaN_3 and hence the number of moles of N_2 produced. Finally, we can calculate the volume of N_2 using the ideal gas equation.

Solution First we calculate number of moles of N_2 produced by 60.0 g NaN_3 using the following sequence of conversions



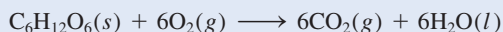
so that

$$\begin{aligned} \text{moles of } N_2 &= 60.0 \text{ g } \cancel{NaN_3} \times \frac{1 \text{ mol } \cancel{NaN_3}}{65.02 \text{ g } \cancel{NaN_3}} \times \frac{3 \text{ mol } N_2}{2 \text{ mol } \cancel{NaN_3}} \\ &= 1.38 \text{ mol } N_2 \end{aligned}$$

The volume of 1.38 moles of N_2 can be obtained by using the ideal gas equation:

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(1.38 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(80 + 273 \text{ K})}{(823/760) \text{ atm}} \\ &= 36.9 \text{ L} \end{aligned}$$

Practice Exercise The equation for the metabolic breakdown of glucose ($C_6H_{12}O_6$) is the same as the equation for the combustion of glucose in air:



Calculate the volume of CO_2 produced at $37^\circ C$ and 1.00 atm when 5.60 g of glucose is used up in the reaction.



An air bag can protect the driver in an automobile collision.

Similar problem: 5.60.





The air in submerged submarines and space vehicles needs to be purified continuously.

EXAMPLE 5.13

Aqueous lithium hydroxide solution is used to purify air in spacecrafts and submarines because it absorbs carbon dioxide, which is an end product of metabolism, according to the equation



The pressure of carbon dioxide inside the cabin of a submarine having a volume of $2.4 \times 10^5 \text{ L}$ is $7.9 \times 10^{-3} \text{ atm}$ at 312 K . A solution of lithium hydroxide (LiOH) of negligible volume is introduced into the cabin. Eventually the pressure of CO_2 falls to $1.2 \times 10^{-4} \text{ atm}$. How many grams of lithium carbonate are formed by this process?

Strategy How do we calculate the number of moles of CO_2 reacted from the drop in CO_2 pressure? From the ideal gas equation we write

$$n = P \times \left(\frac{V}{RT} \right)$$

At constant T and V , the change in pressure of CO_2 , ΔP , corresponds to the change in the number of moles of CO_2 , Δn . Thus,

$$\Delta n = \Delta P \times \left(\frac{V}{RT} \right)$$

What is the conversion factor between CO_2 and Li_2CO_3 ?

Solution The drop in CO_2 pressure is $(7.9 \times 10^{-3} \text{ atm}) - (1.2 \times 10^{-4} \text{ atm})$ or $7.8 \times 10^{-3} \text{ atm}$. Therefore, the number of moles of CO_2 reacted is given by

$$\begin{aligned} \Delta n &= 7.8 \times 10^{-3} \text{ atm} \times \frac{2.4 \times 10^5 \text{ L}}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(312 \text{ K})} \\ &= 73 \text{ mol} \end{aligned}$$

From the chemical equation we see that $1 \text{ mol CO}_2 \approx 1 \text{ mol Li}_2\text{CO}_3$, so the amount of Li_2CO_3 formed is also 73 moles. Then, with the molar mass of Li_2CO_3 (73.89 g), we calculate its mass:

$$\begin{aligned} \text{mass of Li}_2\text{CO}_3 \text{ formed} &= 73 \text{ mol Li}_2\text{CO}_3 \times \frac{73.89 \text{ g Li}_2\text{CO}_3}{1 \text{ mol Li}_2\text{CO}_3} \\ &= 5.4 \times 10^3 \text{ g Li}_2\text{CO}_3 \end{aligned}$$

Practice Exercise A 2.14-L sample of hydrogen chloride (HCl) gas at 2.61 atm and 28°C is completely dissolved in 668 mL of water to form hydrochloric acid solution. Calculate the molarity of the acid solution. Assume no change in volume.

