5

A tornado is a violently rotating column of air extending from a thunderstorm to the ground. The models show the major constituents in a tornado: nitrogen, oxygen, water, and carbon dioxide molecules and an argon atom.

Gases

A LOOK AHEAD

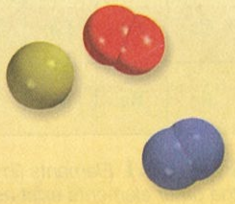
- We begin by examining the substances that exist as gases and their general properties. (5.1)
- We learn units for expressing gas pressure and the characteristics of atmospheric pressure. (5.2)
- Next, we study the relationship among pressure, volume, temperature, and amount of a gas in terms of various 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)
- The chapter ends with a discussion of the correction for the nonideal behavior of gases using the van der Waals equation. (5.8)

Interactive Activity Summary

1. Animation: Gas Laws (5.3)
2. Interactivity: Boyle's Law (5.3)
3. Interactivity: Volume in Gas Laws (5.3)
4. Interactivity: Dalton's Law (5.6)
5. Animation: Collecting a Gas over Water (5.6)
6. Animation: Diffusion of Gases (5.7)

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

Gases, the subject of this chapter, are simpler than liquids or solids in many ways. Molecular motion in gases is totally random, and the forces of attraction between gas molecules are so small that each molecule moves freely and essentially independently of other molecules. Subjected to changes in temperature and pressure, 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.



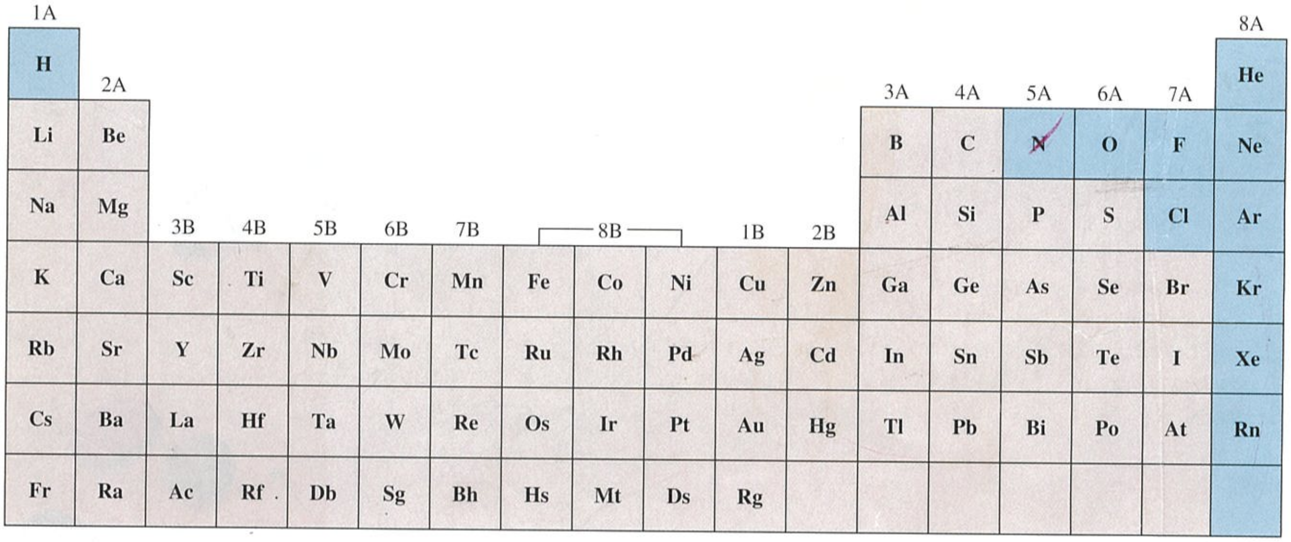
5.1 Substances That Exist as Gases

We live at the bottom of an ocean of air whose composition by volume is roughly 78 percent N_2, 21 percent O_2, and 1 percent other gases, including CO_2. Today, the chemistry of this vital mixture of gases has become a source of great interest because of the detrimental effects of environmental pollution. The chemistry of the atmosphere and polluting gases is discussed in Chapter 17. Here we will focus generally on the behavior of substances that exist as gases under normal atmospheric conditions, which are defined as 25°C and 1 atmosphere (atm) pressure.

Figure 5.1 shows the elements that are gases under normal atmospheric conditions. Note that hydrogen, nitrogen, oxygen, fluorine, and chlorine exist as gaseous diatomic molecules: H_2, N_2, O_2, F_2, and Cl_2. An allotrope of oxygen, ozone (O_3), is also a gas at room temperature. All the elements in Group 8A, the noble gases, are monatomic gases: He, Ne, Ar, Kr, Xe, and Rn.

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

The behavior of molecular compounds is more varied. Some—for example, CO, CO_2, HCl, NH_3, and CH_4 (methane)—are gases, but the majority of molecular compounds are liquids or solids at room temperature. However, on heating they are converted to gases much more easily than ionic compounds. In other words, molecular compounds usually boil at much lower temperatures than ionic compounds do. There is no simple rule to help us determine whether a certain molecular compound is a gas under normal atmospheric conditions. To make such a determination we need to understand the nature and magnitude of the attractive forces among the molecules, called *intermolecular forces* (discussed in Chapter 11). In general, the stronger these attractions, the less likely a compound can exist as a gas at ordinary temperatures.



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Figure 5.1 *Elements (in blue) 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 (O_3) is also a gas.*

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

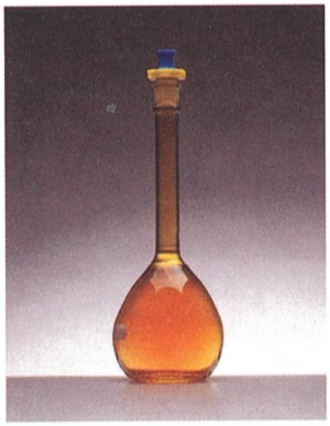
Elements	Compounds
H_2 (molecular hydrogen)	HF (hydrogen fluoride)
N_2 (molecular nitrogen)	HCl (hydrogen chloride)
O_2 (molecular oxygen)	HBr (hydrogen bromide)
O_3 (ozone)	HI (hydrogen iodide)
F_2 (molecular fluorine)	CO (carbon monoxide)
Cl_2 (molecular chlorine)	CO_2 (carbon dioxide)
He (helium)	NH_3 (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO_2 (nitrogen dioxide)
Kr (krypton)	N_2O (nitrous oxide)
Xe (xenon)	SO_2 (sulfur dioxide)
Rn (radon)	H_2S (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.

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.

Of the gases listed in Table 5.1, only O_2 is essential for our survival. Hydrogen sulfide (H_2S) and hydrogen cyanide (HCN) are deadly poisons. Several others, such as CO, NO_2, O_3, and SO_2, 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 F_2, Cl_2, and NO_2. The dark-brown color of NO_2 is sometimes visible in polluted air. All gases have the following physical characteristics:

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


NO_2 gas.

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

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

$$\text{velocity} = \frac{\text{distance moved}}{\text{elapsed time}}$$

The SI unit for velocity is m/s, although we also use cm/s.

Acceleration is the change in velocity with time, or

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

Acceleration is measured in m/s^2 (or cm/s^2).

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

$$\text{force} = \text{mass} \times \text{acceleration}$$

1 N is roughly equivalent to the force exerted by Earth's gravity on an apple.

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

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

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

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

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

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

Atmospheric Pressure

The atoms and molecules of the gases in the atmosphere, like those of all other matter, are subject to Earth's gravitational pull. As a consequence, the atmosphere is much denser near the surface of Earth than at high altitudes. (The air outside the pressurized cabin of an airplane at 9 km is too thin to breathe.) In fact, the density of air decreases very rapidly with increasing distance from Earth. 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

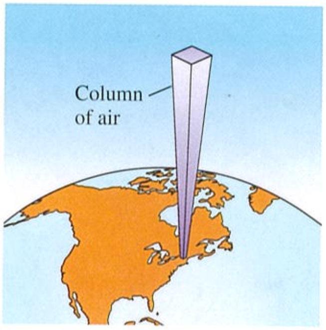


Figure 5.2 *A column of air extending from sea level to the upper atmosphere.*

[†] Sir Issac 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.

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 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

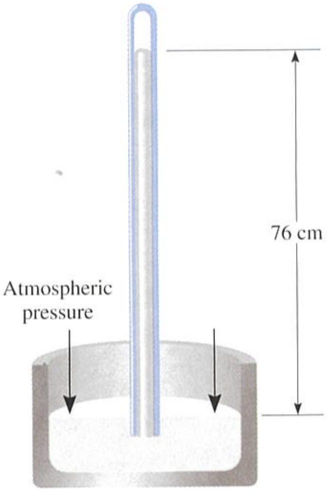


Figure 5.3 *A barometer for measuring atmospheric pressure. Above the mercury in the tube is a vacuum. The column of mercury is supported by the atmospheric pressure.*

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

and

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

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 Pa = 1 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 atm = 760 mmHg, the following conversion factor is needed to obtain the pressure in atmospheres

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

(Continued)

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

Solution The pressure in the cabin is given by

$$\text{pressure} = 688\ \cancel{\text{mmHg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}}$$
$$= \boxed{0.905\ \text{atm}}$$

Similar problem: 5.13.

Practice Exercise Convert 749 mmHg to atmospheres.

Example 5.2

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

Strategy Here we are asked to convert mmHg to kPa. Because

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

the conversion factor we need is

$$\frac{1.01325 \times 10^5\ \text{Pa}}{760\ \text{mmHg}}$$

Solution The pressure in kPa is

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

Similar problem: 5.14.

Practice Exercise Convert 295 mmHg to kilopascals.

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*

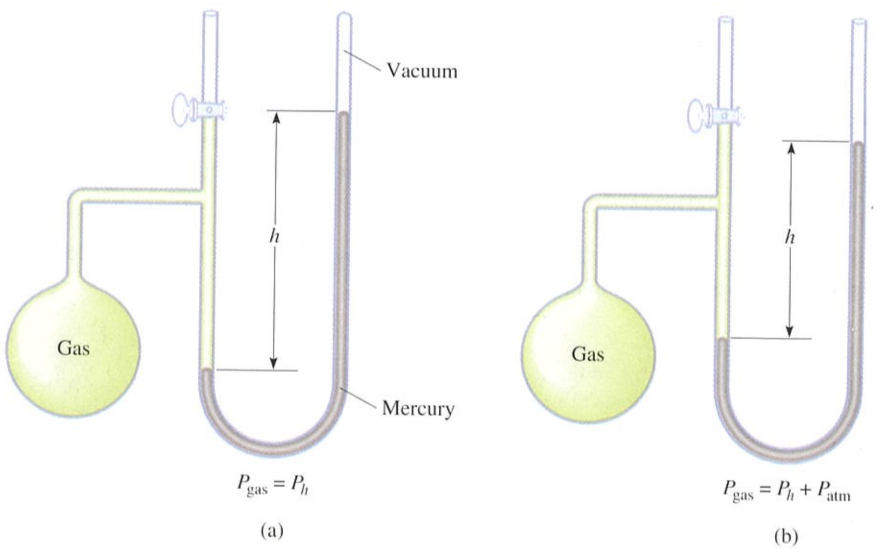


Figure 5.4 *Two types of manometers used to measure gas pressures. (a) Gas pressure is less than atmospheric pressure. (b) Gas pressure is greater than atmospheric pressure.*

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.

5.3 The Gas Laws

Animation:
The Gas Laws
ARIS, Animations

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.*

Interactivity:
Boyle's Law
ARIS, Interactives

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)].

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

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

[†] 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.

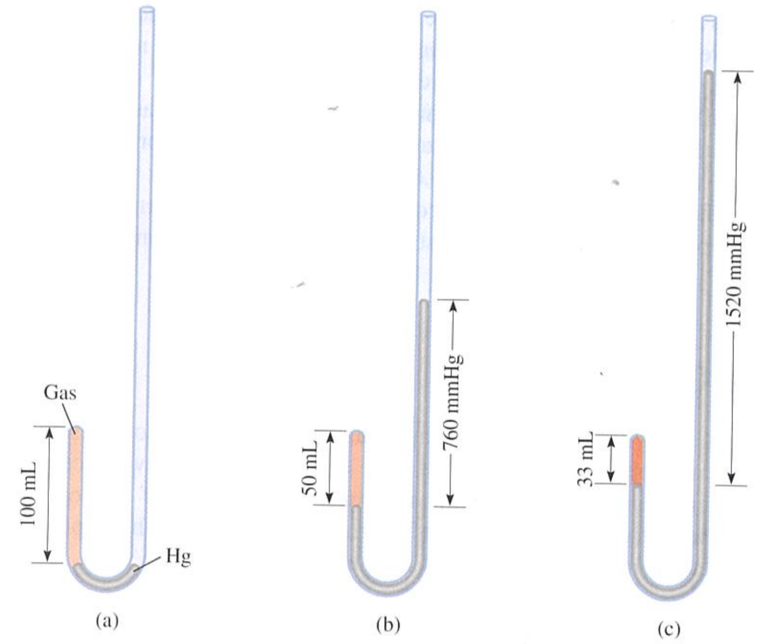


Figure 5.5 *Apparatus for studying the relationship between pressure and volume of a gas. (a) The levels of mercury are equal and the pressure of the gas is equal to the atmospheric pressure (760 mmHg). The gas volume is 100 mL. (b) Doubling the pressure by adding more mercury reduces the gas volume 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.*

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

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

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

$$P = k_1 \times \frac{1}{V} \tag{5.1a}$$

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

$$PV = k_1 \tag{5.1b}$$

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.

