

3

Gas Laws and the Kinetic Theory

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- Key Concepts**
- 3-1** Avogadro's law. $n = kV$.
 - 3-2** The pressure of a gas, units of pressure.
 - 3-3** Boyle's law relating pressure and volume. $P = a/V$.
 - 3-4** Charles' law relating volume and temperature. $V = bT$. Absolute zero and the Kelvin scale.
 - 3-5** The combined gas law: $PV = nRT$. Standard temperature and pressure. Ideal and nonideal behavior.
 - 3-6** The kinetic molecular theory. Molecular motion, molecular energy, and temperature.
 - 3-7** Predictions of the kinetic molecular theory. Molecular size and speed. Dalton's law of partial pressures. Graham's law of effusion.
 - 3-8** Real gases and deviations from ideal behavior. The van der Waals gas law.

Scientific research consists in seeing what everyone else has seen, but thinking what no one else has thought.

A. Szent-Gyorgyi (b. 1893)

The word *gas* comes from *gaos*, a Dutch form of the word *chaos*. Gases were the last substances to be understood chemically. Solids and liquids were easy to identify and differentiate, but the idea of different kinds of “ayres” came only slowly. Carbon dioxide was not prepared from limestone until 1756. Hydrogen was discovered in 1766; nitrogen, in 1772; and oxygen, in 1781. Although gases were late in being identified, they were the first substances whose physical properties could be explained in terms of simple laws. It is fortunate that when matter in this most elusive state is subjected to changes in temperature and pressure, it behaves according to rules much simpler than those that solids and liquids follow. Moreover, one of the best tests of the atomic theory is its ability to account for the behavior of gases. This is the story of the present chapter.

Given any trapped sample of gas, we can measure its mass, its volume, its pressure against the walls of a container, its viscosity, its temperature, and its rate of conducting heat and sound. We can also measure the rate at which it effuses through an orifice into another container, and the rate at which it diffuses through another gas. In this chapter we shall show that these properties are not independent of one another, that they can all be related by a simple theory which assumes that gases consist of moving and colliding particles.

3-1 AVOGADRO'S LAW

One of the most important hypotheses in the development of atomic theory was made by Amedeo Avogadro (1776–1856) in 1811. He proposed that equal volumes of all gases, at a specified temperature and pressure, contain equal numbers of molecules. This means that the density of a gas—in weight per unit volume—in grams per milliliter must be proportional to the molecular weight of the gas. If Avogadro's ideas had not been ignored for another 50 years, the process of arriving at a dependable set of atomic weights for the elements would have taken much less time. (The entire story is told in Chapter 6.) It was a belated tribute to an unjustly ignored scientist to call the number of molecules per mole **Avogadro's number**.

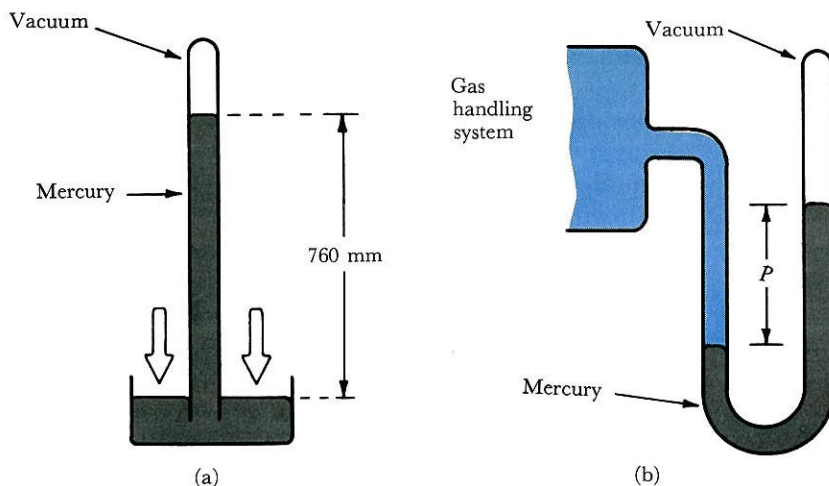
If we accept Avogadro's principle, then the number of molecules, n , and also the number of moles, is proportional to V , the volume of the gas:

$$n = \text{number of moles} = kV \quad (\text{at constant } P \text{ and } T) \quad (3-1)$$

In this equation, k is a proportionality constant; it changes with temperature and pressure. We shall be looking for other such relationships for gases—relationships connecting the pressure, P , the volume, V , the temperature, T , and the number of moles in a sample, n .

3-2 THE PRESSURE OF A GAS

If a glass tube, closed at one end, is filled with mercury (Hg), and the open end is inverted in a pool of mercury as in Figure 3-1a, the level of mercury in the tube will fall until the mercury column stands about 760 millimeters (mm) above the surface of the pool. The pressure produced at the pool surface by the weight of the mercury column is balanced exactly by the pressure of the surrounding atmosphere. Because there is a balance of opposing pressures, more mercury will not flow into or out of the tube. A device such as this (called a *barometer*) can measure atmospheric pressure, as Italian mathematician and physicist Evangelista Torricelli (1608–1647) first realized. He showed that it was the *pressure* at the bottom of the mercury column that mattered, and not the total weight of mercury; thus, the height of mercury in a barometer tube is independent of the size or shape of the tube. Atmospheric pressure at sea level supports a column of mercury 760 mm high. Because mercury columns were used so often in early pressure experiments, the “millimeter of mercury” became a common unit of pressure. Pressure is force per unit area ($P = F/A$), and the SI unit of pressure is the pascal (Pa), defined as 1 newton per square meter (N m^{-2}). (The newton, as you may recall from Chapter 2, is the force that will impart an acceleration of 1 m sec^{-2} to a 1-kg mass; $1 \text{ N} = 1 \text{ kg m sec}^{-2}$.)

**Figure 3-1**

Measuring gas pressure. (a) Torricellian barometer. When a mercury-filled tube is inverted in a dish of mercury, the level in the tube falls, thereby leaving a vacuum at the top of the tube. Only a trace of mercury vapor is present in the space at the top. The height of the column is determined by the pressure of the atmosphere on the mercury in the reservoir. (b) In a gas-handling system, pressure P (in millimeters of Hg) is determined by measuring the difference in heights of the two mercury columns of a manometer. If the system is evacuated completely, the levels are equal.

Example 1

The density of liquid mercury is 13.596 g cm^{-3} . How would you express a pressure of 1 mm Hg in pascals?

Solution

Imagine a sheet of mercury 1 m square and 1 mm thick. Converting first to centimeters for convenience, we would find its volume to be

$$0.100 \text{ cm} \times 100 \text{ cm} \times 100 \text{ cm} = 1000 \text{ cm}^3$$

and its mass to be

$$1000 \text{ cm}^3 \times 13.596 \text{ g cm}^{-3} = 13,596 \text{ g or } 13.596 \text{ kg}$$

Since force is equal to mass times acceleration, and the acceleration of gravity at sea level, g , is 9.806 m sec^{-2} , the force exerted by the mercury on its supporting table would be

$$F = mg$$

$$F = 13.596 \text{ kg} \times 9.806 \text{ m sec}^{-2} = 133.32 \text{ kg m sec}^{-2}, \text{ or } 133.32 \text{ N}$$

Since the area of the sheet is 1 m^2 , the pressure on the table would be

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

$$P = \frac{133.32 \text{ N}}{1 \text{ m}^2} = 133.32 \text{ N m}^{-2} = 133.32 \text{ pascals (Pa)}$$

Example 2

Standard sea level pressure is exactly 760 mm Hg. Express this in pascals.