5.6 Dalton's Law of Partial Pressures

Thus far we have concentrated on the behavior of pure gaseous substances, but experimental studies very often involve mixtures of gases. For example, for a study of air pollution, we may be interested in the pressure-volume-temperature relationship of a sample of air, which contains several gases. In this case, and all cases involving mixtures of gases, the total gas pressure is related to **partial pressures**, that is, the pressures of individual gas components in the mixture. In 1801 Dalton formulated a law,

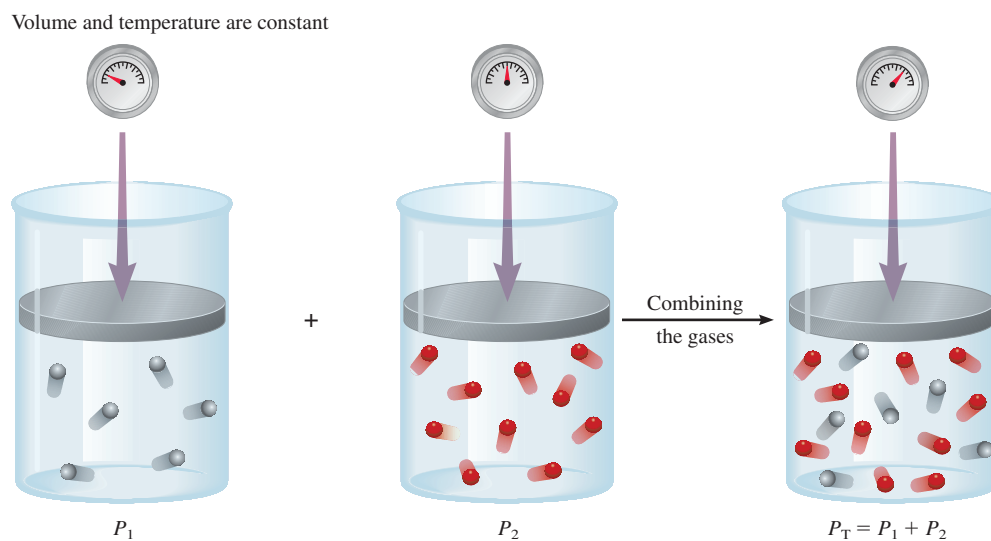


Figure 5.14 Schematic illustration of Dalton's law of partial pressures.

now known as **Dalton's law of partial pressures**, which states that *the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone*. Figure 5.14 illustrates Dalton's law.

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

$$P_T = P_1 + P_2 + P_3 + \dots$$

where P_1, P_2, P_3, \dots are the partial pressures of components 1, 2, 3,

X_A is called the mole fraction of A. The **mole fraction** is a *dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present*. In general, the mole fraction of component i in a mixture is given by

$$X_i = \frac{n_i}{n_T} \quad (5.13)$$

where n_i and n_T are the number of moles of component i and the total number of moles present, respectively. The mole fraction is always smaller than 1. We can now express the partial pressure of A as

$$P_A = X_A P_T$$

Similarly,

$$P_B = X_B P_T$$

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

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

For gas mixtures, the sum of partial pressures must equal the total pressure and the sum of mole fractions must equal 1.

If a system contains more than two gases, then the partial pressure of the i th component is related to the total pressure by

$$P_i = X_i P_T \quad (5.14)$$

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

From mole fractions and total pressure, we can calculate the partial pressures of individual components, as Example 5.14 shows. A direct application of Dalton's law of partial pressures to scuba diving is discussed in the Chemistry in Action essay on p. 202.

EXAMPLE 5.14

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

Strategy What is the relationship between the partial pressure of a gas and the total gas pressure? How do we calculate the mole fraction of a gas?

Solution According to Equation (5.14), the partial pressure of Ne (P_{Ne}) is equal to the product of its mole fraction (X_{Ne}) and the total pressure (P_{T})

$$P_{\text{Ne}} = X_{\text{Ne}} P_{\text{T}}$$

↑ ↑ ↑
 want to calculate need to find given

Using Equation (5.13), we calculate the mole fraction of Ne as follows:

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

Therefore,

$$\begin{aligned} P_{\text{Ne}} &= X_{\text{Ne}} P_{\text{T}} \\ &= 0.607 \times 2.00 \text{ atm} \\ &= \mathbf{1.21 \text{ atm}} \end{aligned}$$

Similarly,

$$\begin{aligned} P_{\text{Ar}} &= X_{\text{Ar}} P_{\text{T}} \\ &= 0.10 \times 2.00 \text{ atm} \\ &= \mathbf{0.20 \text{ atm}} \end{aligned}$$

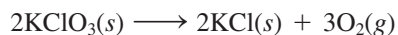
and

$$\begin{aligned} P_{\text{Xe}} &= X_{\text{Xe}} P_{\text{T}} \\ &= 0.293 \times 2.00 \text{ atm} \\ &= \mathbf{0.586 \text{ atm}} \end{aligned}$$

Check Make sure that the sum of the partial pressures is equal to the given total pressure; that is, $(1.21 + 0.20 + 0.586) \text{ atm} = 2.00 \text{ atm}$.