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

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

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

$$\begin{aligned} \text{income} &\propto \text{number of tickets sold} \\ &= C \times \text{number of tickets sold} \end{aligned}$$

where C, the proportionality constant, is the price per ticket.

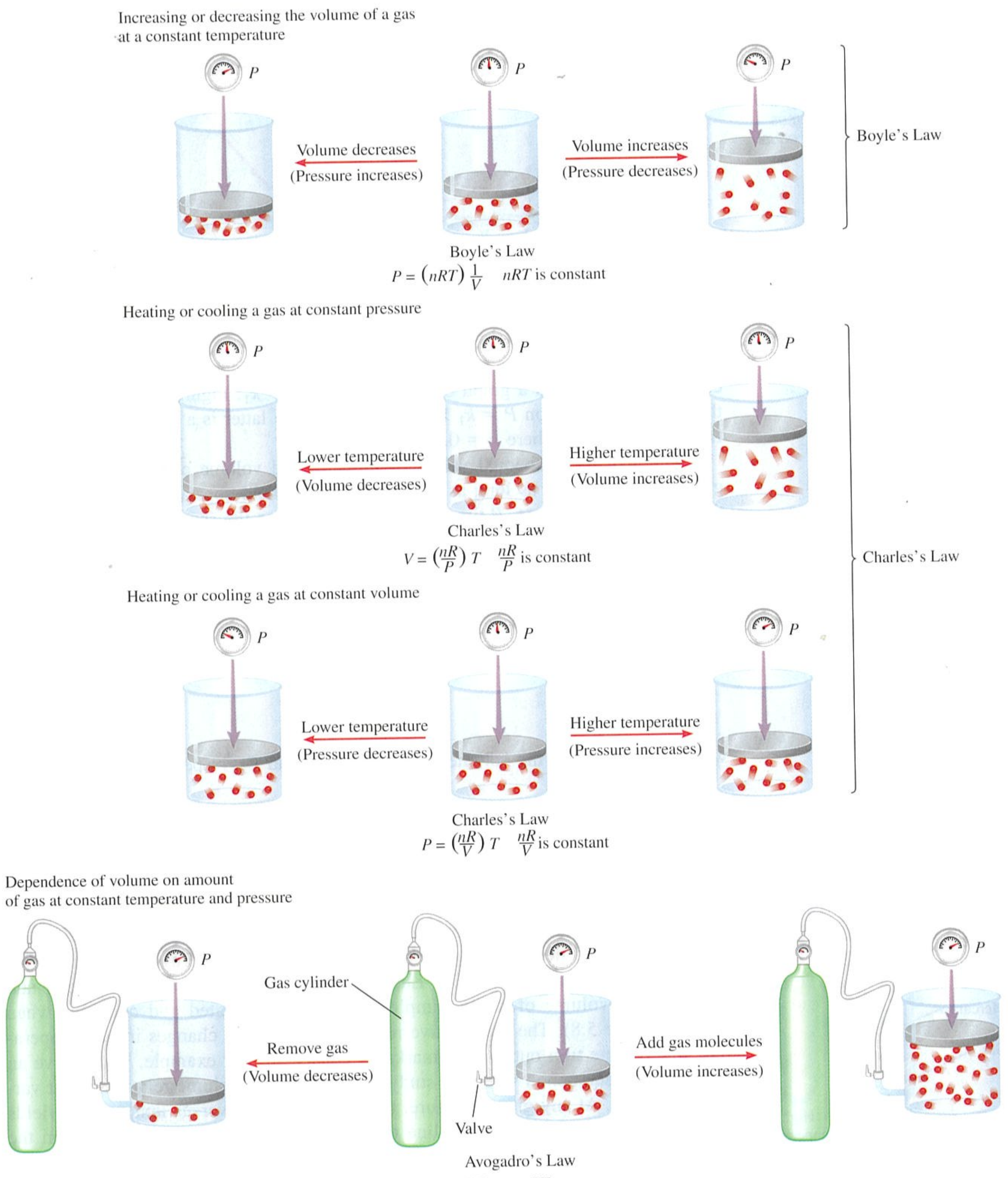


Figure 5.6 *Schematic illustrations of Boyle's law, Charles's law, and Avogadro's law.*

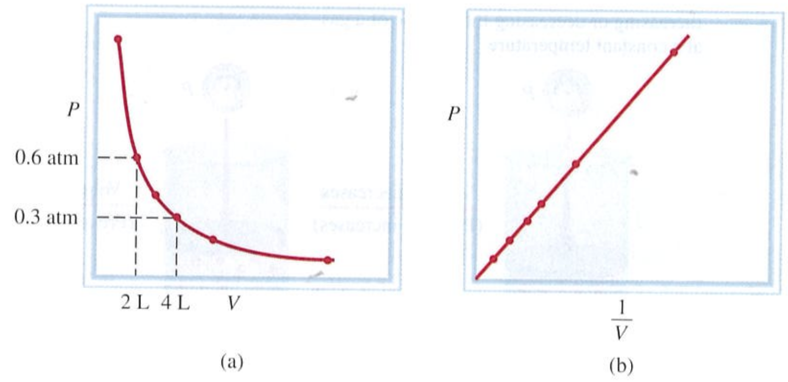


Figure 5.7 *Graphs showing variation of the volume of a gas with the pressure exerted on the gas, at constant temperature. (a) P versus V. Note that the volume of the gas doubles as the pressure is halved. (b) P versus 1/V. The slope of the line is equal to k_1.*

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 $b = 0$.

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

$$P_1V_1 = P_2V_2 \tag{5.2}$$

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

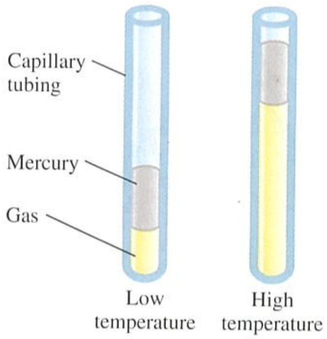


Figure 5.8 *Variation of the volume of a gas sample with temperature, at constant pressure. The pressure exerted on the gas is the sum of the atmospheric pressure and the pressure due to the weight of the mercury.*

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

---

[†] 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.

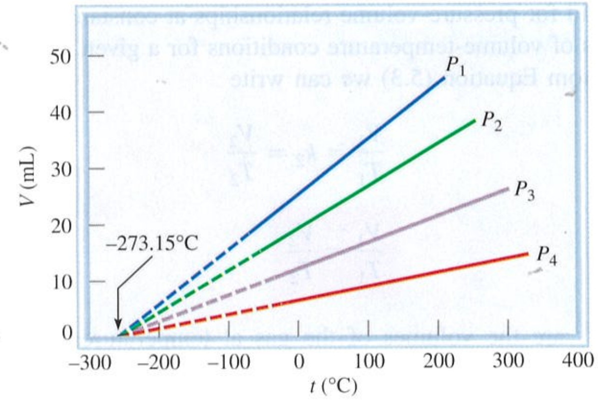


Figure 5.9 *Variation of the volume of a gas sample with temperature, at constant pressure. Each line represents the variation at a certain pressure. The pressures increase from P_1 to P_4. All gases ultimately condense (become liquids) if they are cooled to sufficiently low temperatures; the solid portions 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.*

straight line for the volume-temperature plot, but we get the *same* zero-volume temperature intercept 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 °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 °C. By convention, we use T to denote absolute (kelvin) temperature and t to indicate temperature on the Celsius scale.

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

$$V \propto T$$
$$V = k_2 T$$

or

$$\frac{V}{T} = k_2 \tag{5.3}$$

where k_2 is the proportionality constant. Equation (5.3) is known as ***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

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{5.4}$$

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

Another form of Charles's law shows that at constant amount of gas and volume, the pressure of a gas is proportional to temperature

$$P \propto T$$
$$P = k_3T$$

or

$$\frac{P}{T} = k_3 \tag{5.5}$$

From Figure 5.6 we see that $k_3 = nR/V$. Starting with Equation (5.5), we have

$$\frac{P_1}{T_1} = k_3 = \frac{P_2}{T_2}$$

or

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \tag{5.6}$$

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

Avogadro's name first appeared in Section 3.2.

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

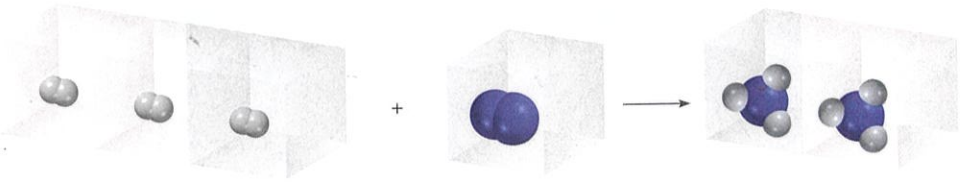
$$V \propto n$$
$$V = k_4n \tag{5.7}$$

where n represents the number of moles and k_4 is the proportionality constant. Equation (5.7) is the mathematical expression of ***Avogadro's law,*** which states that *at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.* From Figure 5.6 we see that $k_4 = RT/P$.

Interactivity:
Volume in Gas Laws
ARIS, Interactives

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:

$$\underset{\text{3 mol}}{3H_2(g)} + \underset{\text{1 mol}}{N_2(g)} \longrightarrow \underset{\text{2 mol}}{2\,NH_3(g)}$$



$3H_2(g)$	+	$N_2(g)$	⟶	$2NH_3(g)$
3 molecules	+	1 molecule	⟶	2 molecules
3 moles	+	1 mole	⟶	2 moles
3 volumes	+	1 volume	⟶	2 volumes

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

$$\underset{\text{3 volumes}}{3H_2(g)} + \underset{\text{1 volume}}{N_2(g)} \longrightarrow \underset{\text{2 volumes}}{2NH_3(g)}$$

The volume ratio of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to molecular hydrogen and molecular nitrogen (the reactants) combined 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:

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

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

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

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

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

$$V = R\frac{nT}{P}$$

or

$$PV = nRT \tag{5.8}$$

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.

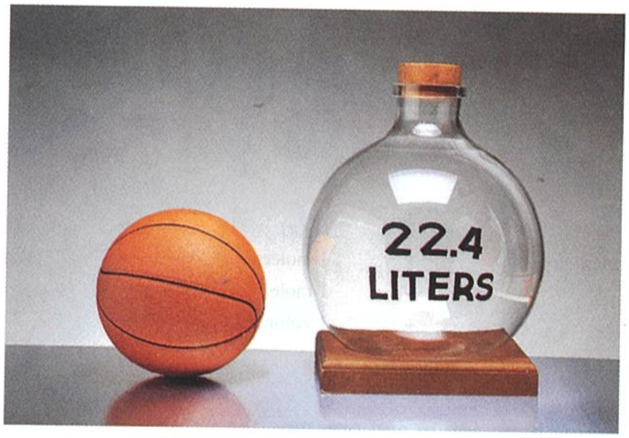


Figure 5.11 *A comparison of the molar volume at STP (which is approximately 22.4 L) with a basketball.*

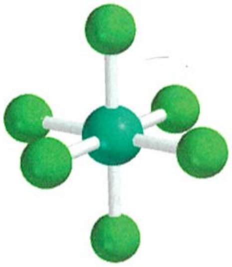
Before we can apply the ideal gas equation to a real system, we must evaluate the gas constant *R*. At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an ideal gas. Experiments show that under these conditions, 1 mole of an ideal gas occupies 22.414 L, which is somewhat greater than the 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

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

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

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 °C in calculations are exact so that they do not affect the number of significant figures.



SF_6

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?

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

(Continued)

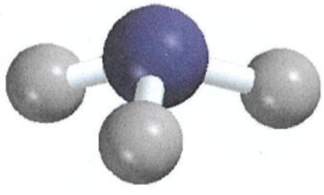
$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(1.82\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(69.5 + 273)\ \text{K}}{5.43\ \text{L}} \\ &= 9.42\ \text{atm} \end{aligned}$$

Similar problem: 5.32.

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



NH_3

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

$$\text{grams of } NH_3 \longrightarrow \text{moles of } NH_3 \longrightarrow \text{liters of } NH_3 \text{ at STP}$$

so the volume of NH_3 is given by

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

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.

Similar problem: 5.40.