Solution

From Example 1, we know that a pressure of 1 mm Hg is equal to 133.3 Pa. Therefore,

$$760 \text{ mm Hg} \times 133.32 \text{ Pa mm}^{-1} = 101,323 \text{ Pa}$$

The pascal is too small a unit to be convenient for measuring gas pressures, just as the cubic meter is too large to be convenient for measuring liquid volumes. Hence we shall follow a long-established tradition of measuring gas pressures in standard atmospheres, where

$$1 \text{ atmosphere (atm)} = 101,325 \text{ Pa} = 760 \text{ mm Hg}$$

The atmosphere then becomes an auxiliary or secondary unit to the strict SI, like the liter for volume, and the charge on the electron for ionic charges.

Example 3

At 8000 ft in the Colorado Rockies, the pressure of the atmosphere is approximately three-quarters what it is at sea level. Express this pressure in standard atmospheres, in pascals, and in millimeters of mercury.

Solution

The pressure is 0.750 atm, 76,000 Pa, or 570 mm Hg.

3-3 BOYLE'S LAW RELATING PRESSURE AND VOLUME

Robert Boyle (1627–1691), who gave us the first operational definition of an element (see Chapter 6), was also interested in phenomena occurring in evacuated spaces. When devising vacuum pumps for removing air from vessels, he noticed a property familiar to anyone who has used a hand pump for inflating a tire or football, or who has squeezed a balloon without breaking

it: As air is compressed, it pushes back with increased vigor. Boyle called this the “spring of the air,” and measured it with the simple device shown in Figure 3-2a and b.

Boyle trapped a quantity of air in the closed end of the J-tube as in Figure 3-2a, and then compressed it by pouring increasing amounts of mercury into the open end (b). At any point in the experiment, the total pressure on the enclosed gas is the atmospheric pressure *plus* that produced

Figure 3-2

Dependence of volume of gas sample on pressure. (a) The simple J-tube apparatus used by Boyle to measure pressure and volume. When the height of the column is equal in the open and closed parts of the tube, the pressure exerted on the gas sample is equal to atmospheric pressure. (b) The pressure on the gas is increased by adding mercury to the tube. (c) The gas burette, a device employing the same principle as the J-tube apparatus. The gas is at atmospheric pressure. (d) The pressure on the gas is increased by raising the mercury reservoir. In (a) and (b) the cross section of the J-tube is assumed constant, so the height of the gas sample is a measure of volume. In (c) and (d) the volume of the gas is measured by the calibrated burette.

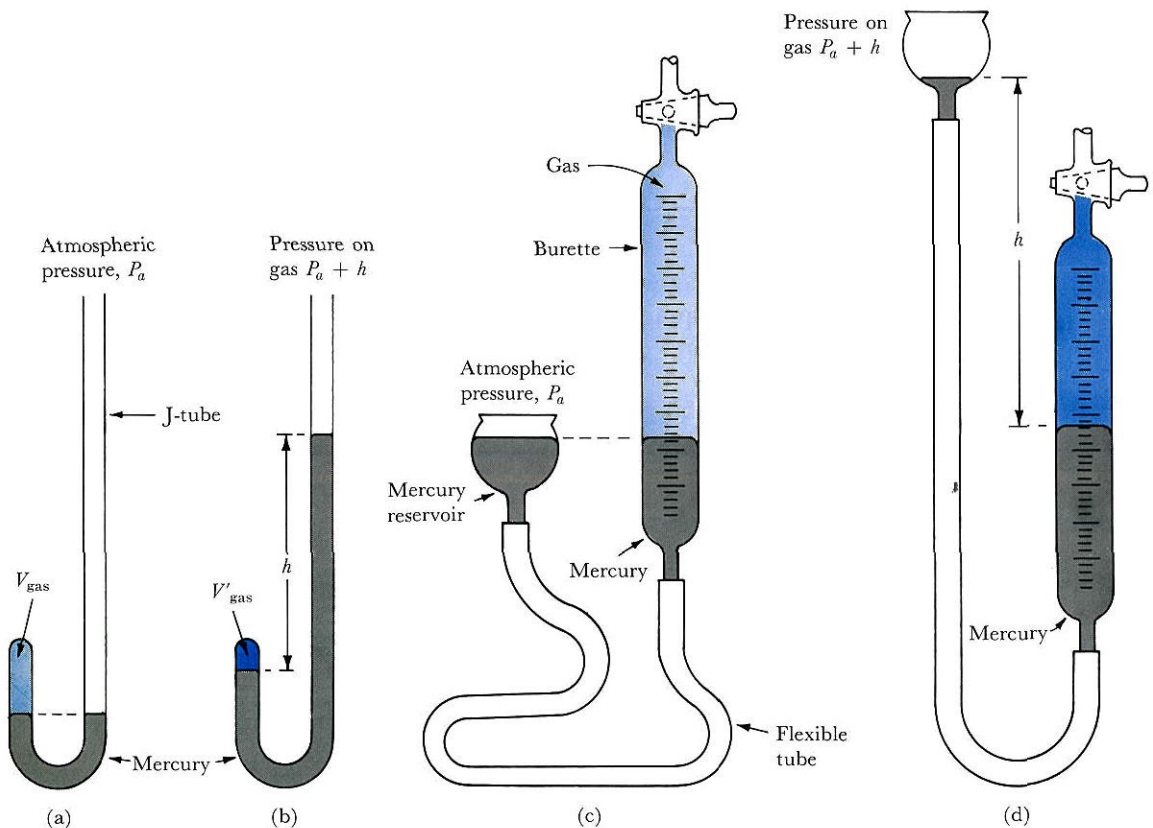


Table 3-1**Boyle's Original Data Relating Pressure and Volume for Atmospheric Air^a**

	Volume (index marks along uniform bore tubing) ^b	Pressure (inches of mercury) ^c	$P \times V$
A	48	$29\frac{2}{16}$	1400
	46	$30\frac{9}{16}$	1406
	44	$31\frac{15}{16}$	1408
	42	$33\frac{8}{16}$	1410
	40	$35\frac{5}{16}$	1412
	38	37	1408
	36	$39\frac{5}{16}$	1416
	34	$41\frac{10}{16}$	1420
	32	$44\frac{3}{16}$	1416
	30	$47\frac{1}{16}$	1414
	28	$50\frac{5}{16}$	1410
	26	$54\frac{5}{16}$	1412
	24	$58\frac{13}{16}$	1414
	23	$61\frac{5}{16}$	1411
	22	$64\frac{1}{16}$	1411
	21	$67\frac{1}{16}$	1410
	20	$70\frac{11}{16}$	1415
	19	$74\frac{7}{16}$	1410
	18	$77\frac{14}{16}$	1403
	17	$82\frac{12}{16}$	1410
	16	$87\frac{14}{16}$	1407
	15	$93\frac{1}{16}$	1398
	14	$100\frac{7}{16}$	1408
	13	$107\frac{13}{16}$	1395
B	12	$111\frac{9}{16}$	1342

^aReprinted by permission from J. B. Conant, *Harvard Case Histories in Experimental Science*, Harvard University Press, Cambridge, 1957, Vol. 1, p. 53.

^bEnd data points A and B correspond to those labels on Figure 3-3.

^cThe height, h , in Figure 3-2b, plus $29\frac{1}{8}$ inches for atmospheric pressure.

by the excess mercury, which has height h in the open tube. Boyle's original pressure–volume data on air are given in Table 3-1. Although he did not take special pains to keep the temperature of the gas constant, it probably varied only slightly. Boyle did note that the heat from a candle flame produced a drastic alteration in the behavior of air.

Analysis of Data

After a scientist obtains data such as those in Table 3-1, he then attempts to infer a mathematical equation relating the two mutually dependent quantities that he has measured. One technique is to plot various powers of each quantity against one another until a straight line is obtained. The general equation for a straight line is

$$y = ax + b \quad (3-2)$$

in which x and y are variables and a and b are constants. If b is zero, the line passes through the origin.