Practice Exercise A sample of natural gas contains 8.24 moles of methane (CH_4), 0.421 mole of ethane (C_2H_6), and 0.116 mole of propane (C_3H_8). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?

Dalton's law of partial pressures is useful for calculating volumes of gases collected over water. For example, when potassium chlorate (KClO_3) is heated, it decomposes to KCl and O_2 :



The oxygen gas can be collected over water, as shown in Figure 5.15. Initially, the inverted bottle is completely filled with water. As oxygen gas is generated, the gas bubbles rise to the top and displace water from the bottle. This method of collecting

When collecting a gas over water, the total pressure (gas plus water vapor) is equal to the atmospheric pressure.

Figure 5.15 An apparatus for collecting gas over water. The oxygen generated by heating potassium chlorate (KClO_3) in the presence of a small amount of manganese dioxide (MnO_2), which speeds up the reaction, is bubbled through water and collected in a bottle as shown. Water originally present in the bottle is pushed into the trough by the oxygen gas.

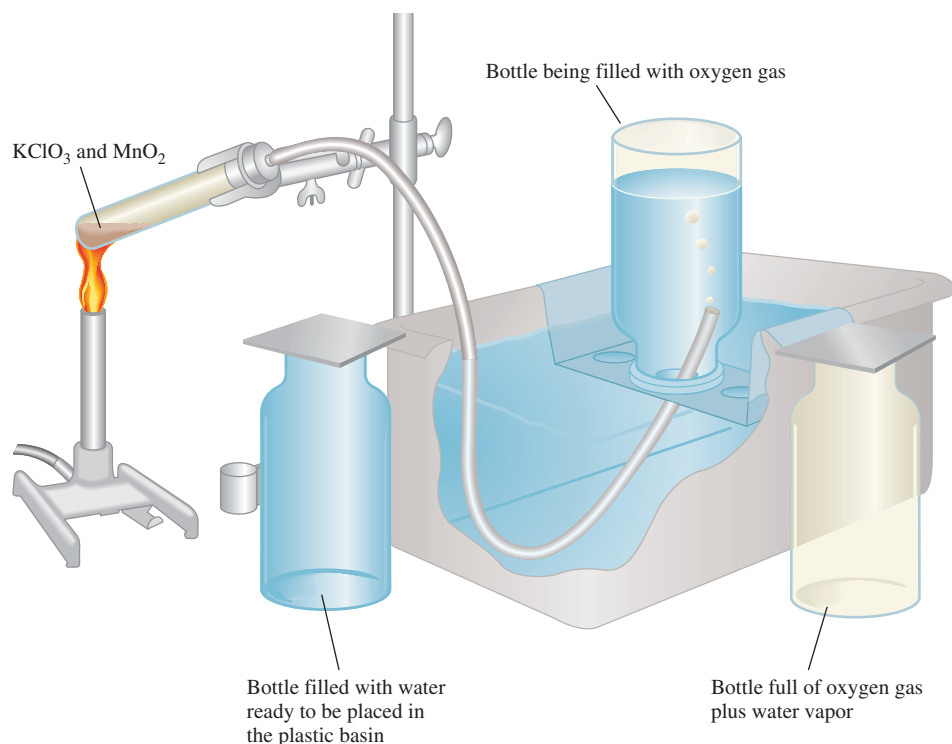


TABLE 5.3

Pressure of Water Vapor at Various Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

a gas is based on the assumptions that the gas does not react with water and that it is not appreciably soluble in it. These assumptions are valid for oxygen gas, but not for gases such as NH_3 , which dissolves readily in water. The oxygen gas collected in this way is not pure, however, because water vapor is also present in the bottle. The total gas pressure is equal to the sum of the pressures exerted by the oxygen gas and the water vapor:

$$P_T = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

Consequently, we must allow for the pressure caused by the presence of water vapor when we calculate the amount of O_2 generated. Table 5.3 shows the pressure of water vapor at various temperatures. These data are plotted in Figure 5.16.