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. From Equation (5.8),

$$R = \frac{P_1V_1}{n_1T_1}\ \text{(before change)} \quad \text{and} \quad R = \frac{P_2V_2}{n_2T_2}\ \text{(after change)}$$

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

Therefore,

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \tag{5.9}$$

It is interesting to note that all the gas laws discussed in Section 5.3 can be derived from Equation (5.9). If $n_1 = n_2$, as is usually the case because the amount of gas normally does not change, the equation then becomes

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{5.10}$$

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


A scientific research helium balloon.

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)

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

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

$$P_1V_1 = P_2V_2$$

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

Initial Conditions	Final Conditions
$P_1 = 1.0$ atm	$P_2 = 0.40$ atm
$V_1 = 0.55$ L	$V_2 = ?$

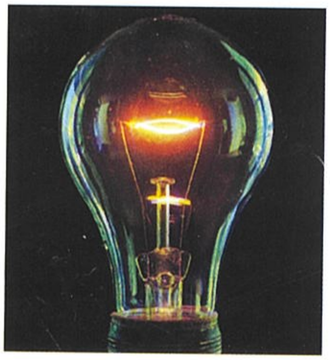
Therefore,

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

Similar problem: 5.19.

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.


Electric lightbulbs are usually filled with argon.

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).

(Continued)

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
$P_1 = 1.20$ atm	$P_2 = ?$
$T_1 = (18 + 273)$ K $= 291$ K	$T_2 = (85 + 273)$ K $= 358$ K

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

The final pressure is given by

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

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.

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.

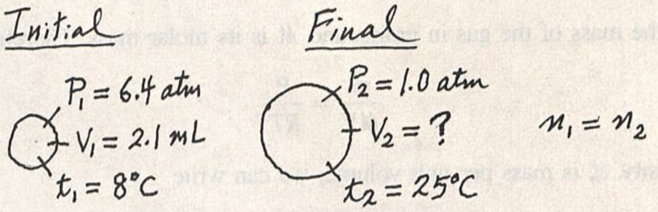
Practice Exercise A sample of oxygen gas initially at 0.97 atm is cooled from 21°C to −68°C at constant volume. What is its final pressure (in atm)?

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.

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)

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

(*Continued*)

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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
$P_1 = 6.4$ atm	$P_2 = 1.0$ atm
$V_1 = 2.1$ mL	$V_2 = ?$
$T_1 = (8 + 273)$ K $= 281$ K	$T_2 = (25 + 273)$ K $= 298$ 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.

Similar problem: 5.35.

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

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT} \tag{5.11}$$

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.

CO_2

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 ($T = 273 + 55 = 328$ K) and use 44.01 g for the molar mass of CO_2:

$$d = \frac{P\mathcal{M}}{RT}$$

$$= \frac{(0.990 \text{ atm})(44.01 \text{ g/mol})}{(0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(328 \text{ K})} = \boxed{1.62 \text{ g/L}}$$

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

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.

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

$$= \frac{(1 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(328 \text{ K})}{0.990 \text{ atm}}$$

$$= 27.2 \text{ L}$$

Therefore, the density of CO_2 is given by

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

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/cm^3.

Similar problem: 5.48.

Practice Exercise What is the density (in g/L) of uranium hexafluoride (UF_6) at 779 mmHg and 62°C?

The Molar Mass of a Gaseous Substance

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

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

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.*

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)

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

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

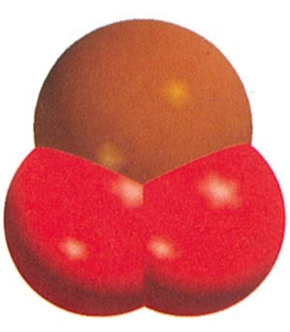
$$\begin{aligned}n &= \frac{PV}{RT}\\ &= \frac{(2.88\ \text{atm})(1.00\ \text{L})}{(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(309\ \text{K})}\\ &= 0.1135\ \text{mol}\end{aligned}$$

Therefore, the molar mass is given by

$$\mathcal{M} = \frac{7.71\ \text{g}}{0.1135\ \text{mol}} = 67.9\ \text{g/mol}$$

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

(Continued)



ClO_2

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.

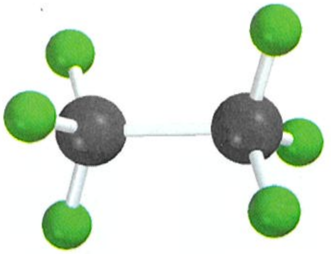
Similar problems: 5.43, 5.47.

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?

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.



Si_2F_6

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. 88) 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

$$n_{Si} = 33.0\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 1.17\ \text{mol Si}$$

$$n_F = 67.0\ \cancel{\text{g F}} \times \frac{1\ \text{mol F}}{19.00\ \cancel{\text{g F}}} = 3.53\ \text{mol F}$$

Therefore, the empirical formula is $Si_{1.17}F_{3.53}$, 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 $(SiF_3)_2$ or Si_2F_6.

Similar problem: 5.49.

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

5.5 Gas Stoichiometry

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

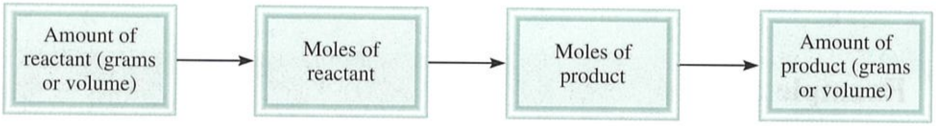
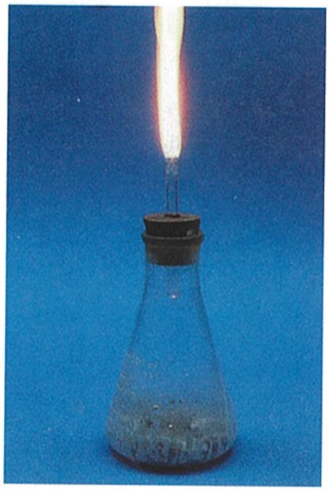


Figure 5.13 *Stoichiometric calculations involving gases.*



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

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.

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$$

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 mol $O_2 \simeq$ 2 mol C_2H_2; therefore, we can also write 5 L $O_2 \simeq$ 2 L C_2H_2. The volume of O_2 that will react with 7.64 L C_2H_2 is given by

$$\text{volume of } O_2 = 7.64\ \cancel{\text{L}\ C_2H_2} \times \frac{5\ \text{L}\ O_2}{2\ \cancel{\text{L}\ C_2H_2}}$$

$$= \boxed{19.1\ \text{L}}$$

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}):

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)$$

Similar problem: 5.26.

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

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:

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

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°C and 823 mmHg by the decomposition of 60.0 g of NaN_3.

(Continued)

Strategy From the balanced equation we see that 2 mol NaN_3 ≏ 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

$$\text{grams of } NaN_3 \longrightarrow \text{moles of } NaN_3 \longrightarrow \text{moles of } N_2$$

so that

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

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

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

Similar problem: 5.60.

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:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

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

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

$$2LiOH(aq) + CO_2(g) \longrightarrow Li_2CO_3(aq) + H_2O(l)$$

The pressure of carbon dioxide inside the cabin of a submarine having a volume of 2.4×10^5 L is 7.9×10^{-3} 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 1.2×10^{-4} atm. How many grams of lithium carbonate are formed by this process?

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

Strategy How do we calculate the number of moles of CO_2 reacted from the drop in CO_2 pressure? What is the conversion factor between CO_2 and Li_2CO_3?

Solution First we calculate the number of moles of CO_2 consumed in the reaction. The drop in CO_2 pressure, which is $(7.9 \times 10^{-3}$ atm$) - (1.2 \times 10^{-4}$ atm$)$, or

(Continued)

7.8×10^{-3} atm, corresponds to the consumption of CO_2. Using the ideal gas equation, we write

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

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

From the chemical equation we see that 1 mol $CO_2 \simeq$ 1 mol Li_2CO_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:

$$\text{mass of } Li_2CO_3 \text{ formed} = 73\ \cancel{\text{mol } Li_2CO_3} \times \frac{73.89\ \text{g } Li_2CO_3}{1\ \cancel{\text{mol } Li_2CO_3}}$$

$$= \boxed{5.4 \times 10^{3}\ \text{g } Li_2CO_3}$$

Similar problem: 5.99.

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, 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.

Interactivity:
Dalton's Law
ARIS, Interactives

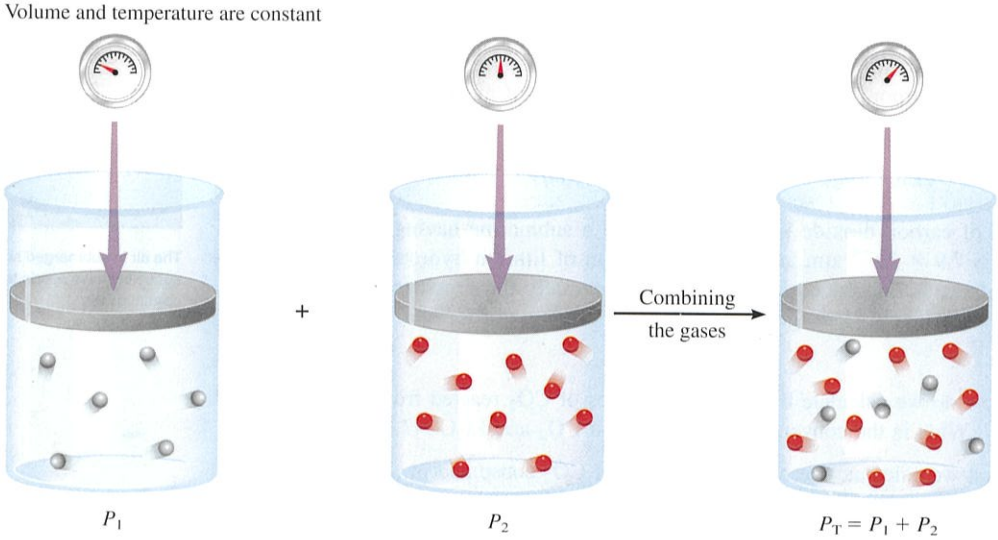


Figure 5.14 *Schematic illustration of Dalton's law of partial pressures.*

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

$$P_A = \frac{n_A RT}{V}$$

where n_A is the number of moles of A present. Similarly, the pressure exerted by gas B is

$$P_B = \frac{n_B RT}{V}$$

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

$$\begin{aligned} P_T &= P_A + P_B \\ &= \frac{n_A RT}{V} + \frac{n_B RT}{V} \\ &= \frac{RT}{V}(n_A + n_B) \\ &= \frac{nRT}{V} \end{aligned}$$

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

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

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

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

$$\begin{aligned} \frac{P_A}{P_T} &= \frac{n_A RT/V}{(n_A + n_B)RT/V} \\ &= \frac{n_A}{n_A + n_B} \\ &= X_A \end{aligned}$$

where 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

$$X_i = \frac{n_i}{n_T} \tag{5.13}$$

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,

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

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

$$X_{\text{A}} + X_{\text{B}} = \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{B}}} + \frac{n_{\text{B}}}{n_{\text{A}} + n_{\text{B}}} = 1$$

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

$$P_i = X_iP_{\text{T}} \tag{5.14}$$

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. 198.

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})

$$\underset{\text{want to calculate}}{\underset{\nearrow}{P_{\text{Ne}}}} = \overset{\text{need to find}}{\overset{\swarrow}{X_{\text{Ne}}}}\underset{\text{given}}{\underset{\nwarrow}{P_{\text{T}}}}$$

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

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

Therefore

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

(Continued)

Similarly,

$$P_{\text{Ar}} = X_{\text{Ar}}P_{\text{T}}$$
$$= 0.10 \times 2.00 \text{ atm}$$
$$= 0.20 \text{ atm}$$

and

$$P_{\text{Xe}} = X_{\text{Xe}}P_{\text{T}}$$
$$= 0.293 \times 2.00 \text{ atm}$$
$$= 0.586 \text{ atm}$$

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) atm = 2.00 atm.

Similar problem: 5.63.

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?