Figure 3-3 shows several possible plots of the data for pressure, P , and volume, V , given in Table 3-1. The plots of P versus $1/V$ and V versus $1/P$ are straight lines through the origin. A plot of the logarithm of P versus the logarithm of V is also a straight line with negative slope of -1 . From these plots the equivalent equations are deduced:

$$P = \frac{a}{V} \quad (3-3a)$$

$$V = \frac{a}{P} \quad (3-3b)$$

and

$$\log V = \log a - \log P \quad (3-3c)$$

These equations represent variants of the usual formulation of Boyle's law: *For a given number of moles of gas molecules, the pressure is inversely proportional to the volume if the temperature is held constant.*

When the relationship between two measured quantities is as simple as this one, it can be deduced numerically as well. If each value of P is multiplied by the corresponding value of V , the products all are nearly the same for a single sample of gas at constant temperature (Table 3-1). Thus,

$$PV = a \simeq 1410 \quad (3-3d)$$

Equation 3-3d represents the hyperbola obtained by plotting P versus V (Figure 3-3a). This experimental function relating P and V now can be checked by plotting PV against P to see if a horizontal straight line is obtained (Figure 3-3e).

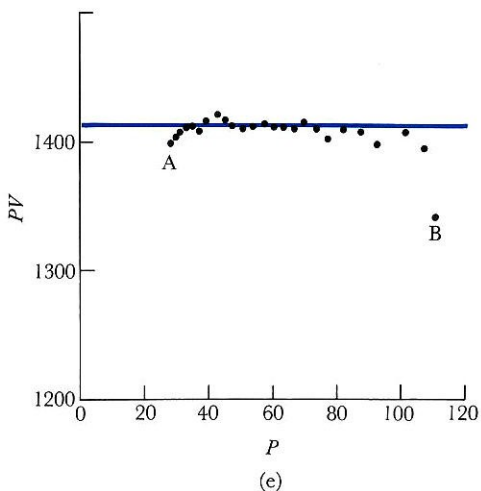
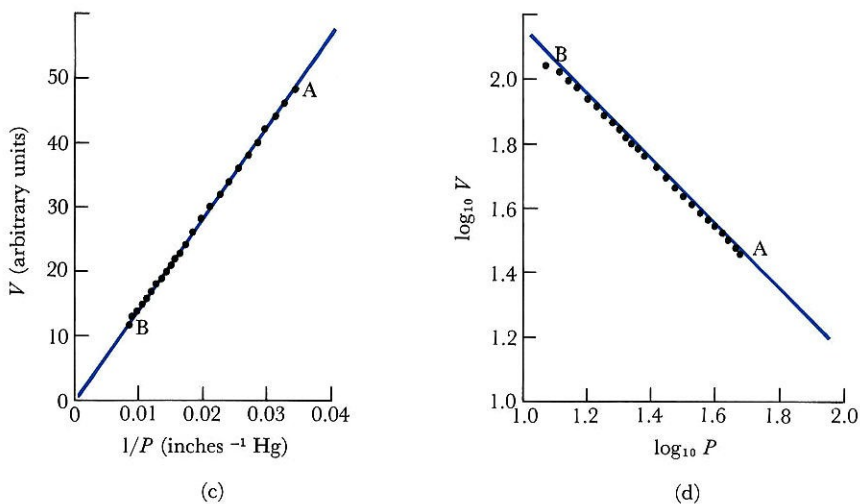
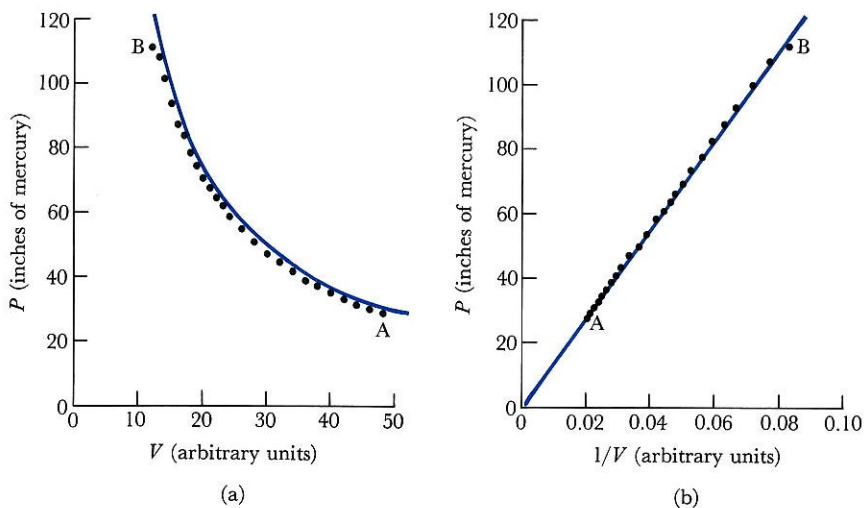
Boyle found that for a given quantity of any gas at constant temperature, the relationship between P and V is given reasonably precisely by

$$PV = \text{constant} \quad (\text{at constant } T \text{ and } n) \quad (3-4)$$

For comparing the same gas sample at constant temperature under different pressure and volume conditions, Boyle's law can be written conveniently as

$$P_1V_1 = P_2V_2 \quad (3-5)$$

with the subscripts 1 and 2 representing the different conditions.

**Figure 3-3**

Plots of Boyle's data of Table 3-1 on various scales. (a) P versus V , which gives a hyperbola. (b) P versus $1/V$. (c) V versus $1/P$. (d) $\log V$ versus $\log P$. (e) PV versus P . A and B mark the same end data points in each plot. If the data are plotted as P versus $1/V$ (or V versus $1/P$), the curve obeys the linear equation $y = ax + b$, in which P is the y -coordinate and $1/V$ is the x coordinate. The proportionality constant a can be determined from the slope of the straight line in (b), or from the height of the horizontal line in (e). Note how sensitive plot (e), with its expanded vertical scale, is to errors in the data (and possibly unsuspected trends).

Example 4

Plastic bags of peanuts or potato chips purchased in Aspen, Colorado, are frequently puffed up because the air sealed inside at sea level has expanded under the lower surrounding pressure at the 8000-ft elevation. If 100 cm^3 of air are sealed inside a bag at sea level, what volume will the air occupy at the same temperature in Aspen? (Assume that the bag is so wrinkled that it does not limit gas expansion, and see Example 3 for missing data.)

Solution

Use Boyle's law in the form of equation 3-5, with subscript 1 representing sea level and subscript 2 representing 8000 ft. Then $P_1 = 1.000 \text{ atm}$, $V_1 = 100 \text{ cm}^3$, $P_2 = 0.750 \text{ atm}$, and V_2 is to be calculated:

$$P_1 V_1 = P_2 V_2$$

$$1.000 \text{ atm} \times 100 \text{ cm}^3 = 0.750 \text{ atm} \times V_2$$

$$V_2 = 133 \text{ cm}^3$$

3-4 CHARLES' LAW RELATING VOLUME AND TEMPERATURE

We know that air expands on heating, thereby decreasing its density. For this reason, balloons rise when inflated with warm air. About 100 years after Boyle derived his law, Jacques Charles (1746–1823), in France, measured the effect of changing temperature on the volume of an air sample. This measurement can be made quite easily with the device shown in Figure 3-4.

Figure 3-4

Experimental determination of the relationship between volume and temperature of a gas. The apparatus consists of a small capillary tube and a thermometer mounted on a ruled scale and immersed in a hot oil bath. As the system cools, the oil rises in the tube, and the length of air space and the temperature are measured at intervals. For a tube of constant bore, the length of the air space is a measure of the gas volume. So long as the bottom of the air space in the capillary is maintained at the same depth below the surface of the oil bath, the pressure in the capillary will be constant.