Example 5.15 shows how to use Dalton's law to calculate the amount of a gas collected over water.

EXAMPLE 5.15

Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in Figure 5.15. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24°C is 22.4 mmHg.

Strategy To solve for the mass of O_2 generated, we must first calculate the partial pressure of O_2 in the mixture. What gas law do we need? How do we convert pressure of O_2 gas to mass of O_2 in grams?

(Continued)

Solution From Dalton's law of partial pressures we know that

$$P_T = P_{O_2} + P_{H_2O}$$

Therefore,

$$\begin{aligned} P_{O_2} &= P_T - P_{H_2O} \\ &= 762 \text{ mmHg} - 22.4 \text{ mmHg} \\ &= 740 \text{ mmHg} \end{aligned}$$

From the ideal gas equation we write

$$PV = nRT = \frac{m}{\mathcal{M}}RT$$

where m and \mathcal{M} are the mass of O_2 collected and the molar mass of O_2 , respectively. Rearranging the equation we obtain

$$\begin{aligned} m &= \frac{PV\mathcal{M}}{RT} = \frac{(740/760)\text{atm}(0.128 \text{ L})(32.00 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 + 24) \text{ K}} \\ &= 0.164 \text{ g} \end{aligned}$$

Check The density of the oxygen gas is $(0.164 \text{ g}/0.128 \text{ L})$, or 1.28 g/L , which is a reasonable value for gases under atmospheric conditions (see Example 5.8).

Practice Exercise Hydrogen gas generated when calcium metal reacts with water is collected as shown in Figure 5.15. The volume of gas collected at 30°C and pressure of 988 mmHg is 641 mL . What is the mass (in grams) of the hydrogen gas obtained? The pressure of water vapor at 30°C is 31.82 mmHg .

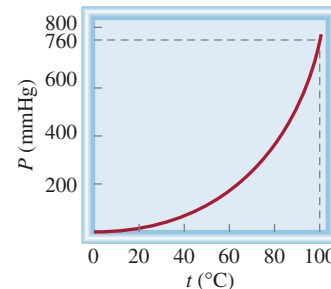


Figure 5.16 The pressure of water vapor as a function of temperature. Note that at the boiling point of water (100°C) the pressure is 760 mmHg , which is exactly equal to 1 atm .

The Kinetic Molecular Theory of Gases

The gas laws help us to predict the behavior of gases, but they do not explain what happens at the molecular level to cause the changes we observe in the macroscopic world. For example, why does a gas expand on heating?

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

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be “points”; that is, they possess mass but have negligible volume.
2. Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic. In other words, energy can be transferred from one molecule to another as a result of a collision. Nevertheless, the total energy of all the molecules in a system remains the same.
3. Gas molecules exert neither attractive nor repulsive forces on one another.

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

Application to the Gas Laws

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

- **Compressibility of Gases.** Because molecules in the gas phase are separated by large distances (assumption 1), gases can be compressed easily to occupy less volume.
- **Boyle’s Law.** The pressure exerted by a gas results from the impact of its molecules on the walls of the container. The collision rate, or the number of molecular collisions with the walls per second, is proportional to the number density (that is, number of molecules per unit volume) of the gas. Decreasing the volume of a given amount of gas increases its number density and hence its collision rate. For this reason, the pressure of a gas is inversely proportional to the volume it occupies; as volume decreases, pressure increases and vice versa.
- **Charles’s Law.** Because the average kinetic energy of gas molecules is proportional to the sample’s absolute temperature (assumption 4), raising the temperature increases the average kinetic energy. Consequently, molecules will collide with the walls of the container more frequently and with greater impact if the gas

is heated, and thus the pressure increases. The volume of gas will expand until the gas pressure is balanced by the constant external pressure (see Figure 5.8).

Another way of stating Avogadro's law is that at the same pressure and temperature, equal volumes of gases, whether they are the same or different gases, contain equal numbers of molecules.