Animation:
Collecting a Gas over Water
ARIS, Animations

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:

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$

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 a gas is based on the assumptions that the gas does not react with water and that it

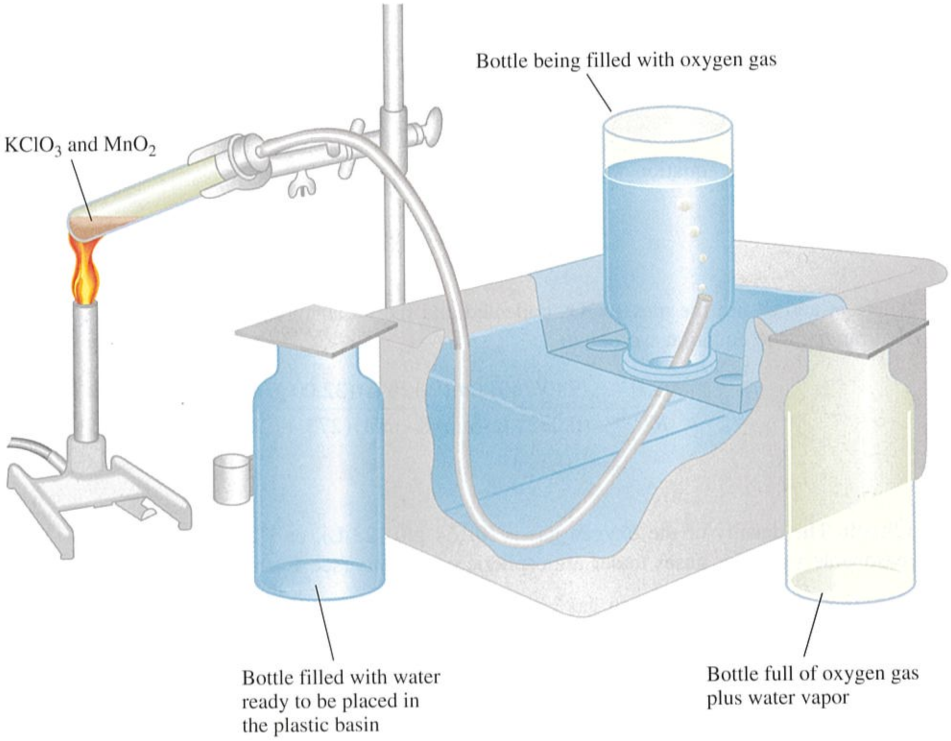


Figure 5.15 *An apparatus for collecting gas over water. The oxygen generated by heating potassium chlorate ($KClO_3$) in the presence of a small amount of manganese dioxide (MnO_2), which speeds up the reaction, is bubbled through water and collected in a bottle as shown. Water originally present in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

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:

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

Consequently, we must allow for the pressure caused by the presence of water vapor when we calculate the amount of 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.

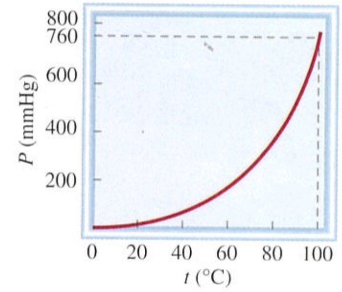


Figure 5.16 *The pressure of water vapor as a function of temperature. Note that at the boiling point of water (100°C) the pressure is 760 mmHg, which is exactly equal to 1 atm.*

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

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?

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 g/0.128 L), or 1.28 g/L, which is a reasonable value for gases under atmospheric conditions (see Example 5.8).

Similar problem: 5.68.

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.

5.7 The Kinetic Molecular Theory of Gases

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

In the nineteenth century, a number of physicists, notably Ludwig Boltzmann[†] and James Clerk Maxwell,[‡] found that the physical properties of gases can be explained in terms of the motion of individual molecules. This molecular movement is a form of *energy,* which we define as the capacity to do work or to produce change. In mechanics, *work* is defined as force times distance. Because energy can be measured as work, we can write

$$\begin{aligned} \text{energy} &= \text{work done} \\ &= \text{force} \times \text{distance} \end{aligned}$$

The ***joule (J)***[§] is *the SI unit of energy*

$$\begin{aligned} 1\ \text{J} &= 1\ \text{kg m}^2/\text{s}^2 \\ &= 1\ \text{N m} \end{aligned}$$

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

$$1\ \text{kJ} = 1000\ \text{J}$$

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

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

The kinetic theory of gases treats molecules as hard spheres without internal structure.

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

$$\overline{\text{KE}} = \tfrac{1}{2}m\overline{u^2}$$

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

[‡] James Clerk Maxwell (1831–1879). Scottish physicist. Maxwell was one of the great theoretical physicists of the nineteenth century; his work covered many areas in physics, including kinetic theory of gases, thermodynamics, and electricity and magnetism.

[§] James Prescott Joule (1818–1889). English physicist. As a young man, Joule was tutored by John Dalton. He is most famous for determining the mechanical equivalent of heat, the conversion between mechanical energy and thermal energy.

CHEMISTRY *in Action*

Scuba Diving and the Gas Laws

Scuba diving is an exhilarating sport, and, thanks in part to the gas laws, it is also a safe activity for trained individuals who are in good health. ("Scuba" is an acronym for self-contained underwater breathing apparatus.) Two applications of the gas laws to this popular pastime are the development of guidelines for returning safely to the surface after a dive and the determination of the proper mix of gases to prevent a potentially fatal condition during a dive.

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

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

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

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

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

where P_T is the total pressure. However, because volume is directly proportional to the number of moles of gas present (at

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

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

where N is the number of molecules.

Assumption 4 enables us to write

$$\begin{aligned} \overline{\mathrm{KE}} &\propto T \\ \tfrac{1}{2}m\overline{u^2} &\propto T \\ \tfrac{1}{2}m\overline{u^2} &= CT \end{aligned} \tag{5.15}$$

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

According to the kinetic molecular theory, gas pressure is the result of collisions between molecules and the walls of their container. It depends on the frequency of collision per unit area and on how "hard" the molecules strike the constant temperature and pressure), we can now write

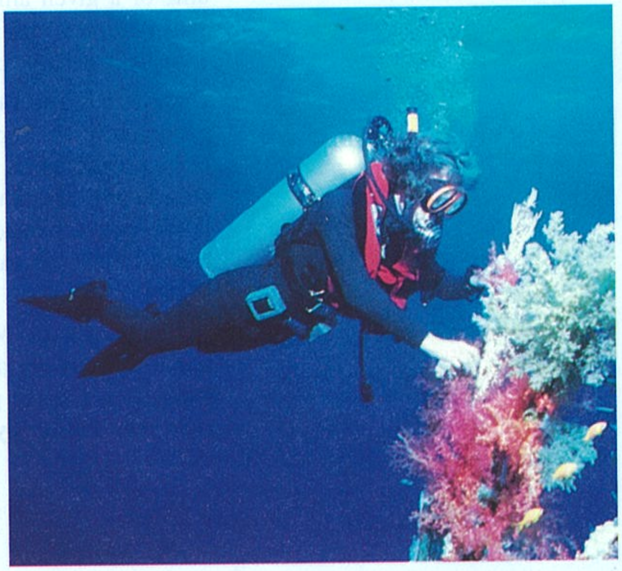
$$P_{O_2} = \frac{V_{O_2}}{V_{O_2} + V_{N_2}} P_T$$

Thus, the composition of air is 20 percent oxygen gas and 80 percent nitrogen gas by volume. When a diver is submerged, the pressure of the water on the diver is greater than atmospheric pressure. The air pressure inside the body cavities (for example, lungs, sinuses) must be the same as the pressure of the surrounding water; otherwise they would collapse. A special valve automatically adjusts the pressure of the air breathed from a scuba tank to ensure that the air pressure equals the water pressure at all times. For example, at a depth where the total pressure is 2.0 atm, the oxygen content in air should be reduced to 10 percent by volume to maintain the same partial pressure of 0.20 atm; that is,

$$P_{O_2} = 0.20 \text{ atm} = \frac{V_{O_2}}{V_{O_2} + V_{N_2}} \times 2.0 \text{ atm}$$

$$\frac{V_{O_2}}{V_{O_2} + V_{N_2}} = \frac{0.20 \text{ atm}}{2.0 \text{ atm}} = 0.10 \text{ or } 10\%$$

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



A scuba diver.

wall. The theory also provides a molecular interpretation of temperature. According to Equation (5.15), the absolute temperature of a gas is a measure of the average kinetic energy of the molecules. In other words, the absolute temperature is an 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.

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

$$P \propto \frac{n}{V}T$$

For two gases, 1 and 2, we write

$$P_1 \propto \frac{n_1T_1}{V_1} = C\frac{n_1T_1}{V_1}$$
$$P_2 \propto \frac{n_2T_2}{V_2} = C\frac{n_2T_2}{V_2}$$

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

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

Distribution of Molecular Speeds

The kinetic theory of gases 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

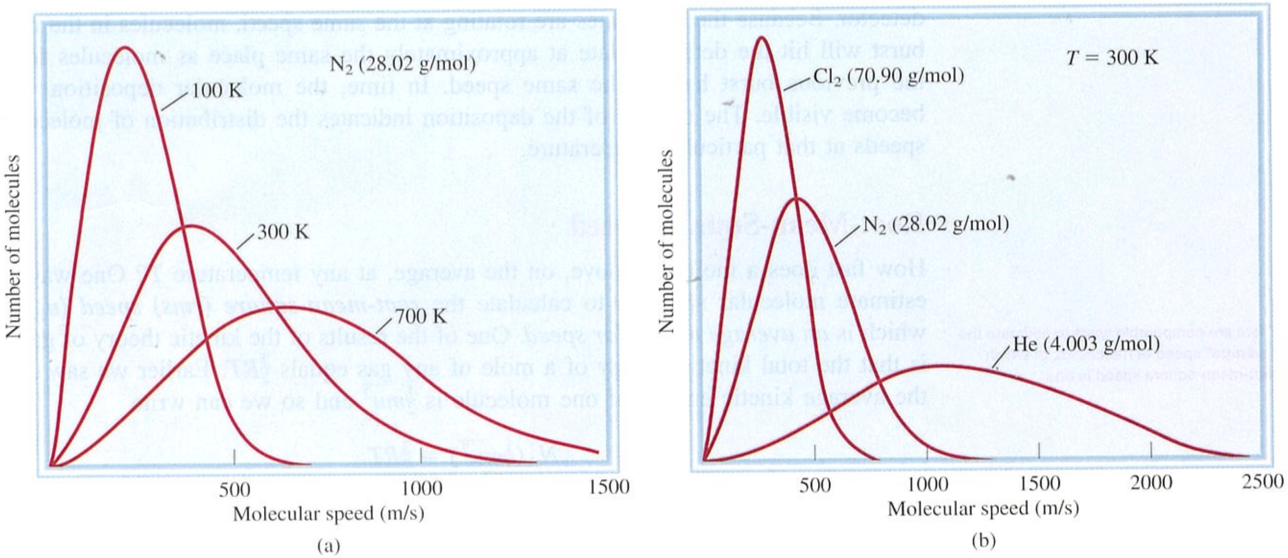


Figure 5.17 *(a) The distribution of speeds for nitrogen gas at three different temperatures. At the higher temperatures, more molecules are moving at faster speeds. (b) The distribution of speeds for three gases at 300 K. At a given temperature, the lighter molecules are moving faster, on the average.*

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 than the slower-moving ones. Eventually, a layer of deposit will accumulate on the

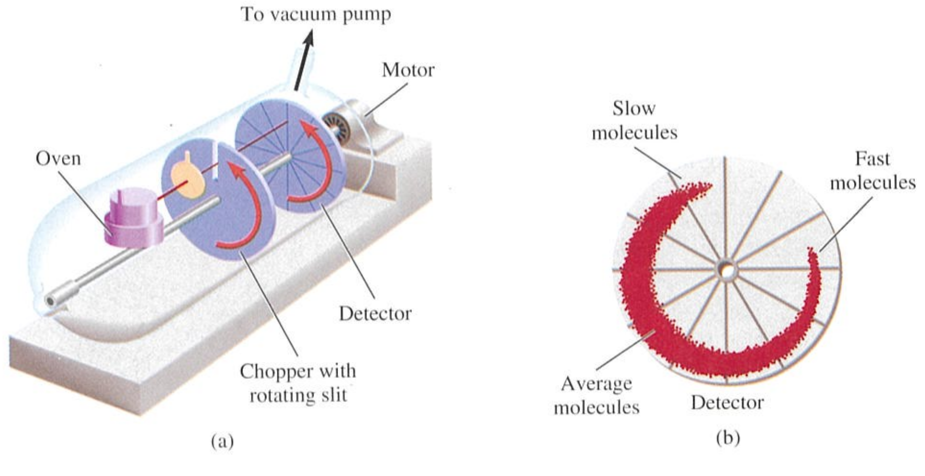


Figure 5.18 *(a) Apparatus for studying molecular speed distribution at a certain temperature. The vacuum pump causes the molecules to travel from left to right as shown. (b) The spread of the deposit on the detector gives the range of molecular speeds, and the density of the deposit is proportional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

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.

Root-Mean-Square Speed

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

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

$$N_A(\tfrac{1}{2}m\overline{u^2}) = \tfrac{3}{2}RT$$

where N_A is Avogadro's number. Because $N_A m = \mathcal{M}$, the above equation can be rearranged to give

$$\overline{u^2} = \frac{3RT}{\mathcal{M}}$$

Taking the square root of both sides gives

$$\sqrt{\overline{u^2}} = u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}} \qquad (5.16)$$

Equation (5.16) shows that the root-mean-square speed of a gas increases with the square root of its temperature (in kelvins). Because $\mathcal{M}$ appears in the denominator, it follows that the heavier the gas, the more slowly its molecules move. If we substitute 8.314 J/K · mol for R (see Appendix 2) and convert the molar mass to kg/mol, then u_{rms} will be calculated in meters per second (m/s). This procedure is illustrated in Example 5.16.