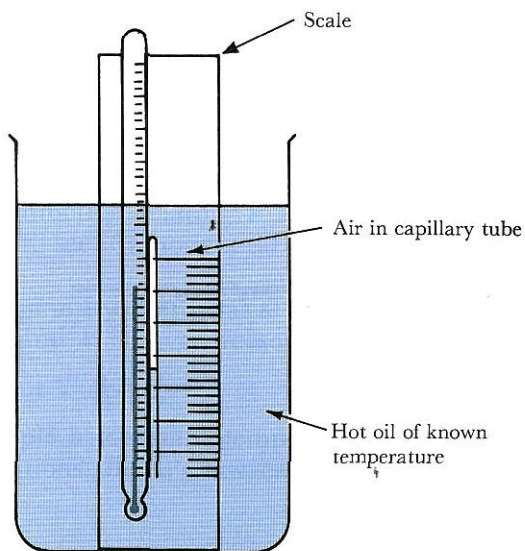
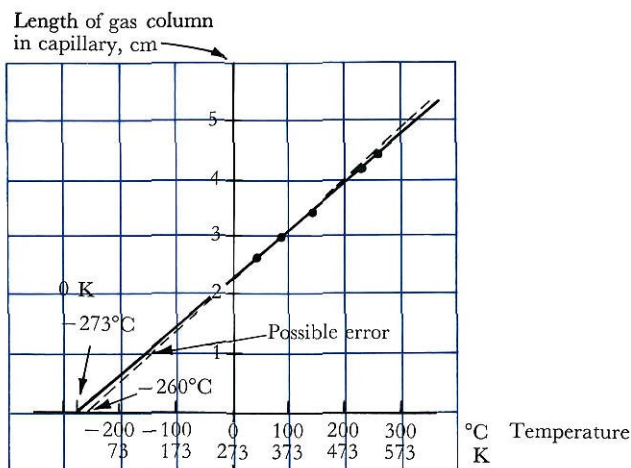


Figure 3-5

A plot of data obtained with the apparatus in Figure 3-4, showing that volume is proportional to the absolute temperature. Just such a plot employing the Celsius scale of temperature was originally used to locate the absolute zero of temperature. Notice how easily a small error in the slope of the line through the data points could produce a large error in the value of absolute zero. It should be clear that, if at all possible, such long extrapolations should be avoided.



Some sample data are plotted in Figure 3-5; these show that a graph of V versus T is a straight line with an extrapolated intercept of -273° on the Celsius scale of temperature, or -460° on the Fahrenheit scale. Charles expressed his law as

$$V = c(t + 273)$$

where V is the volume of gas sample, t is the temperature on the Celsius scale, and c is a proportionality constant.

Later, Lord Kelvin (1824–1907) suggested that the intercept of -273°C represented an absolute minimum of temperature below which it is not possible to go. Scientists now use Kelvin's absolute scale of temperature with $0\text{ K} = -273.15^\circ\text{C}$ and $0^\circ\text{C} = 273.15\text{ K}$. Charles' law is expressed as

$$V = cT \quad (\text{at constant } P \text{ and } n) \quad (3-6)$$

where T is the absolute Kelvin temperature (i.e., $T = t + 273.15$). Equation 3-6 indicates that *at constant pressure the volume of a given number of moles of gas is directly proportional to the absolute temperature*. For light gases such as hydrogen and helium, Charles' law is so accurate that gas thermometers often replace mercury thermometers for precise temperature measurement (Figure 3-6). A mercury thermometer calibrated to read 0°C in a water–ice mixture and 100°C in boiling water is inaccurate by as much as 0.1 degree (deg) at intermediate points, whereas a hydrogen thermometer is much more accurate throughout this region.

If the same gas sample is being compared at constant pressure but different temperatures and volumes, then Charles' law can be written as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{V_1}{V_2} = \frac{T_1}{T_2} \quad (3-7)$$

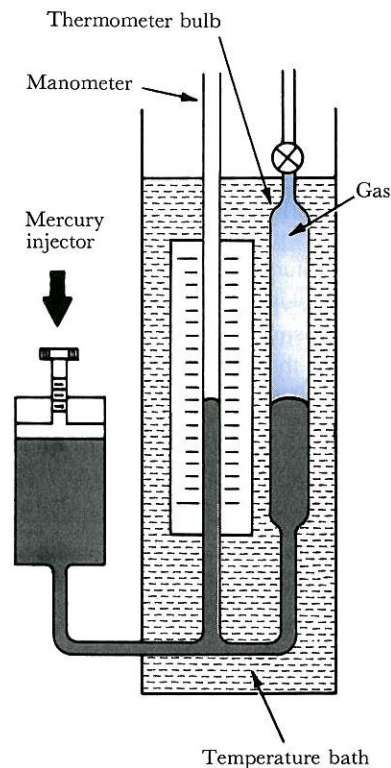


Figure 3-6

A simple gas thermometer. The gas volume is a measure of the absolute temperature. The scale can be calibrated with the freezing point (0°C) and boiling point (100°C) of water. The mercury is injected into or removed from the apparatus to maintain constant atmospheric pressure.

This way of writing the expression emphasizes the fact that the ratio of volumes matches the ratio of absolute temperatures, if pressure and the number of moles are constant.

Example 5

The same plastic bag of peanuts mentioned in Example 4 is laid on a windowsill in the sun, where its temperature increases from 20°C to 30°C . If the original volume is 100.0 cm^3 , what is the final volume after warming?

Solution

$V_1 = 100.0\text{ cm}^3$; $T_1 = 20^{\circ}\text{C}$, or 293.15 K ; and $T_2 = 30^{\circ}\text{C}$, or 303.15 K . To calculate V_2 , we use equation 3-7:

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

Substituting our data and solving for V_2 , we get

$$\frac{100.0\text{ cm}^3}{293.15} = \frac{V_2}{303.15}$$

$$V_2 = \frac{303.15}{293.15} \times 100.0 \text{ cm}^3 = 103.4 \text{ cm}^3$$

Notice that the absolute Kelvin temperature (K) must be used, *not* the Celsius temperature.

3-5 THE COMBINED GAS LAW

The three gas equations that we have encountered so far all may be written in terms of the proportionality of volume to another quantity:

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

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

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

(The symbol \propto means “is proportional to.”) Therefore, the volume must be proportional to the product of these three terms, or

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

or

$$PV = nRT \quad (3-8)$$

where R is the proportionality constant. Equation 3-8 is known as the **ideal gas law**. It contains all of our earlier laws as special cases and, in addition, predicts more relationships that can be tested. For example, the French chemist and physicist Joseph Gay-Lussac verified the prediction that, at constant volume, the pressure of a fixed amount of gas is proportional to its absolute temperature. (In effect, equation 3-8 is a definition of the ideal gas; the differences between real gases and the hypothetical ideal gas are discussed in Section 3-8.)

The gas law is often useful when expressed in the form of ratios of starting and final variables. Suppose a fixed amount of gas at constant temperature is compressed from P_1 to P_2 , with volumes V_1 and V_2 . Then $P_1 = nRT/V_1$, $P_2 = nRT/V_2$, and the pressure ratio and volume ratio are related by

$$\frac{P_2}{P_1} = \frac{V_1}{V_2} \quad (T, n \text{ constant}) \quad (3-9)$$

This is Boyle's law in ratio form. In a similar way, as we have seen, Charles' law states that the ratio of starting volume to final volume matches the temperature ratio at constant pressure:

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \quad (P, n \text{ constant}) \quad (3-7)$$

Increasing the number of moles of gas at constant temperature and pressure by a certain factor increases the volume by the same factor:

$$\frac{V_2}{V_1} = \frac{n_2}{n_1} \quad (P, T \text{ constant}) \quad (3-10)$$

And increasing the number of moles of gas at constant temperature in a tank of fixed volume by a certain factor increases the pressure inside the tank by the same factor:

$$\frac{P_2}{P_1} = \frac{n_2}{n_1} \quad (T, V \text{ constant}) \quad (3-11)$$

You should be able to derive these equations and also the analogous equation that expresses Gay-Lussac's observations about pressure and temperature at constant volume easily from the ideal gas law.