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

Distribution of Molecular Speeds

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

Figure 5.17(a) shows typical *Maxwell speed distribution curves* for nitrogen gas at three different temperatures. At a given temperature, the distribution curve tells us the number of molecules moving at a certain speed. The peak of each curve represents the *most probable speed*, that is, the speed of the largest number of molecules. Note that the most probable speed increases as temperature increases (the peak shifts toward the right). Furthermore, the curve also begins to flatten out with increasing temperature, indicating that larger numbers of molecules are moving at greater speed. Figure 5.17(b) shows the speed distributions of three gases at the *same* temperature. The difference in the curves can be explained by noting that lighter molecules move faster, on average, than heavier ones.

The distribution of molecular speeds can be demonstrated with the apparatus shown in Figure 5.18. A beam of atoms (or molecules) exits from an oven at a known temperature and passes through a pinhole (to collimate the beam). Two circular plates mounted on the same shaft are rotated by a motor. The first plate is called the “chopper” and the second is the detector. The purpose of the chopper is to allow small bursts of atoms (or molecules) to pass through it whenever the slit is aligned with the beam. Within each burst, the faster-moving molecules will reach the detector earlier

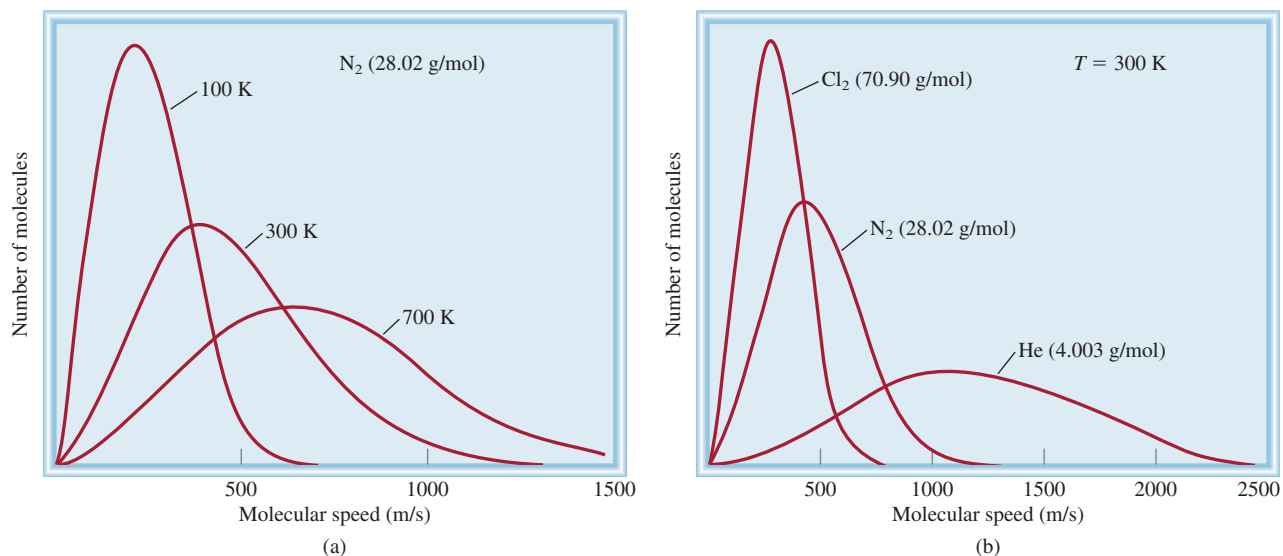


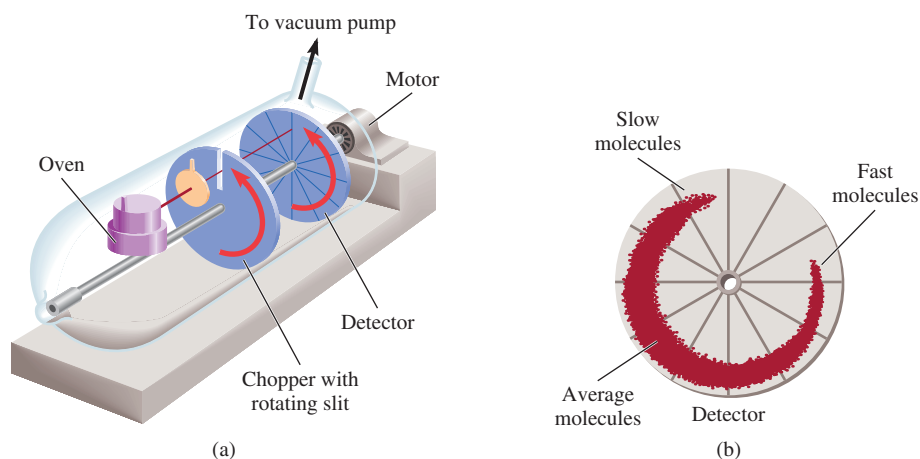
Figure 5.17 (a) The distribution of speeds for nitrogen gas at three different temperatures. At the higher temperatures, more molecules are moving at faster speeds. (b) The distribution of speeds for three gases at 300 K. At a given temperature, the lighter molecules are moving faster, on the average.