Example 5.16

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

Strategy To calculate the root-mean-square speed we need Equation (5.16). What units should we use for R and $\mathcal{M}$ so that u_{rms} will be expressed in m/s?

Solution To calculate u_{rms}, the units of R should be 8.314 J/K · mol and, because 1 J = 1 kg m^2/s^2, the molar mass must be in kg/mol. The molar mass of He is 4.003 g/mol, or 4.003×10^{-3} kg/mol. From Equation (5.16),

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{\mathcal{M}}} \\ &= \sqrt{\frac{3(8.314\ \text{J/K}\cdot\text{mol})(298\ \text{K})}{4.003 \times 10^{-3}\ \text{kg/mol}}} \\ &= \sqrt{1.86 \times 10^{6}\ \text{J/kg}} \end{aligned}$$

(Continued)

Using the conversion factor 1 J = 1 kg m²/s² we get

$$\begin{aligned} u_{\text{rms}} &= \sqrt{1.86 \times 10^6 \text{ kg m}^2/\text{kg} \cdot \text{s}^2} \\ &= \sqrt{1.86 \times 10^6 \text{ m}^2/\text{s}^2} \\ &= 1.36 \times 10^3 \text{ m/s} \end{aligned}$$

The procedure is the same for N_2, the molar mass of which is 28.02 g/mol, or 2.802×10^{-2} kg/mol so that we write

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mole})(298 \text{ K})}{2.802 \times 10^{-2} \text{ kg/mol}}} \\ &= \sqrt{2.65 \times 10^5 \text{ m}^2/\text{s}^2} \\ &= 515 \text{ m/s} \end{aligned}$$

Check Because He is a lighter gas, we expect it to move faster, on average, than N_2. A quick way to check the answers is to note that the ratio of the two u_{rms} values ($1.36 \times 10^3/515 \approx 2.6$) should be equal to the square root of the ratios of the molar masses of N_2 to He, that is, $\sqrt{28/4} \approx 2.6$.

Similar problems: 5.77, 5.78.

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

The calculation in Example 5.16 has an interesting relationship to the composition of Earth's atmosphere. 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.

The Chemistry in Action essay on p. 205 describes a fascinating phenomenon involving gases at extremely low temperatures.

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

Gas Diffusion and Effusion

We will now discuss two phenomena based on gaseous motion.

Gas Diffusion

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

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.

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

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).*

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,*** is expressed mathematically as

Animation:
Diffusion of Gases
ARIS, Animations

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \tag{5.17}$$

where r_1 and r_2 are the diffusion rates of gases 1 and 2, and $\mathcal{M}_1$ and $\mathcal{M}_2$ are their molar masses, respectively.

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 $^{235}UF_6$ and $^{238}UF_6$. 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.

Example 5.17 shows an application of Graham's law.

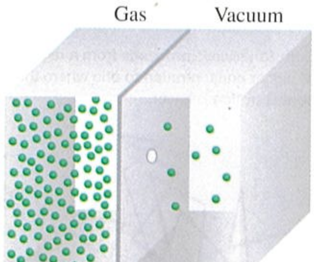


Figure 5.21 *Gas effusion. Gas molecules move from a high-pressure region (left) to a low-pressure one through a pinhole.*

Example 5.17

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min. Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier. Calculate the molar mass of the unknown gas, and suggest what this gas might be.

(Continued)

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

CHEMISTRY in Action

Super Cold Atoms

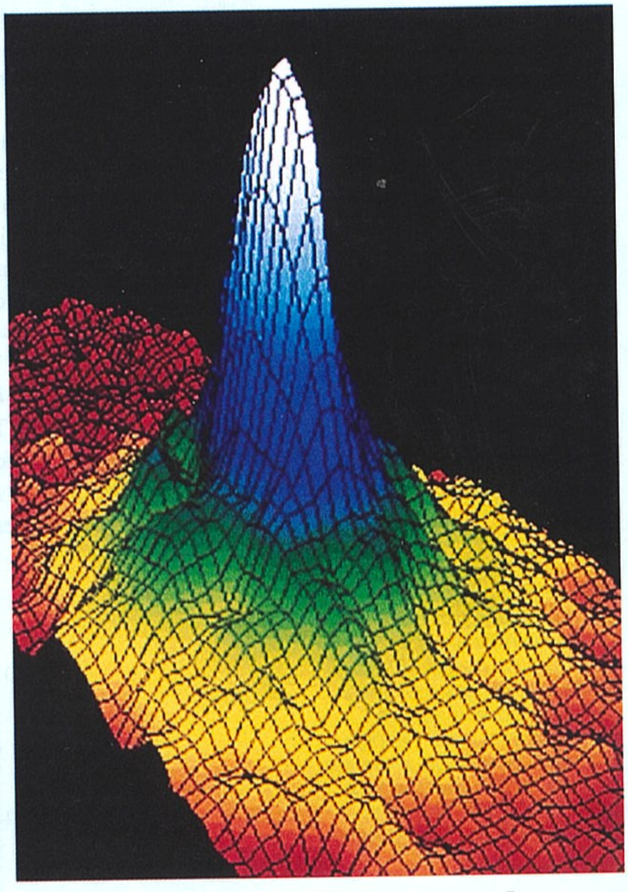
What happens to a gas when cooled to nearly absolute zero? More than 70 years ago, Albert Einstein, extending work by the Indian physicist Satyendra Nath Bose, predicted that at extremely low temperatures gaseous atoms of certain elements would "merge" or "condense" to form a single entity and a new form of matter. Unlike ordinary gases, liquids, and solids, this supercooled substance, which was named the *Bose-Einstein condensate* (*BEC*), would contain no individual atoms because the original atoms would overlap one another, leaving no space in between.

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

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

The figure shows the Maxwell velocity distribution[†] of the Rb atoms at this temperature. The colors indicate the number of atoms having velocity specified by the two horizontal axes. The blue and white portions represent atoms that have merged to form the BEC.

Within weeks of the Colorado team's discovery, a group of scientists at Rice University, using similar techniques, succeeded in producing a BEC with lithium atoms and in 1998 scientists at the Massachusetts Institute of Technology were able to produce a BEC with hydrogen atoms. Since then, many advances have been made in understanding the properties of the BEC in general and experiments are being extended to molecular systems. It is expected that studies of the BEC will shed light on atomic properties that are still not fully understood (see Chapter 7) and on the mechanism of superconductivity (see the Chemistry in Action essay on this topic in Chapter 11). An additional benefit might be the development of better lasers. Other applications will depend on further study of the BEC itself. Nevertheless, the discovery of a new form of matter has to be one of the foremost scientific achievements of the twentieth century.



Maxwell velocity distribution of Rb atoms at about 1.7×10^{-7} K. The velocity increases from the center (zero) outward along the two axes. The red color represents the lowest number of Rb atoms and the white color the highest. The average speed in the white region is about 0.5 mm/s.

[†] Velocity distribution differs from speed distribution in that velocity has both magnitude and direction. Thus, velocity can have both positive and negative values but speed can have only zero or positive values.

Strategy The rate of effusion is the number of molecules passing through a porous hole in a given time. The longer the time it takes, the slower is the rate of effusion. Therefore, Equation (5.17) can be written as $r_1/r_2 = t_2/t_1 = \sqrt{\mathcal{M}_2/\mathcal{M}_1}$, where t_1 and t_2 are the times for effusion for gases 1 and 2, respectively.

Solution From the molar mass of Br_2, we write

$$\frac{1.50 \text{ min}}{4.73 \text{ min}} = \sqrt{\frac{\mathcal{M}}{159.8 \text{ g/mol}}}$$

where $\mathcal{M}$ is the molar mass of the unknown gas. Solving for $\mathcal{M}$, we obtain

$$\mathcal{M} = \left(\frac{1.50 \text{ min}}{4.73 \text{ min}}\right)^2 \times 159.8 \text{ g/mol}$$
$$= \boxed{16.1 \text{ g/mol}}$$

Because the molar mass of carbon is 12.01 g and that of hydrogen is 1.008 g, the gas is methane (CH_4).

Similar problems: 5.83, 5.84.

Practice Exercise It takes 192 s for an unknown gas to effuse through a porous wall and 84 s for the same volume of N_2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

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

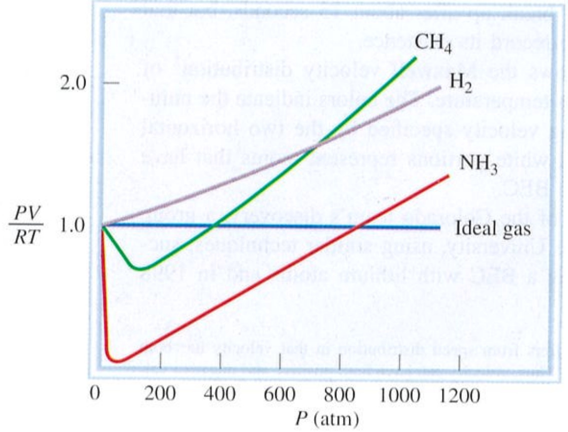


Figure 5.22 *Plot of PV/RT versus P of 1 mole of a gas at 0°C. For 1 mole of an ideal gas, PV/RT is equal to 1, no matter what the pressure of the gas is. For real gases, we observe various deviations from ideality at high pressures. At very low pressures, all gases exhibit ideal behavior; that is, their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

pressure increases. Attractive forces operate among molecules at relatively short distances. At atmospheric pressure, the molecules in a gas are far apart and the attractive forces are negligible. At high pressures, the density of the gas increases; the molecules are much closer to one another. Intermolecular forces can then be significant enough to affect the motion of the molecules, and the gas will not behave ideally.

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

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

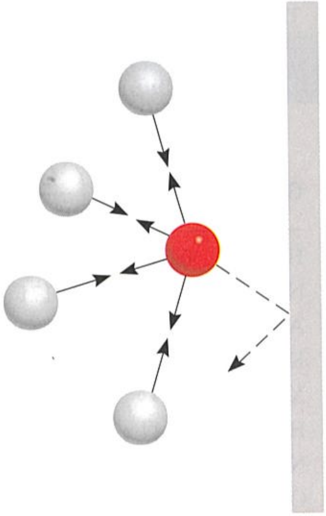


Figure 5.23 *Effect of intermolecular forces on the pressure exerted by a gas. The speed of a molecule that is moving toward the container wall (red sphere) is reduced by the attractive forces exerted by its neighbors (gray spheres). Consequently, the impact this molecule makes with the wall is not as 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.*

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. Van der Waals suggested that the pressure exerted by an ideal gas, P_{ideal}, is related to the experimentally measured pressure, P_{real}, by the equation

$$P_{\text{ideal}} = \underset{\substack{\uparrow \\ \text{observed} \\ \text{pressure}}}{P_{\text{real}}} + \underset{\substack{\uparrow \\ \text{correction} \\ \text{term}}}{\frac{an^2}{V^2}}$$

where a is a constant and n and V are the number of moles and volume of the container, respectively. The correction term for pressure (an^2/V^2) can be understood as follows. The intermolecular interaction that gives rise to nonideal behavior depends on how frequently any two molecules approach each other closely. The frequency of such "encoumters" increases with the square of the number of molecules per unit volume (n^2/V^2), because the probability of finding each of the two molecules in a particular region is proportional to n/V. Thus, a is just a proportionality constant.

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

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

$$\underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\substack{\text{corrected} \\ \text{pressure}}}\underbrace{(V - nb)}_{\substack{\text{corrected} \\ \text{volume}}} = nRT \tag{5.18}$$

Equation (5.18), *relating P, V, T, and n for a nonideal gas,* is known as the ***van der Waals equation.*** The van der Waals constants a and b are selected to give the best possible agreement between Equation (5.18) and observed behavior of a particular 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.

TABLE 5.4

van der Waals Constants of Some Common Gases

Gas	a $\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0371
H_2O	5.46	0.0305

Table 5.4 lists the values of a and b for a number of gases. The value of a indicates how strongly molecules of a given type of gas attract one another. We see that helium atoms have the weakest attraction for one another, because helium has the smallest a value. There is also a rough correlation between molecular size and b. Generally, the larger the molecule (or atom), the greater b is, but the relationship between b and molecular (or atomic) size is not a simple one.

Example 5.18 compares the pressure of a gas calculated using the ideal gas equation and the van der Waals equation.

Example 5.18

Given that 3.50 moles of NH_3 occupy 5.20 L at 47°C, calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the van der Waals equation.

Strategy To calculate the pressure of NH_3 using the ideal gas equation, we proceed as in Example 5.3. What corrections are made to the pressure and volume terms in the van der Waals equation?