Example 6

An old-fashioned diving bell is simply a cylinder closed at the top and open at the bottom, like an inverted drinking glass, with benches around the inside for the divers to sit on. Air pressure alone keeps the water out. A diver sitting in a bell that has an air volume of 8000 liters wants to drive the water level down by increasing the volume to 10,000 liters, because his feet are getting wet. If he filled the bell with 650 moles of an O_2 - N_2 mixture to begin with, how many more moles of gas will he have to release into the bell to obtain his desired volume increase?

Solution

This is a problem in changes of volume with number of moles; pressure and temperature remain constant. Therefore we use equation 3-10, with $V_1 = 8000$ liters, $V_2 = 10,000$ liters, and $n_1 = 650$ moles. We need to calculate n_2 . Substituting our data in equation 3-10 and solving for n_2 , we get

$$\begin{aligned} \frac{10,000 \text{ liters}}{8000 \text{ liters}} &= \frac{n_2}{650 \text{ moles}} \\ n_2 &= \frac{10,000 \text{ liters}}{8000 \text{ liters}} \times 650 \text{ moles} = 813 \text{ moles} \end{aligned}$$

Hence $813 - 650 = 163$ moles of gas must be added.

Notice that it makes no difference to the problem whether the gas is pure or a mixture of N_2 and O_2 . Within the limits of validity of the ideal

gas expression, all gases behave the same way with respect to pressure, volume, and temperature, if measured in moles rather than in grams. The ideal gas expression itself can be written as a ratio, in a form useful for considering simultaneous pressure, temperature, and volume changes in a fixed quantity of gas:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (3-12)$$

Example 7

When a weather balloon is filled with hydrogen gas at 1.000 atm pressure and 25°C, it has a diameter of 3.00 m and a volume of 14,100 liters. At high altitude the atmospheric pressure drops to half its sea-level value; the temperature is -40°C . What then is the volume of the balloon? What is its diameter?

Solution

We have $P_1 = 1.000$ atm; $V_1 = 14,100$ liters; $T_1 = 25^\circ\text{C}$, or 298.15 K; $P_2 = 0.500$ atm; $T_2 = -40^\circ\text{C}$, or 233.15 K. Rearranging equation 3-12 to solve for V_2 , we get

$$\begin{aligned} V_2 &= \frac{T_2}{T_1} \times \frac{P_1}{P_2} \times V_1 = \frac{233.15 \text{ K}}{298.15 \text{ K}} \times \frac{1.000 \text{ atm}}{0.500 \text{ atm}} \times 14,100 \text{ liters} \\ &= 22,100 \text{ liters} \end{aligned}$$

Assuming that the balloon is spherical, we can find its diameter, d , by using the formula $V = \frac{4}{3}\pi r^3$ or $V = 4\pi r^3/3$. The diameter then is 3.48 m.

Notice that in Example 7 the temperature drop alone would have brought about a volume decrease to $233.15/298.15 = 0.782$ of the initial volume, and the pressure drop alone would have brought about a twofold volume increase. The actual increase, by a factor of 1.56, is the product of these two effects.

The numerical value of the gas constant, R , in the ideal gas law (equation 3-8) depends on the units in which pressure and volume are measured—assuming that only the absolute, or Kelvin, temperature scale is used. If pressure is in atmospheres and volume is in liters, then $R = 0.082054$ liter atm K^{-1} mole $^{-1}$. But, as you can see from Appendix 1, R also can be expressed as 8.3143 J K^{-1} mole $^{-1}$. We shall show in Chapter 15 that the product PV has the units of work or energy.

Example 8

How much volume will 75.0 g of hydrogen gas occupy at 1.000 atm pressure and 298 K?

Solution

To answer this question we must use the full ideal gas equation, equation 3-8, with $P = 1.000$ atm, $R = 0.08205$ liter atm K^{-1} mole $^{-1}$, $T = 298$ K, and $n = 75.0$ g/ 2.016 g mole $^{-1} = 37.2$ moles. Thus

$$V = \frac{nRT}{P} = \frac{37.2 \text{ moles} \times 0.08205 \text{ liter atm K}^{-1} \text{ mole}^{-1} \times 298 \text{ K}}{1.000 \text{ atm}}$$

$$= 910 \text{ liters}$$

Example 9

A 1000-liter tank is filled to a pressure of 10.00 atm at 298 K, requiring 11.5 kg of gas. How many moles of gas are present? What is the molecular weight of the gas? Assuming the gas to be a pure element, can you identify it?

Solution

$V = 1000$ liters, $P = 10.00$ atm, and $T = 298$ K. Hence,

$$n = \frac{PV}{RT} = \frac{10.00 \text{ atm} \times 1000 \text{ liters}}{0.08205 \text{ liter atm K}^{-1} \text{ mole}^{-1} \times 298 \text{ K}}$$

$$= 409 \text{ moles}$$

We convert the weight of the gas in kilograms to grams (11.5 kg = $11,500$ g) and then calculate the molecular weight (mol wt):

$$\text{Mol wt} = \frac{11,500 \text{ g}}{409 \text{ moles}} = 28.1 \text{ g mole}^{-1}$$

Since we are assuming that the gas is an element, it must be N_2 .

Example 10

An 8-liter boiler is designed to withstand pressures up to 1000 atm. If 1.50 kg of water vapor is in the boiler, to what temperature can it be heated before the boiler explodes?

Solution

$P = 1000$ atm, $V = 8.00$ liters. To find the number of moles, we divide the number of grams of water (1.50 kg = 1500 g) by the molecular weight of water. Hence, $n = 1500$ g/ 18.0 g mole $^{-1} = 83.3$ moles. Therefore,

$$T = \frac{PV}{nR} = \frac{1000 \times 8.00}{83.3 \times 0.08205} \text{ K} = 1170 \text{ K or } 897^\circ\text{C}$$

Standard Temperature and Pressure

It is frequently useful to compare volumes of gases involved in physical and chemical processes. Such comparisons are interpreted most easily if the

gases are at the same temperature and pressure, although generally it is inconvenient to make all measurements under such carefully controlled conditions; 0°C (273 K) and 1.000 atm have been designated arbitrarily as **standard temperature and pressure (STP)**. If we know the volume of a sample of gas at any condition, we can easily calculate the volume it would have as an ideal gas at STP by employing the combined gas law. This calculated volume is useful even if the substance itself becomes a liquid or solid at STP.

Example 11

In an experiment, 300 cm³ of steam are at 1.000 atm pressure and 150°C. What is the ideal volume at STP?

Solution

We can use equation 3-7, substituting the subscript STP for the subscript 2. Rearranging the equation to solve for V_{STP} , we get

$$\begin{aligned} V_{\text{STP}} &= V_1 \frac{T_{\text{STP}}}{T_1} \\ &= 300 \text{ cm}^3 \times \frac{273 \text{ K}}{423 \text{ K}} = 194 \text{ cm}^3 \end{aligned}$$

This is the volume that the steam would occupy at STP *if* it behaved like an ideal gas instead of condensing.

At STP, 1 mole of an ideal gas occupies 22.414 liters, as can be seen from the ideal gas law:

$$\begin{aligned} \text{Volume per mole} &= \frac{V}{n} = \frac{RT}{P} \\ &= \frac{0.082054 \text{ liter atm K}^{-1} \text{ mole}^{-1} \times 273.15 \text{ K}}{1.0000 \text{ atm}} \\ &= 22.414 \text{ liters mole}^{-1} \end{aligned}$$

This volume is often called a **standard molar volume**.