than the slower-moving ones. Eventually, a layer of deposit will accumulate on the detector. Because the two plates are rotating at the same speed, molecules in the next burst will hit the detector plate at approximately the same place as molecules from the previous burst having the same speed. In time, the molecular deposition will become visible. The density of the deposition indicates the distribution of molecular speeds at that particular temperature.

There are comparable ways to estimate the "average" speed of molecules, of which root-mean-square speed is one.

$$\frac{1}{2} \quad \frac{3}{2}$$

Figure 5.18 (a) Apparatus for studying molecular speed distribution at a certain temperature. The vacuum pump causes the molecules to travel from left to right as shown. (b) The spread of the deposit on the detector gives the range of molecular speeds, and the density of the deposit is proportional to the number of molecules moving at different speeds.





Jupiter. The interior of this massive planet consists mainly of hydrogen.

Diffusion always proceeds from a region of higher concentration to one where the concentration is lower.

Unlike Jupiter, Earth does not have appreciable amounts of hydrogen or helium in its atmosphere. Why is this the case? A smaller planet than Jupiter, Earth has a weaker gravitational attraction for these lighter molecules. A fairly straightforward calculation shows that to escape Earth's gravitational field, a molecule must possess an escape velocity equal to or greater than 1.1×10^4 m/s. Because the average speed of helium is considerably greater than that of molecular nitrogen or molecular oxygen, more helium atoms escape from Earth's atmosphere into outer space. Consequently, only a trace amount of helium is present in our atmosphere. On the other hand, Jupiter, with a mass about 320 times greater than that of Earth, retains both heavy and light gases in its atmosphere.

Gas Diffusion and Effusion

We will now discuss two phenomena based on gaseous motion.

Gas Diffusion

A direct demonstration of gaseous random motion is provided by **diffusion**, the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties. Despite the fact that molecular speeds are very great, the diffusion process takes a relatively long time to complete. For example, when a bottle of concentrated ammonia solution is opened at one end of a lab bench, it takes some time before a person at the other end of the bench can smell it. The reason is that a molecule experiences numerous collisions while moving from one end of the bench to the other, as shown in Figure 5.19. Thus, diffusion of gases always happens gradually, and not instantly as molecular speeds seem to suggest. Furthermore, because the root-mean-square speed of a light gas is greater than that of a heavier gas (see Example 5.16), a lighter gas will diffuse through a certain space more quickly than will a heavier gas. Figure 5.20 illustrates gaseous diffusion.

In 1832 the Scottish chemist Thomas Graham[†] found that *under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their molar masses*. This statement, now known as **Graham's law of diffusion**.

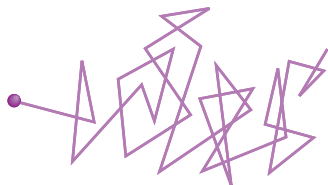


Figure 5.19 The path traveled by a single gas molecule. Each change in direction represents a collision with another molecule.

[†]Thomas Graham (1805–1869). Scottish chemist. Graham did important work on osmosis and characterized a number of phosphoric acids.



Figure 5.20 A demonstration of gas diffusion. NH_3 gas (from a bottle containing aqueous ammonia) combines with HCl gas (from a bottle containing hydrochloric acid) to form solid NH_4Cl . Because NH_3 is lighter and therefore diffuses faster, solid NH_4Cl first appears nearer the HCl bottle (on the right).