Solution (a) We have the following data:

$$\begin{aligned} V &= 5.20\ \text{L} \\ T &= (47 + 273)\ \text{K} = 320\ \text{K} \\ n &= 3.50\ \text{mol} \\ R &= 0.0821\ \text{L} \cdot \text{atm/K} \cdot \text{mol} \end{aligned}$$

Substituting these values in the ideal gas equation, we write

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(3.50\ \text{mol})(0.0821\ \text{L} \cdot \text{atm/K} \cdot \text{mol})(320\ \text{K})}{5.20\ \text{L}} \\ &= 17.7\ \text{atm} \end{aligned}$$

(b) We need Equation (5.18). It is convenient to first calculate the correction terms in Equation (5.18) separately. From Table 5.4, we have

$$\begin{aligned} a &= 4.17\ \text{atm} \cdot \text{L}^2/\text{mol}^2 \\ b &= 0.0371\ \text{L/mol} \end{aligned}$$

so that the correction terms for pressure and volume are

$$\begin{aligned} \frac{an^2}{V^2} &= \frac{(4.17\ \text{atm} \cdot \text{L}^2/\text{mol}^2)(3.50\ \text{mol})^2}{(5.20\ \text{L})^2} = 1.89\ \text{atm} \\ nb &= (3.50\ \text{mol})(0.0371\ \text{L/mol}) = 0.130\ \text{L} \end{aligned}$$

Finally, substituting these values in the van der Waals equation, we have

$$\begin{aligned} (P + 1.89\ \text{atm})(5.20\ \text{L} - 0.130\ \text{L}) &= (3.50\ \text{mol})(0.0821\ \text{L} \cdot \text{atm/K} \cdot \text{mol})(320\ \text{K}) \\ P &= 16.2\ \text{atm} \end{aligned}$$

Check Based on your understanding of nonideal gas behavior, is it reasonable that the pressure calculated using the van der Waals equation should be smaller than that using the ideal gas equation? Why?

Similar problem: 5.89.

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

Summary of Facts and Concepts

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

Key Words

Absolute temperature scale, p. 179
Absolute zero, p. 179
Atmospheric pressure, p. 172
Avogadro's law, p. 180
Barometer, p. 173
Boyle's law, p. 175
Charles's and Gay-Lussac's law, p. 179
Charles's law, p. 179
Dalton's law of partial pressures, p. 192
Diffusion, p. 203
Effusion, p. 204
Gas constant (R), p. 181
Graham's law of diffusion, p. 204
Ideal gas, p. 181
Ideal gas equation, p. 181
Joule (J), p. 197
Kelvin temperature scale, p. 179
Kinetic energy (KE), p. 197
Kinetic molecular theory of gases, p. 197
Manometer, p. 174
Mole fraction, p. 193
Newton (N), p. 172
Partial pressure, p. 192
Pascal (Pa), p. 172
Pressure, p. 172
Root-mean-square (rms) speed (u_{rms}), p. 202
Standard atmospheric pressure (1 atm), p. 173
Standard temperature and pressure (STP), p. 182
van der Waals equation, p. 207

Questions and Problems

Substances That Exist as Gases

Review Questions

5.1 Name five elements and five compounds that exist as gases at room temperature.

5.2 List the physical characteristics of gases.

Pressure of a Gas

Review Questions

5.3 Define pressure and give the common units for pressure.

5.4 Describe how a barometer and a manometer are used to measure gas pressure.

5.5 Why is mercury a more suitable substance to use in a barometer than water?

5.6 Explain why the height of mercury in a barometer is independent of the cross-sectional area of the tube. Would the barometer still work if the tubing were tilted at an angle, say 15° (see Figure 5.3)?

5.7 Would it be easier to drink water with a straw on top of Mt. Everest or at the foot? Explain.

5.8 Is the atmospheric pressure in a mine that is 500 m below sea level greater or less than 1 atm?

5.9 What is the difference between a gas and a vapor? At 25°C, which of the following substances in the gas phase should be properly called a gas and which should be called a vapor: molecular nitrogen (N_2), mercury?

5.10 If the maximum distance that water may be brought up a well by a suction pump is 34 ft (10.3 m), how is it possible to obtain water and oil from hundreds of feet below the surface of Earth?

5.11 Why is it that if the barometer reading falls in one part of the world, it must rise somewhere else?

5.12 Why do astronauts have to wear protective suits when they are on the surface of the moon?

Problems

5.13 Convert 562 mmHg to atm.

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

The Gas Laws

Review Questions

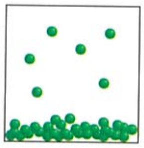
5.15 State the following gas laws in words and also in the form of an equation: Boyle's law, Charles's law, Avogadro's law. In each case, indicate the conditions under which the law is applicable, and give the units for each quantity in the equation.

5.16 Explain why a helium weather balloon expands as it rises in the air. Assume that the temperature remains constant.

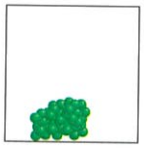
Problems

5.17 A gaseous sample of a substance is cooled at constant pressure. Which of the following diagrams best represents the situation if the final temperature is (a) above the boiling point of the substance and (b) below the boiling point but above the freezing point of the substance?

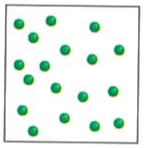
(a)



(b)

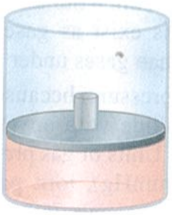


(c)

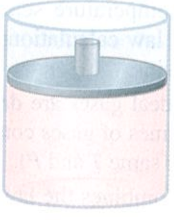


(d)

5.18 Consider the following gaseous sample in a cylinder fitted with a movable piston. Initially there are *n* moles of the gas at temperature *T*, pressure *P*, and volume *V*.



Choose the cylinder that correctly represents the gas after each of the following changes. (1) The pressure on the piston is tripled at constant *n* and *T*. (2) The temperature is doubled at constant *n* and *P*. (3) *n* moles of another gas are added at constant *T* and *P*. (4) *T* is halved and pressure on the piston is reduced to a quarter of its original value.



(a)

(b)

(c)

5.19 A gas occupying a volume of 725 mL at a pressure of 0.970 atm is allowed to expand at constant temperature until its pressure reaches 0.541 atm. What is its final volume?

5.20 At 46°C a sample of ammonia gas exerts a pressure of 5.3 atm. What is the pressure when the volume of the gas is reduced to one-tenth (0.10) of the original value at the same temperature?

5.21 The volume of a gas is 5.80 L, measured at 1.00 atm. What is the pressure of the gas in mmHg if the volume is changed to 9.65 L? (The temperature remains constant.)

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

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

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

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

5.26 Molecular chlorine and molecular fluorine combine to form a gaseous product. Under the same conditions of temperature and pressure it is found that one volume of Cl_2 reacts with three volumes of F_2 to yield two volumes of the product. What is the formula of the product?

The Ideal Gas Equation

Review Questions

5.27 List the characteristics of an ideal gas. Write the ideal gas equation and also state it in words. Give the units for each term in the equation.

5.28 Use Equation (5.9) to derive all the gas laws.

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

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

Problems

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

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

5.33 What volume will 5.6 moles of sulfur hexafluoride (SF_6) gas occupy if the temperature and pressure of the gas are 128°C and 9.4 atm?

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

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

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

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

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

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

5.40 Calculate its volume (in liters) of 88.4 g of CO_2 at STP.

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

5.42 Dry ice is solid carbon dioxide. A 0.050-g sample of dry ice is placed in an evacuated 4.6-L vessel at 30°C. Calculate the pressure inside the vessel after all the dry ice has been converted to CO_2 gas.

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

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

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

5.46 Assuming that air contains 78 percent N_2, 21 percent O_2, and 1 percent Ar, all by volume, how many molecules of each type of gas are present in 1.0 L of air at STP?

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

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

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

5.50 A compound has the empirical formula SF_4. At 20°C, 0.100 g of the gaseous compound occupies a volume of 22.1 mL and exerts a pressure of 1.02 atm. What is the molecular formula of the gas?

Gas Stoichiometry

Problems

5.51 Consider the formation of nitrogen dioxide from nitric oxide and oxygen:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

If 9.0 L of NO are reacted with excess O_2 at STP, what is the volume in liters of the NO_2 produced?

5.52 Methane, the principal component of natural gas, is used for heating and cooking. The combustion process is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

If 15.0 moles of CH_4 are reacted, what is the volume of CO_2 (in liters) produced at 23.0°C and 0.985 atm?

5.53 When coal is burned, the sulfur present in coal is converted to sulfur dioxide (SO_2), which is responsible for the acid rain phenomenon.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

If 2.54 kg of S are reacted with oxygen, calculate the volume of SO_2 gas (in mL) formed at 30.5°C and 1.12 atm.

5.54 In alcohol fermentation, yeast converts glucose to ethanol and carbon dioxide:

$$C_6H_{12}O_6(s) \longrightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

If 5.97 g of glucose are reacted and 1.44 L of CO_2 gas are collected at 293 K and 0.984 atm, what is the percent yield of the reaction?

5.55 A compound of P and F was analyzed as follows: Heating 0.2324 g of the compound in a 378-cm^3 container turned all of it to gas, which had a pressure of 97.3 mmHg at 77°C. Then the gas was mixed with calcium chloride solution, which turned all of the F to 0.2631 g of CaF_2. Determine the molecular formula of the compound.

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

5.57 What is the mass of the solid NH_4Cl formed when 73.0 g of NH_3 are mixed with an equal mass of HCl? What is the volume of the gas remaining, measured at 14.0°C and 752 mmHg? What gas is it?

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

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

5.60 Ethanol (C_2H_5OH) burns in air:

$$C_2H_5OH(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$$

Balance the equation and determine the volume of air in liters at 35.0°C and 790 mmHg required to burn 227 g of ethanol. Assume that air is 21.0 percent O_2 by volume.

Dalton's Law of Partial Pressures

Review Questions

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

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

Problems

5.63 A mixture of gases contains 0.31 mol CH_4, 0.25 mol C_2H_6, and 0.29 mol C_3H_8. The total pressure is 1.50 atm. Calculate the partial pressures of the gases.

5.64 A 2.5-L flask at 15°C contains a mixture of N_2, He, and Ne at partial pressures of 0.32 atm for N_2, 0.15 atm for He, and 0.42 atm for Ne. (a) Calculate the total pressure of the mixture. (b) Calculate the volume in liters at STP occupied by He and Ne if the N_2 is removed selectively.

5.65 Dry air near sea level has the following composition by volume: N_2, 78.08 percent; O_2, 20.94 percent; Ar, 0.93 percent; CO_2, 0.05 percent. The atmospheric pressure is 1.00 atm. Calculate (a) the partial pressure of each gas in atm and (b) the concentration of each gas in moles per liter at 0°C. (*Hint:* Because volume is proportional to the number of moles present, mole fractions of gases can be expressed as ratios of volumes at the same temperature and pressure.)

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

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

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

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

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

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

The hydrogen gas produced is collected over water at 25.0°C using an arrangement similar to that shown in Figure 5.15. The volume of the gas is 7.80 L, and the pressure is 0.980 atm. Calculate the amount of zinc metal in grams consumed in the reaction. (Vapor pressure of water at 25°C = 23.8 mmHg.)

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

5.70 A sample of ammonia (NH_3) gas is completely decomposed to nitrogen and hydrogen gases over heated iron wool. If the total pressure is 866 mmHg, calculate the partial pressures of N_2 and H_2.

Kinetic Molecular Theory of Gases

Review Questions

5.71 What are the basic assumptions of the kinetic molecular theory of gases?

5.72 How does the kinetic molecular theory explain Boyle's law, Charles's law, Avogadro's law, and Dalton's law of partial pressures?

5.73 What does the Maxwell speed distribution curve tell us? Does Maxwell's theory work for a sample of 200 molecules? Explain.

5.74 Which of the following statements is correct? (a) Heat is produced by the collision of gas molecules against one another. (b) When a gas is heated, the molecules collide with one another more often.

5.75 Uranium hexafluoride (UF_6) is a much heavier gas than helium, yet at a given temperature, the average kinetic energies of the samples of the two gases are the same. Explain.

5.76 What is the difference between gas diffusion and effusion? State Graham's law and define the terms in Equation (5.17).

Problems

5.77 Compare the root-mean-square speeds of O_2 and UF_6 at 65°C.

5.78 The temperature in the stratosphere is $-23°C$. Calculate the root-mean-square speeds of N_2, O_2, and O_3 molecules in this region.

5.79 The average distance traveled by a molecule between successive collisions is called *mean free path*. For a given amount of a gas, how does the mean free path of a gas depend on (a) density, (b) temperature at constant volume, (c) pressure at constant temperature, (d) volume at constant temperature, and (e) size of the atoms?

5.80 At a certain temperature the speeds of six gaseous molecules in a container are 2.0 m/s, 2.2 m/s, 2.6 m/s, 2.7 m/s, 3.3 m/s, and 3.5 m/s. Calculate the root-mean-square speed and the average speed of the molecules. These two average values are close to each other, but the root-mean-square value is always the larger of the two. Why?

5.81 Based on your knowledge of the kinetic theory of gases, derive Graham's law [Equation (5.17)].

5.82 The ^{235}U isotope undergoes fission when bombarded with neutrons. However, its natural abundance is only 0.72 percent. To separate it from the more abundant ^{238}U isotope, uranium is first converted to UF_6, which is easily vaporized above room temperature. The mixture of the $^{235}UF_6$ and $^{238}UF_6$ gases is then subjected to many stages of effusion. Calculate the separation factor, that is, the enrichment of ^{235}U relative to ^{238}U after one stage of effusion.