Ideality and Nonideality

The equations describing the various gas laws are exact mathematical expressions. Measurements of volume, pressure, and temperature more accurate than those of Boyle and Charles show that gases only *approach* the behavior that the equations express. Gases depart radically from so-called ideal behavior when under high pressure or at temperatures near the boiling

point of the corresponding liquids. Thus, the gas laws, or more precisely the ideal gas laws, accurately describe the actual behavior of a real gas only at low pressures and at temperatures far above the boiling point of the substance in question. In Section 3-8 we shall return to the problem of how to correct the simple ideal gas law for the behavior of real gases.

3-6 THE KINETIC MOLECULAR THEORY OF GASES

At STP, 1 mole of carbon dioxide gas occupies 22.2 liters (ideally 22.4 liters), whereas the same amount of dry ice (solid CO_2) has a volume of only about 28 cm^3 (assuming a density of dry ice of 1.56 g cm^{-3}). This greater volume of the gas, plus the fact that a gas is compressed or expanded so easily, suggests strongly that much of a gas is empty space. But how does a system that is mostly empty space exert pressure on its surroundings? Experiments such as the one in Figure 3-7 indicate that gas molecules move, and move in straight lines. They also collide with the walls of the container, with one another, and with any other objects that may be in the container with the gas (Figure 3-8). As we shall see, the collision with the container walls produces pressure. It is unnecessary to assume any forces between molecules and container to account for pressure.

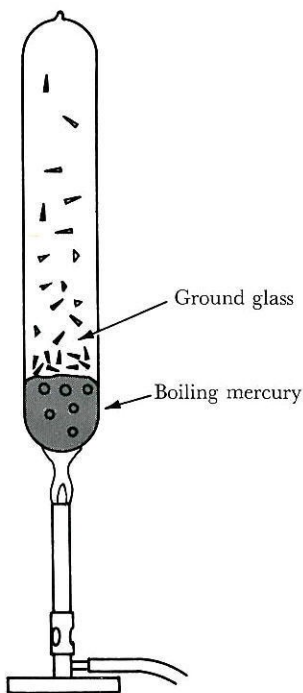
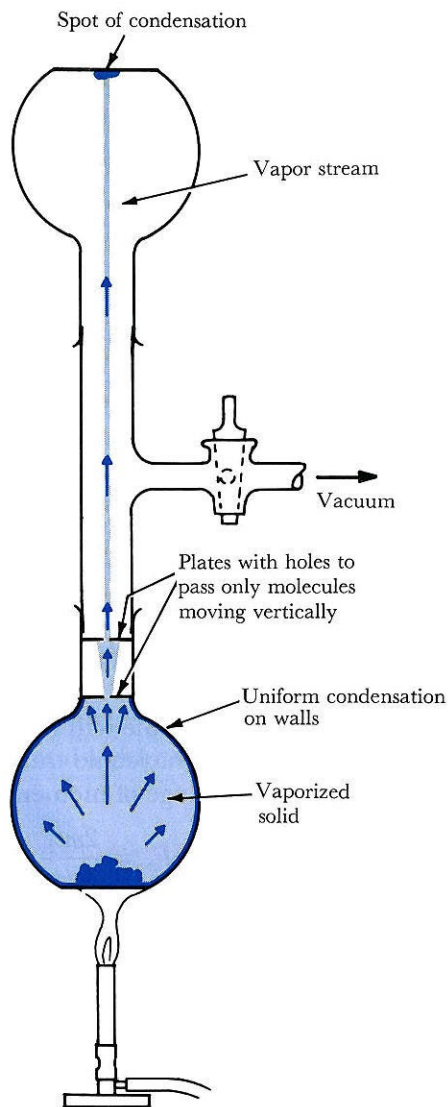
We can explain many observed properties of gases by a simple theory of molecular behavior that was developed in the latter half of the nineteenth century by Ludwig Boltzmann (1844–1906), James Clerk Maxwell (1831–1879), and others. This **kinetic molecular theory** has three assumptions:

1. A gas is composed of molecules that are extremely far from one another in comparison with their own dimensions. They can be considered as essentially shapeless, volumeless points, or small, hard spheres.
2. These gas molecules are in a state of constant random motion, which is interrupted only by collisions of the molecules with each other and with the walls of the container.
3. The molecules exert no forces on one another or on the container other than through the impact of collision. Furthermore, these collisions are **elastic**; that is, no energy is lost as friction during collision.

Our experience with colliding bodies such as a tennis ball bouncing on pavement is that some kinetic energy is lost on collision: The energy is transformed into heat as a result of what we call **friction**. A bouncing tennis ball gradually “dies down” and comes to rest because its collisions with the pavement are subject to friction and are therefore **inelastic**. If molecular collisions involved friction, the molecules gradually would slow down and lose kinetic energy, thereby hitting the walls with decreasing change of momentum, so the pressure would drop slowly to zero. This process does not

Figure 3-7

An experiment to test whether gas molecules move in straight lines. Two flasks are joined by a straight tube with a side arm and stopcock. The bottom flask contains material, such as iodine, that can be vaporized by heating. The flasks are evacuated and the material heated, thereby producing vapor. Molecules leave the solid in random directions, and condensation occurs uniformly over the entire surface of the bottom flask. However, only molecules moving vertically can pass through the collimating holes in the connecting tube and into the top flask. These molecules pass straight through and form a single spot directly opposite the source material. A high vacuum (low pressure) is required to prevent molecular collisions from randomizing molecular motion in the connection tube and upper flask.

**Figure 3-8**

An experiment demonstrating collisions of gas molecules with large solid particles. Particles of ground glass are kept suspended like dust particles in air by bombardment with moving mercury molecules. The heavy molecules (mainly monatomic Hg) leaving the surface of the boiling mercury have high kinetic energy, some of which is transferred to the glass particles on collision.

take place; therefore, we must postulate that **molecular collisions are frictionless, that is, perfectly elastic**. In other words, the total kinetic energy of colliding molecules remains constant.

The Phenomenon of Pressure and Boyle's Law

This simple model is adequate to explain pressure and to provide a molecular explanation of Boyle's law. Consider a container, which we will make cubical for simplicity, with a side of length l (Figure 3-9b). Suppose that the container is evacuated completely except for one molecule of mass m that moves with a velocity v having components v_x , v_y , and v_z parallel to the x , y , and z edges of the box (see Figure 3-9a).*

Let us look first at what happens when the molecule rebounds from a collision with one of the YZ walls, which are perpendicular to the x axis.

Pressure is force per unit area, and force is the rate of change of momentum (mass times velocity) with time. When a molecule bounces off the shaded wall in Figure 3-9b, it exchanges momentum of $2mv_x$ with the wall; for the particle begins with momentum in the x direction of $-mv_x$ and ends with momentum $+mv_x$. The velocity components in the y and z directions are not changed during a collision with the YZ wall and do not enter into the calculation. No matter how many collisions the molecule has with an XY or an XZ wall along the way, if the x component of velocity is v_x , the molecule will return to collide with the original YZ wall in a time $2l/v_x$. If the molecule transfers momentum of $2mv_x$ every $2l/v_x$ sec, then the rate of change of momentum with time, or the force, F_x , is

$$F_x = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}$$

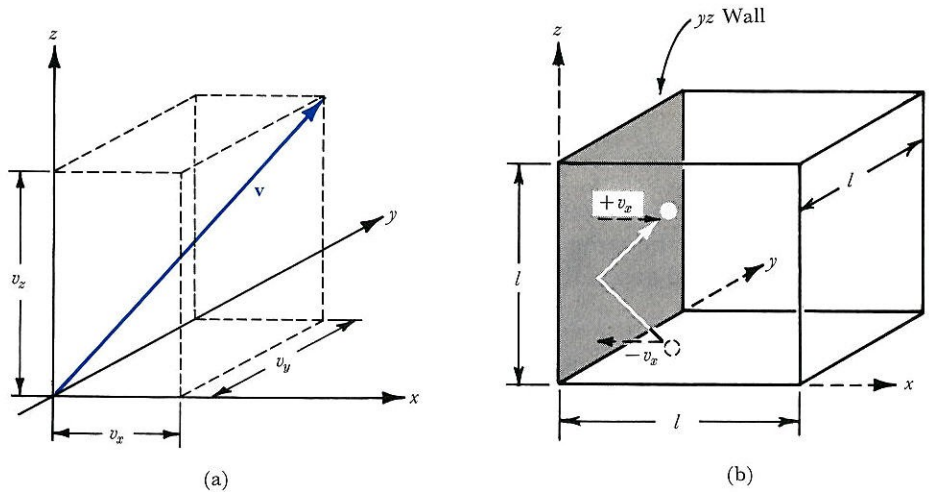
The force per unit area, or the pressure, is

$$P_x = \frac{mv_x^2}{l \cdot l^2} = \frac{mv_x^2}{l^3} = \frac{mv_x^2}{V} \quad (3-13)$$