Gas Effusion

Whereas diffusion is a process by which one gas gradually mixes with another, *effusion* is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening. Figure 5.21 shows the effusion of a gas into a vacuum. Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion [see Equation (5.17)]. A helium-filled rubber balloon deflates faster than an air-filled one because the rate of effusion through the pores of the rubber is faster for the lighter helium atoms than for the air molecules. Industrially, gas effusion is used to separate uranium isotopes in the forms of gaseous $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$. By subjecting the gases to many stages of effusion, scientists were able to obtain highly enriched ^{235}U isotope, which was used in the construction of atomic bombs during World War II.

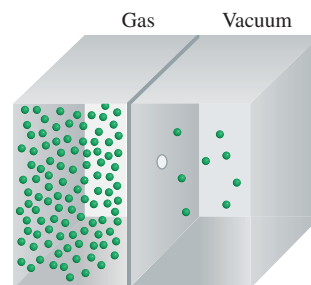


Figure 5.21 Gas effusion. Gas molecules move from a high-pressure region (left) to a low-pressure one through a pinhole.

5.8 Deviation from Ideal Behavior

The gas laws and the kinetic molecular theory assume that molecules in the gaseous state do not exert any force, either attractive or repulsive, on one another. The other assumption is that the volume of the molecules is negligibly small compared with that of the container. A gas that satisfies these two conditions is said to exhibit *ideal behavior*.

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

Figure 5.22 shows PV/RT plotted against P for three real gases and an ideal gas at a given temperature. This graph provides a test of ideal gas behavior. According to the ideal gas equation (for 1 mole of gas), PV/RT equals 1, regardless of the actual gas pressure. (When $n = 1$, $PV = nRT$ becomes $PV = RT$, or $PV/RT = 1$.) For real gases, this is true only at moderately low pressures (≤ 5 atm); significant deviations occur as pressure increases. Attractive forces operate among molecules at relatively short distances. At atmospheric pressure, the molecules in a gas are far apart and the attractive forces are negligible. At high pressures, the density of the gas increases; the molecules are much closer to one another. Intermolecular forces can then be significant enough to affect the motion of the molecules, and the gas will not behave ideally.

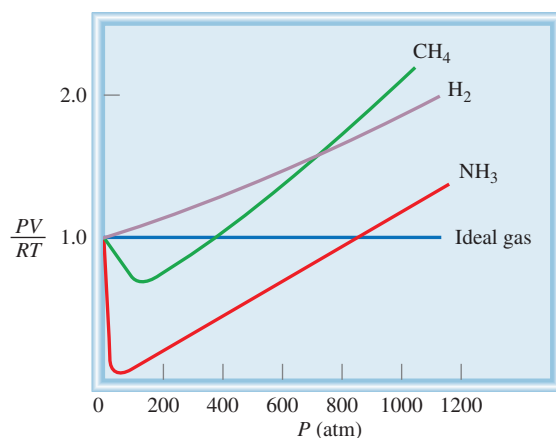


Figure 5.22 Plot of PV/RT versus P of 1 mole of a gas at 0°C . For 1 mole of an ideal gas, PV/RT is equal to 1, no matter what the pressure of the gas is. For real gases, we observe various deviations from ideality at high pressures. At very low pressures, all gases exhibit ideal behavior; that is, their PV/RT values all converge to 1 as P approaches zero.

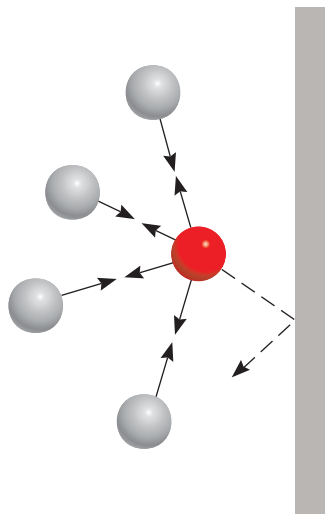


Figure 5.23 *Effect of intermolecular forces on the pressure exerted by a gas. The speed of a molecule that is moving toward the container wall (red sphere) is reduced by the attractive forces exerted by its neighbors (gray spheres). Consequently, the impact this molecule makes with the wall is not as great as it would be if no intermolecular forces were present. In general, the measured gas pressure is lower than the pressure the gas would exert if it behaved ideally.*

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

Consider the approach of a particular molecule toward the wall of a container (Figure 5.23). The intermolecular attractions exerted by its neighbors tend to soften the impact made by this molecule against the wall. The overall effect is a lower gas pressure than we would expect for an ideal gas.