5.83 A gas evolved from the fermentation of glucose is found to effuse through a porous barrier in 15.0 min. Under the same conditions of temperature and pressure, it takes an equal volume of N_2 12.0 min to effuse through the same barrier. Calculate the molar mass of the gas and suggest what the gas might be.

5.84 Nickel forms a gaseous compound of the formula $Ni(CO)_x$. What is the value of x given the fact that under the same conditions of temperature and pressure, methane (CH_4) effuses 3.3 times faster than the compound?

Deviation from Ideal Behavior

Review Questions

5.85 Cite two pieces of evidence to show that gases do not behave ideally under all conditions.

5.86 Under what set of conditions would a gas be expected to behave most ideally? (a) High temperature and low pressure, (b) high temperature and high pressure, (c) low temperature and high pressure, (d) low temperature and low pressure.

5.87 Write the van der Waals equation for a real gas. Explain the corrective terms for pressure and volume.

5.88 (a) A real gas is introduced into a flask of volume V. Is the corrected volume of the gas greater or less than V? (b) Ammonia has a larger a value than neon does (see Table 5.4). What can you conclude about the relative strength of the attractive forces between molecules of ammonia and between atoms of neon?

Problems

5.89 Using the data shown in Table 5.4, calculate the pressure exerted by 2.50 moles of CO_2 confined in a volume of 5.00 L at 450 K. Compare the pressure with that predicted by the ideal gas equation.

5.90 At 27°C, 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

Additional Problems

5.91 Discuss the following phenomena in terms of the gas laws: (a) the pressure increase in an automobile tire on a hot day, (b) the "popping" of a paper bag, (c) the expansion of a weather balloon as it rises in the air, (d) the loud noise heard when a lightbulb shatters.

5.92 Under the same conditions of temperature and pressure, which of the following gases would behave most ideally: Ne, N_2, or CH_4? Explain.

5.93 Nitroglycerin, an explosive compound, decomposes according to the equation

$$4C_3H_5(NO_3)_3(s) \longrightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g)$$

Calculate the total volume of gases when collected at 1.2 atm and 25°C from 2.6×10^2 g of nitroglycerin.

What are the partial pressures of the gases under these conditions?

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

5.95 When ammonium nitrite (NH_4NO_2) is heated, it decomposes to give nitrogen gas. This property is used to inflate some tennis balls. (a) Write a balanced equation for the reaction. (b) Calculate the quantity (in grams) of NH_4NO_2 needed to inflate a tennis ball to a volume of 86.2 mL at 1.20 atm and 22°C.

5.96 The percent by mass of bicarbonate (HCO_3^-) in a certain Alka-Seltzer product is 32.5 percent. Calculate the volume of CO_2 generated (in mL) at 37°C and 1.00 atm when a person ingests a 3.29-g tablet. (*Hint:* The reaction is between HCO_3^- and HCl acid in the stomach.)

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

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

$$\mathrm{Ni}(s) + 4\mathrm{CO}(g) \longrightarrow \mathrm{Ni(CO)_4}(g)$$

This reaction separates nickel from other solid impurities. (a) Starting with 86.4 g of Ni, calculate the pressure of $Ni(CO)_4$ in a container of volume 4.00 L. (Assume the above reaction goes to completion.) (b) At temperatures above 43°C, the pressure of the gas is observed to increase much more rapidly than predicted by the ideal gas equation. Explain.

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

5.100 A healthy adult exhales about 5.0×10^2 mL of a gaseous mixture with each breath. Calculate the number of molecules present in this volume at 37°C and 1.1 atm. List the major components of this gaseous mixture.

5.101 Sodium bicarbonate ($NaHCO_3$) is called baking soda because when heated, it releases carbon dioxide gas, which is responsible for the rising of cookies, doughnuts, and bread. (a) Calculate the volume (in liters) of CO_2 produced by heating 5.0 g of $NaHCO_3$ at 180°C and 1.3 atm. (b) Ammonium bicarbonate (NH_4HCO_3) has also been used for the same purpose. Suggest one advantage and one disadvantage of using NH_4HCO_3 instead of $NaHCO_3$ for baking.

5.102 A barometer having a cross-sectional area of 1.00 cm^2 at sea level measures a pressure of 76.0 cm of mercury. The pressure exerted by this column of mercury is equal to the pressure exerted by all the air on 1 cm^2 of Earth's surface. Given that the density of mercury is 13.6 g/mL and the average radius of Earth is 6371 km, calculate the total mass of Earth's atmosphere in kilograms. (*Hint:* The surface area of a sphere is $4\pi r^2$ where r is the radius of the sphere.)

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

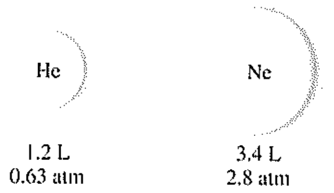
$$2\mathrm{NaOH}(aq) + 2\mathrm{Al}(s) + 6\mathrm{H_2O}(l) \longrightarrow 2\mathrm{NaAl(OH)_4}(aq) + 3\mathrm{H_2}(g)$$

The heat generated in this reaction helps melt away obstructions such as grease, and the hydrogen gas released stirs up the solids clogging the drain. Calculate the volume of H_2 formed at 23°C and 1.00 atm if 3.12 g of Al are treated with an excess of NaOH.

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

5.105 Propane (C_3H_8) burns in oxygen to produce carbon dioxide gas and water vapor. (a) Write a balanced equation for this reaction. (b) Calculate the number of liters of carbon dioxide measured at STP that could be produced from 7.45 g of propane.

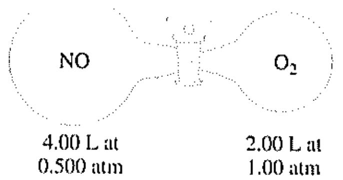
5.106 Consider the following apparatus. Calculate the partial pressures of helium and neon after the stopcock is open. The temperature remains constant at 16°C.



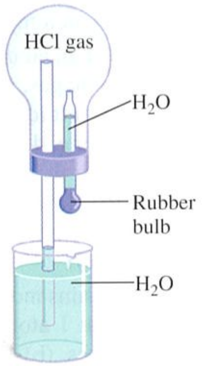
5.107 Nitric oxide (NO) reacts with molecular oxygen as follows:

$$2\mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{NO_2}(g)$$

Initially NO and O_2 are separated as shown here. When the valve is opened, the reaction quickly goes to completion. Determine what gases remain at the end and calculate their partial pressures. Assume that the temperature remains constant at 25°C.



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

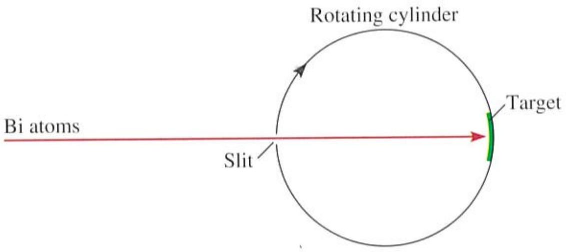


5.109 Describe how you would measure, by either chemical or physical means, the partial pressures of a mixture of gases of the following composition: (a) CO_2 and H_2, (b) He and N_2.

5.110 A certain hydrate has the formula $MgSO_4 \cdot xH_2O$. A quantity of 54.2 g of the compound is heated in an oven to drive off the water. If the steam generated exerts a pressure of 24.8 atm in a 2.00-L container at 120°C, calculate x.

5.111 A mixture of Na_2CO_3 and $MgCO_3$ of mass 7.63 g is reacted with an excess of hydrochloric acid. The CO_2 gas generated occupies a volume of 1.67 L at 1.24 atm and 26°C. From these data, calculate the percent composition by mass of Na_2CO_3 in the mixture.

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



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

5.114 Commercially, compressed oxygen is sold in metal cylinders. If a 120-L cylinder is filled with oxygen to a pressure of 132 atm at 22°C, what is the mass (in grams) of O_2 present? How many liters of O_2 gas at 1.00 atm and 22°C could the cylinder produce? (Assume ideal behavior.)

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

5.116 Ethylene gas (C_2H_4) is emitted by fruits and is known to be responsible for their ripening. Based on this information, explain why a bunch of bananas ripens faster in a closed paper bag than in a bowl.

5.117 About 8.0×10^6 tons of urea $[(NH_2)_2CO]$ are used annually as a fertilizer. The urea is prepared at 200°C and under high-pressure conditions from carbon dioxide and ammonia (the products are urea and steam). Calculate the volume of ammonia (in liters) measured at 150 atm needed to prepare 1.0 ton of urea.

5.118 Some ballpoint pens have a small hole in the main body of the pen. What is the purpose of this hole?

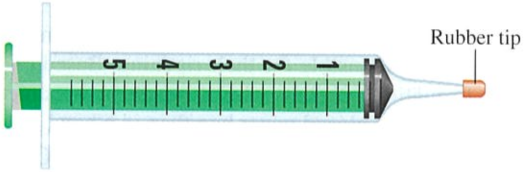
5.119 The gas laws are vitally important to scuba divers. The pressure exerted by 33 ft of seawater is equivalent to 1 atm pressure. (a) A diver ascends quickly to the surface of the water from a depth of 36 ft without exhaling gas from his lungs. By what factor will the volume of his lungs increase by the time he reaches the surface? Assume that the temperature is constant. (b) The partial pressure of oxygen in air is about 0.20 atm. (Air is 20 percent oxygen by volume.) In deep-sea diving, the composition of air the diver breathes must be changed to maintain this partial pressure. What must the oxygen content (in percent by volume) be when the total pressure exerted on the diver is 4.0 atm? (At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of gases.) (*Hint:* See Chemistry in Action essay on p. 198.)

5.120 Nitrous oxide (N_2O) can be obtained by the thermal decomposition of ammonium nitrate (NH_4NO_3). (a) Write a balanced equation for the reaction. (b) In a certain experiment, a student obtains 0.340 L of the gas at 718 mmHg and 24°C. If the gas weighs 0.580 g, calculate the value of the gas constant.

5.121 Two vessels are labeled A and B. Vessel A contains NH_3 gas at 70°C, and vessel B contains Ne gas at the same temperature. If the average kinetic energy of NH_3 is 7.1×10^{-21} J/molecule, calculate the mean-square speed of Ne atoms in m^2/s^2.

5.122 Which of the following molecules has the largest a value: CH_4, F_2, C_6H_6, Ne?

5.123 The following procedure is a simple though somewhat crude way to measure the molar mass of a gas. A liquid of mass 0.0184 g is introduced into a syringe like the one shown here by injection through the rubber tip using a hypodermic needle. The syringe is then transferred to a temperature bath heated to 45°C, and the liquid vaporizes. The final volume of the vapor (measured by the outward movement of the plunger) is 5.58 mL and the atmospheric pressure is 760 mmHg. Given that the compound's empirical formula is CH_2, determine the molar mass of the compound.



5.124 In 1995 a man suffocated as he walked by an abandoned mine in England. At that moment there was a sharp drop in atmospheric pressure due to a change in the weather. Suggest what might have caused the man's death.

5.125 Acidic oxides such as carbon dioxide react with basic oxides like calcium oxide (CaO) and barium oxide (BaO) to form salts (metal carbonates). (a) Write equations representing these two reactions. (b) A student placed a mixture of BaO and CaO of combined mass 4.88 g in a 1.46-L flask containing carbon dioxide gas at 35°C and 746 mmHg. After the reactions were complete, she found that the CO_2 pressure had dropped to 252 mmHg. Calculate the percent composition by mass of the mixture. Assume volumes of the solids are negligible.

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

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

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

5.129 Atop Mt. Everest, the atmospheric pressure is 210 mmHg and the air density is 0.426 kg/m^3. (a) Calculate the air temperature, given that the molar mass of air is 29.0 g/mol. (b) Assuming no change in air composition, calculate the percent decrease in oxygen gas from sea level to the top of Mt. Everest.

5.130 Relative humidity is defined as the ratio (expressed as a percentage) of the partial pressure of water vapor in the air to the equilibrium vapor pressure (see Table 5.3) at a given temperature. On a certain summer day in North Carolina the partial pressure of water vapor in the air is 3.9×10^3 Pa at 30°C. Calculate the relative humidity.

5.131 Under the same conditions of temperature and pressure, why does one liter of moist air weigh less than one liter of dry air? In weather forecasts, an oncoming low-pressure front usually means imminent rainfall. Explain.

5.132 Air entering the lungs ends up in tiny sacs called alveoli. It is from the alveoli that oxygen diffuses into the blood. The average radius of the alveoli is 0.0050 cm and the air inside contains 14 percent oxygen. Assuming that the pressure in the alveoli is 1.0 atm and the temperature is 37°C, calculate the number of oxygen molecules in one of the alveoli. (*Hint:* The volume of a sphere of radius r is $\frac{4}{3}\pi r^3$.)