*If the idea of the breakdown of a vector such as velocity into its three components, v_x , v_y , and v_z , is unfamiliar, there is another explanation that, although less exact, leads to the same answer. This is to assume that since the motions of a molecule in the x , y , and z directions are unrelated, we can think of the molecules as being divided into three groups: one third moving in the x direction, one third in the y direction, and one third in the z direction. The pressure from one molecule on the YZ wall is then $P_x = mv^2/V$ (analogous to equation 3-13). The pressure from all the molecules moving in a direction perpendicular to that wall is $N/3$ times this value (where N is the total number of molecules), or

$$P_x = \frac{N}{3} \frac{\overline{mv^2}}{V}$$

as in equation 3-21. The rest of the proof is the same. (The bar over v^2 indicates an average over all molecules.)

**Figure 3-9**

(a) The velocity of a molecule of gas resolved into components. We determine the components of the velocity vector \mathbf{v} by dropping perpendiculars from the head and tail of the vector to the coordinate axes. (b) Collision of molecule with wall showing change in direction of x component of velocity.

since the area of the wall is l^2 , and the total volume of the box is $V = l^3$. Similarly, for the other walls,

$$P_y = \frac{mv_y^2}{V} \quad (3-14)$$

$$P_z = \frac{mv_z^2}{V} \quad (3-15)$$

If the box now contains N molecules rather than just one,

$$P_x = N \frac{m\overline{v_x^2}}{V} \quad (3-16)$$

$$P_y = N \frac{m\overline{v_y^2}}{V} \quad (3-17)$$

$$P_z = N \frac{m\overline{v_z^2}}{V} \quad (3-18)$$

in which the quantities $\overline{v^2}$ are the *averages* over all molecules of the squares of the velocity components, since we cannot assume that all molecules have the same velocity.

The total velocity of a molecule is related to its velocity components by

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad (3-19)$$

If the motions of the individual molecules are truly random and unrelated, the average of the square of the velocity component in each direction will be the same. There will be no preferred direction of motion in the gas:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2} \quad (3-20)$$

(As before, the bars over v^2 indicate averages over all molecules.) An immediate consequence of this randomness of motion is that the pressure will be the same on all walls, a fact that certainly agrees with our observations of real gases. Rewriting equations 3-16, 3-17, and 3-18 in terms of $\overline{v^2}$ gives

$$P_x = \frac{N}{3} \frac{m\overline{v^2}}{V} \quad P_y = \frac{N}{3} \frac{m\overline{v^2}}{V} \quad P_z = \frac{N}{3} \frac{m\overline{v^2}}{V}$$

and

$$P_x = P_y = P_z = P = \frac{N}{3} \frac{m\overline{v^2}}{V} \quad (3-21)$$

or

$$PV = \frac{N}{3} m\overline{v^2} \quad (3-22)$$

This last expression looks very much like Boyle's law. Boyle's law maintains that the product of pressure and volume for a gas is constant *at constant temperature*; our derivation from the simple kinetic molecular theory states that the PV product is constant for a given mean velocity of gas molecules. If the theory is correct, the mean velocity of the molecules of a gas cannot depend on either pressure or volume, but only on temperature. The mean molecular kinetic energy is represented by the symbol $\bar{\epsilon}$ (where ϵ is the Greek letter epsilon) and is expressed as $\frac{1}{2}m\overline{v^2}$; furthermore, if N is Avogadro's number, the kinetic energy, E_k , of 1 mole of molecules is $N\bar{\epsilon}$. For a mole of gas, the PV product of Boyle's law is proportional to the kinetic energy per mole:

$$E_k = N\bar{\epsilon} = \frac{1}{2} N m\overline{v^2} \quad (3-23)$$

Multiplying and dividing the right-hand term by 3 and rearranging gives

$$E_k = \left(\frac{3}{2}\right)\left(\frac{1}{3}\right) N m\overline{v^2} = \left(\frac{3}{2}\right)\left(\frac{N}{3}\right) m\overline{v^2} \quad (3-24)$$

Comparison with equation 3-22 shows that

$$PV = \frac{2}{3} E_k \quad (3-25)$$

The combination of this derivation from the kinetic theory and the observed ideal gas law (equation 3-8) tells us that the kinetic energy per mole is directly proportional to the temperature. Or, reversing the statement:

Absolute temperature, T , is an indication of the kinetic energy of gas molecules and ultimately of their mean square velocity. For 1 mole of an ideal gas, $PV = RT$. Substituting the value for PV given in equation 3-25 gives

$$E_k = \frac{3}{2}RT \quad (3-26)$$

But $E_k = N\bar{\epsilon}$, in which $\bar{\epsilon} = \frac{1}{2}m\bar{v}^2$; therefore,

$$T = \frac{2}{3} \frac{N}{R} \frac{1}{2} m\bar{v}^2 = \frac{M\bar{v}^2}{3R} \quad (3-27)$$

in which the molecular weight is $M = Nm$. In short, *temperature is a measure of the motion of molecules*. If we heat a gas and raise its temperature, we do so by increasing the velocity of its molecules. When a gas (or any other substance) cools, its molecular motion diminishes. This molecular motion need not be confined to movement of whole molecules from one place to another, which is the picture that we have drawn for an ideal gas. It also can include *rotations* of entire molecules or of groups on a molecule, and *vibrations* of molecules.

We now can see more clearly what happens when the kinetic energy of macroscopic objects is dissipated as heat. When a speeding car skids to a halt, its braking is achieved by converting its energy of motion into frictional heat. But this conversion means changing the motion of the large object—the automobile—into increased relative motion of the molecules of the brake shoes and drum, the tires, and the pavement. Instead of having rubber molecules in the tires vibrating relatively slowly but moving rapidly as a unit, we have a heated tire with molecules moving more rapidly relative to one another but without a net direction of motion. The motions of the molecules have become less directional and more randomized.

This behavior is typical of all real processes. It is easy to go from coherent motion (the rolling tire) to incoherent motion (the hot but stationary tire); it is not possible to go the other way without paying a price. As we shall see in Chapter 16, in any real process the disorder of the object under examination, plus all of the surroundings with which it interacts, always will increase. In other words, in this world things always get messier. This notion is simply the second law of thermodynamics. The quantity that measures this disorder, and which we shall learn to use later in chemical situations, is called **entropy**, S .

3-7 PREDICTIONS OF THE KINETIC MOLECULAR THEORY

The test of any theory is not its beauty or its internal consistency, but its usefulness in predicting the behavior of real systems correctly. By this criterion, the kinetic molecular theory is a good one, as we shall see.

Molecular Size

Some simple calculations with solid and gaseous carbon dioxide illustrate an important difference between molecular environments in gases and in condensed phases of matter.

Example 12

The density of dry ice, or solid carbon dioxide, is 1.56 g cm^{-3} . Find the volume per mole and the volume per molecule.