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

[†]Johannes Diderck van der Waals (1837–1923). Dutch physicist. van der Waals received the Nobel Prize in Physics in 1910 for his work on the properties of gases and liquids.

Key Equations

$$P_1V_1 = P_2V_2 \quad (5.2)$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (5.4)$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (5.6)$$

$$V = k_4n \quad (5.7)$$

$$PV = nRT \quad (5.8)$$

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \quad (5.9)$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad (5.10)$$

$$d = \frac{PM}{RT} \quad (5.11)$$

$$X_i = \frac{n_i}{n_T} \quad (5.13)$$

$$P_i = X_iP_T \quad (5.14)$$

Boyle's law. For calculating pressure or volume changes.

Charles's law. For calculating temperature or volume changes.

Charles's law. For calculating temperature or pressure changes.

Avogadro's law. Constant P and T .

Ideal gas equation.

For calculating changes in pressure, temperature, volume, or amount of gas.

For calculating changes in pressure, temperature, or volume when n is constant.

For calculating density or molar mass.

Definition of mole fraction.

Dalton's law of partial pressures. For calculating partial pressures.

V^2

Summary of Facts and Concepts

- At 25°C and 1 atm, a number of elements and molecular compounds exist as gases. Ionic compounds are solids rather than gases under atmospheric conditions.
- Gases exert pressure because their molecules move freely and collide with any surface with which they make contact. Units of gas pressure include millimeters of mercury (mmHg), torr, pascals, and atmospheres. One atmosphere equals 760 mmHg, or 760 torr.
- The pressure-volume relationships of ideal gases are governed by Boyle's law: Volume is inversely proportional to pressure (at constant T and n).
- The temperature-volume relationships of ideal gases are described by Charles's and Gay-Lussac's law: Volume is directly proportional to temperature (at constant P and n).
- Absolute zero (-273.15°C) is the lowest theoretically attainable temperature. The Kelvin temperature scale takes 0 K as absolute zero. In all gas law calculations, temperature must be expressed in kelvins.
- The amount-volume relationships of ideal gases are described by Avogadro's law: Equal volumes of gases contain equal numbers of molecules (at the same T and P).
- The ideal gas equation, $PV = nRT$, combines the laws of Boyle, Charles, and Avogadro. This equation describes the behavior of an ideal gas.
- Dalton's law of partial pressures states that each gas in a mixture of gases exerts the same pressure that it would if it were alone and occupied the same volume.

Key Words

Absolute temperature scale, p. 183	Dalton's law of partial pressures, p. 197	Kelvin temperature scale, p. 183	Pressure, p. 176
Absolute zero, p. 183	Diffusion, p. 208	Kinetic energy (KE), p. 203	Root-mean-square (rms) speed (u_{rms}), p. 206
Atmospheric pressure, p. 176	Effusion, p. 209	Kinetic molecular theory of gases, p. 203	Standard atmospheric pressure (1 atm), p. 177
Avogadro's law, p. 184	Gas constant (R), p. 185	Manometer, p. 178	Standard temperature and pressure (STP), p. 186
Barometer, p. 177	Graham's law of diffusion, p. 208	Mole fraction, p. 198	van der Waals equation, p. 212
Boyle's law, p. 179	Ideal gas, p. 185	Newton (N), p. 176	
Charles's and Gay-Lussac's law, p. 183	Ideal gas equation, p. 185	Partial pressure, p. 196	
Charles's law, p. 183	Joule (J), p. 202	Pascal (Pa), p. 176	

Answers to Practice Exercises

5.1 0.986 atm. **5.2** 39.3 kPa. **5.3** 9.29 L. **5.4** 30.6 L.
5.5 4.46×10^3 mmHg. **5.6** 0.68 atm. **5.7** 2.6 atm.
5.8 13.1 g/L. **5.9** 44.1 g/mol. **5.10** B₂H₆. **5.11** 96.9 L.
5.12 4.75 L. **5.13** 0.338 M. **5.14** CH₄: 1.29 atm; C₂H₆:

0.0657 atm; C₃H₈: 0.0181 atm. **5.15** 0.0653 g. **5.16** 321 m/s.
5.17 146 g/mol. **5.18** 30.0 atm; 45.5 atm using the ideal gas equation.