5.133 A student breaks a thermometer and spills most of the mercury (Hg) onto the floor of a laboratory that measures 15.2 m long, 6.6 m wide, and 2.4 m high. (a) Calculate the mass of mercury vapor (in grams) in the room at 20°C. The vapor pressure of mercury at 20°C is 1.7×10^{-6} atm. (b) Does the concentration of mercury vapor exceed the air quality regulation of

0.050 mg Hg/m^3 of air? (c) One way to treat small quantities of spilled mercury is to spray sulfur powder over the metal. Suggest a physical and a chemical reason for this action.

5.134 Nitrogen forms several gaseous oxides. One of them has a density of 1.33 g/L measured at 764 mmHg and 150°C. Write the formula of the compound.

5.135 Nitrogen dioxide (NO_2) cannot be obtained in a pure form in the gas phase because it exists as a mixture of NO_2 and N_2O_4. At 25°C and 0.98 atm, the density of this gas mixture is 2.7 g/L. What is the partial pressure of each gas?

5.136 The Chemistry in Action essay on p. 205 describes the cooling of rubidium vapor to 1.7×10^{-7} K. Calculate the root-mean-square speed and average kinetic energy of a Rb atom at this temperature.

5.137 Lithium hydride reacts with water as follows:

$$\text{LiH}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{LiOH}(aq) + \text{H}_2(g)$$

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

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

5.139 Venus's atmosphere is composed of 96.5 percent CO_2, 3.5 percent N_2, and 0.015 percent SO_2 by volume. Its standard atmospheric pressure is 9.0×10^6 Pa. Calculate the partial pressures of the gases in pascals.

5.140 A student tries to determine the volume of a bulb like the one shown on p. 188. These are her results: Mass of the bulb filled with dry air at 23°C and 744 mmHg = 91.6843 g; mass of evacuated bulb = 91.4715 g. Assume the composition of air is 78 percent N_2, 21 percent O_2, and 1 percent argon. What is the volume (in milliliters) of the bulb? (*Hint:* First calculate the average molar mass of air, as shown in Problem 3.140.)

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

5.142 It has been said that every breath we take, on average, contains molecules that were once exhaled by Wolfgang Amadeus Mozart (1756–1791). The following calculations demonstrate the validity of this statement. (a) Calculate the total number of molecules in the atmosphere. (*Hint:* Use the result in Problem 5.102 and 29.0 g/mol as the molar mass of air.) (b) Assuming the volume of every breath (inhale or exhale) is 500 mL, calculate the number of molecules exhaled in each breath at 37°C, which is the body temperature. (c) If Mozart's lifespan was exactly 35 years, what is the number of molecules he exhaled in that period? (Given that an average person breathes 12 times per minute.) (d) Calculate the fraction of molecules in the atmosphere that was exhaled by Mozart. How many of Mozart's molecules do we breathe in with every inhale of air? Round off your answer to one significant figure. (e) List three important assumptions in these calculations.

5.143 At what temperature will He atoms have the same u_{rms} value as N_2 molecules at 25°C?

5.144 Estimate the distance (in nanometers) between molecules of water vapor at 100°C and 1.0 atm. Assume ideal behavior. Repeat the calculation for liquid water at 100°C, given that the density of water is 0.96 g/cm^3 at that temperature. Comment on your results. (Assume water molecule to be a sphere with a diameter of 0.3 nm.) (*Hint:* First calculate the number density of water molecules. Next, convert the number density to linear density, that is, number of molecules in one direction.)

5.145 Which of the noble gases would not behave ideally under any circumstance? Why?

5.146 A relation known as the barometric formula is useful for estimating the change in atmospheric pressure with altitude. The formula is given by $P = P_0 e^{-g\mathcal{M}h/RT}$, where P and P_0 are the pressures at height h and sea level, respectively, g is the acceleration due to gravity (9.8 m/s^2), $\mathcal{M}$ is the average molar mass of air (29.0 g/mol), and R is the gas constant. Calculate the atmospheric pressure in atm at a height of 5.0 km, assuming the temperature is constant at 5°C and $P_0 = 1.0$ atm.

5.147 A 5.72-g sample of graphite was heated with 68.4 g of O_2 in a 8.00-L flask. The reaction that took place was

$$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$$

After the reaction was complete, the temperature in the flask was 182°C. What was the total pressure inside the flask?

5.148 A 6.11-g sample of a Cu-Zn alloy reacts with HCl acid to produce hydrogen gas. If the hydrogen gas has a volume of 1.26 L at 22°C and 728 mmHg, what is the percent of Zn in the alloy? (*Hint:* Cu does not react with HCl.)

5.149 A stockroom supervisor measured the contents of a partially filled 25.0-gallon acetone drum on a day when the temperature was 18.0°C and atmospheric pressure was 750 mmHg, and found that 15.4 gallons of the solvent remained. After tightly sealing the drum, an assistant dropped the drum while carrying it upstairs to the organic laboratory. The drum was dented and its internal volume was decreased to 20.4 gallons. What is the total pressure inside the drum after the accident? The vapor pressure of acetone at 18.0°C is 400 mmHg. (*Hint:* At the time the drum was sealed, the pressure inside the drum, which is equal to the sum of the pressures of air and acetone, was equal to the atmospheric pressure.)

Special Problems

5.150 In 2.00 min, 29.7 mL of He effuse through a small hole. Under the same conditions of pressure and temperature, 10.0 mL of a mixture of CO and CO_2 effuse through the hole in the same amount of time. Calculate the percent composition by volume of the mixture.

5.151 Referring to Figure 5.22, explain the following: (a) Why do the curves dip below the horizontal line labeled ideal gas at low pressures and then why do they arise above the horizontal line at high pressures? (b) Why do the curves all converge to 1 at very low pressures? (c) Each curve intercepts the horizontal line labeled ideal gas. Does it mean that at that point the gas behaves ideally?

5.152 A mixture of methane (CH_4) and ethane (C_2H_6) is stored in a container at 294 mmHg. The gases are burned in air to form CO_2 and H_2O. If the pressure of CO_2 is 356 mmHg measured at the same temperature and volume as the original mixture, calculate the mole fractions of the gases.

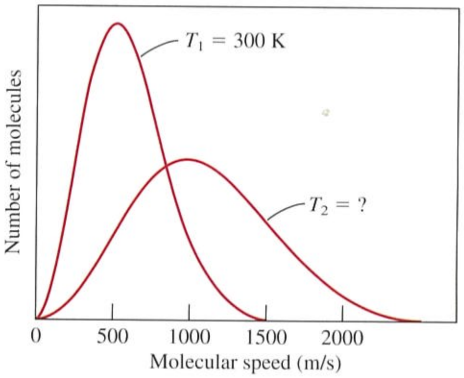
5.153 Use the kinetic theory of gases to explain why hot air rises.

5.154 One way to gain a physical understanding of b in the van der Waals equation is to calculate the "excluded volume." Assume that the distance of closest approach between two similar atoms is the sum of their radii ($2r$). (a) Calculate the volume around each atom into which the center of another atom cannot penetrate. (b) From your result in (a), calculate the excluded volume for 1 mole of the atoms, which is the constant b. How does this volume compare with the sum of the volumes of 1 mole of the atoms?

5.155 A 5.00-mole sample of NH_3 gas is kept in a 1.92 L container at 300 K. If the van der Waals equation is assumed to give the correct answer for the pressure of the gas, calculate the percent error made in using the ideal gas equation to calculate the pressure.

5.156 The root-mean-square speed of a certain gaseous oxide is 493 m/s at 20°C. What is the molecular formula of the compound?

5.157 Referring to Figure 5.17, we see that the maximum of each speed distribution plot is called the most probable speed (u_{mp}) because it is the speed possessed by the largest number of molecules. It is given by $u_{\mathrm{mp}} = \sqrt{2RT/\mathcal{M}}$. (a) Compare u_{mp} with u_{rms} for nitrogen at 25°C. (b) The following diagram shows the Maxwell speed distribution curves for an ideal gas at two different temperatures T_1 and T_2. Calculate the value of T_2.



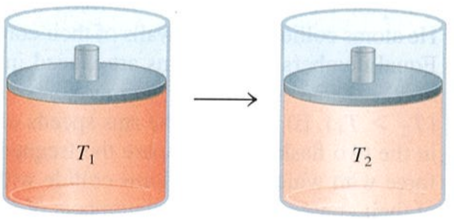
5.158 A gaseous reaction takes place at constant volume and constant pressure in a cylinder shown here. Which of the following equations best describes the reaction? The initial temperature (T_1) is twice that of the final temperature (T_2).

(a) $A + B \longrightarrow C$

(b) $AB \longrightarrow C + D$

(c) $A + B \longrightarrow C + D$

(d) $A + B \longrightarrow 2C + D$



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** B_2H_6. **5.11** 96.9 L. **5.12** 4.75 L. **5.13** 0.338 *M*. **5.14** CH_4: 1.29 atm; C_2H_6: 0.0657 atm; C_3H_8: 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.

CHEMICAL Mystery

Out of Oxygen[†]

In September 1991 four men and four women entered the world's largest glass bubble, known as Biosphere II, to test the idea that humans could design and build a totally self-contained ecosystem, a model for some future colony on another planet. Biosphere II (Earth is considered Biosphere I) was a 3-acre mini-world, complete with a tropical rain forest, savanna, marsh, desert, and working farm that was intended to be fully self-sufficient. This unique experiment was to continue for 2 to 3 years, but almost immediately there were signs that the project could be in jeopardy.

Soon after the bubble had been sealed, sensors inside the facility showed that the concentration of oxygen in Biosphere II's atmosphere had fallen from its initial level of 21 percent (by volume), while the amount of carbon dioxide had risen from a level of 0.035 percent (by volume), or 350 ppm (parts per million). Alarmingly, the oxygen level continued to fall at a rate of about 0.5 percent a month and the level of carbon dioxide kept rising, forcing the crew to turn on electrically powered chemical scrubbers, similar to those on submarines, to remove some of the excess CO_2. Gradually the CO_2 level stabilized around 4000 ppm, which is high but not dangerous. The loss of oxygen did not stop, though. By January 1993—16 months into the experiment—the oxygen concentration had dropped to 14 percent, which is equivalent to the O_2 concentration in air at an elevation of 4360 m (14,300 ft). The crew began having trouble performing normal tasks. For their safety it was necessary to pump pure oxygen into Biosphere II.

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

Identifying the cause of oxygen depiction raised another question. Metabolism produces carbon dioxide. Based on the amount of oxygen consumed by the microbes, the CO_2 level should have been at 40,000 ppm, 10 times what was measured. What happened to the excess gas? After ruling out leakage to the outside world and reactions between CO_2 with compounds in the soils and in water, scientists found that the concrete inside Biosphere II was consuming large amounts of CO_2!

Concrete is a mixture of sand and gravel held together by a binding agent that is a mixture of calcium silicate hydrates and calcium hydroxide. The calcium hydroxide is the key ingredient in the CO_2 mystery. Carbon dioxide diffuses into the porous structure of concrete, then reacts with calcium hydroxide to form calcium carbonate and water:

$$Ca(OH)_2(s) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

Under normal conditions, this reaction goes on slowly. But CO_2 concentrations in Biosphere II were much higher than normal, so the reaction proceeded much faster. In fact, in just over 2 years,

---

[†] Adapted with permission from "Biosphere II: Out of Oxygen," by Joe Alper, CHEM MATTERS, February, 1995, p. 8. Copyright 1995 American Chemical Society.

Vegetation in Biosphere II.

$CaCO_3$ had accumulated to a depth of more than 2 cm in Biosphere II's concrete. Some 10,000 m^2 of exposed concrete was hiding 500,000 to 1,500,000 moles of CO_2.

The water produced in the reaction between $Ca(OH)_2$ and CO_2 created another problem: CO_2 also reacts with water to form carbonic acid (H_2CO_3), and hydrogen ions produced by the acid promote the corrosion of the reinforcing iron bars in the concrete, thereby weakening its structure. This situation was dealt with effectively by painting all concrete surfaces with an impermeable coating.

In the meantime, the decline in oxygen (and hence also the rise in carbon dioxide) slowed, perhaps because there was now less organic matter in the soils and also because new lights in the agricultural areas may have boosted photosynthesis. The project was terminated prematurely and in 1996, the facility was transformed into a science education and research center. As of 2005, the Biosphere is up for sale.

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

Chemical Clues

1. What solution would you use in a chemical scrubber to remove carbon dioxide?
2. Photosynthesis converts carbon dioxide and water to carbohydrates and oxygen gas, while metabolism is the process by which carbohydrates react with oxygen to form carbon dioxide and water. Using glucose ($C_6H_{12}O_6$) to represent carbohydrates, write equations for these two processes.
3. Why was diffusion of O_2 from Biosphere II to the outside world not considered a possible cause for the depletion in oxygen?
4. Carbonic acid is a diprotic acid. Write equations for the stepwise ionization of the acid in water.
5. What are the factors to consider in choosing a planet on which to build a structure like Biosphere II?