Solution

The molecular weight of carbon dioxide is 44.01 amu, so 1 mole of dry ice weighs 44.01 g. To find the volume of 1 mole, divide weight by density:

$$V = \frac{44.01 \text{ g}}{1.56 \text{ g cm}^{-3}} = 28.2 \text{ cm}^3$$

Dividing the volume per mole by Avogadro's number yields the volume per molecule:

$$V = \frac{28.2 \text{ cm}^3}{6.022 \times 10^{23} \text{ molecules}} = 4.68 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1}$$

Since $1 \text{ cm} = 10^8 \text{ \AA}$, the volume per molecule is 46.8 \AA^3 .

The cube root of 46.8 is 3.6, so we should expect the carbon dioxide molecule to fit inside a cube approximately 3.6 Å on edge; therefore the carbon dioxide molecule is about 3.6 Å in diameter. This is roughly what would be expected from other experiments for the size of the carbon dioxide molecule, giving us confidence in the correctness of the picture of dry ice as built up from closely packed molecules of carbon dioxide. Now let's try a comparable calculation for gaseous carbon dioxide.

Example 13

The density of carbon dioxide gas at STP is $1.977 \text{ g liter}^{-1}$. Find the volume per mole and the volume per molecule.

Solution

One mole or 44.01 g of carbon dioxide gas has a volume of

$$V = \frac{44.01 \text{ g}}{1.977 \text{ g liter}^{-1}} = 22.26 \text{ liters or } 22,260 \text{ cm}^3$$

(Notice the small deviation from ideal gas behavior.) The volume per molecule is

$$V = \frac{22,260 \text{ cm}^3}{6.022 \times 10^{23} \text{ molecules}} \times \frac{10^{24} \text{ \AA}^3}{1 \text{ cm}^3} = 36,900 \text{ \AA}^3 \text{ molecule}^{-1}$$

Carbon dioxide gas has a molar volume that is 790 times the volume of the solid. The *volume per molecule* in the gas phase corresponds to a cube that is 33.4 Å on a side (Figure 3-10). Only one part in 790 of the gas volume is actually filled by molecules.

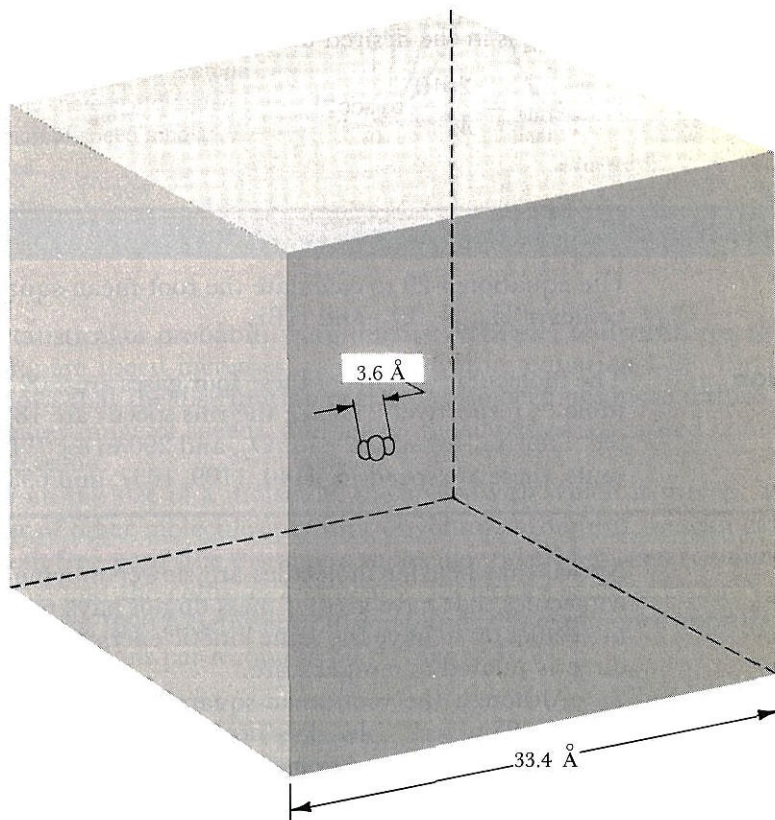


Figure 3-10

The relative size of a CO_2 molecule and the volume per molecule available to it in carbon dioxide gas at STP. Of course, one molecule is not confined to this volume, nor are other molecules excluded from it.

Molecular Speeds

With nothing more than the elementary kinetic theory presented here, we can calculate the **root-mean-square (rms) speed**, v_{rms} , which is the square root of the average of the squares of the speeds of individual molecules. From equation 3-27, v_{rms} is

$$\sqrt{v^2} = v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (3-28)$$

where R is the gas constant, T is the absolute temperature, and M is the molecular weight. This equation is a good example of the absolute necessity of keeping track of units. The gas constant, R , must be expressed as $8.314 \text{ J K}^{-1} \text{ mole}^{-1}$, *not* as $0.08205 \text{ liter atm K}^{-1} \text{ mole}^{-1}$, if the speed is to be expressed in m sec^{-1} . Since $1 \text{ J} = 1 \text{ kg m}^2 \text{ sec}^{-2}$, the units of $3RT/M$ are

$$\frac{(\text{kg m}^2 \text{ sec}^{-2} \text{ K}^{-1} \text{ mole}^{-1})(\text{K})}{(\text{kg mole}^{-1})} = \text{m}^2 \text{ sec}^{-2}$$

and v_{rms} is in the desired units. At STP the expression is

$$v_{\text{rms}} = \frac{2610}{M^{1/2}} \text{ m sec}^{-1} \quad (3-29)$$

Example 14

Use equation 3-29 to calculate the root-mean-square speeds at STP of molecules of H_2 , N_2 , O_2 , and HBr .

Solution

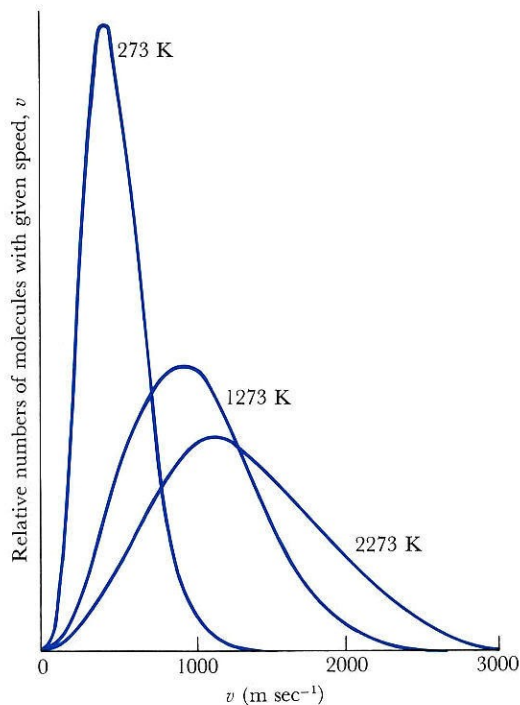
The molecular weights of these four gases are 2.02, 28.01, 32.00, and 80.91 g mole^{-1} , respectively. Hence the rms speeds are 1840 m sec^{-1} for H_2 , 493 m sec^{-1} for N_2 , 461 m sec^{-1} for O_2 , and 290 m sec^{-1} for HBr . In more familiar units, these are speeds of 4140, 1109, 1037, and 653 miles hr^{-1} , respectively.

Notice that heavier molecules are slower moving at a given temperature. Molecules that have greater mass do not have to move as rapidly as lighter molecules do to have the same kinetic energy, and it is kinetic energy that is directly related to temperature.

Although the root-mean-square speed of nitrogen molecules at STP may be 493 m sec^{-1} , this does not mean that all nitrogen molecules travel at this speed. There is a *distribution* of speeds, from zero to values considerably above 493 m sec^{-1} . As individual gas molecules collide and exchange energy, their speeds will vary. The actual distribution of speeds in nitrogen gas at 1 atm pressure and three different temperatures is shown in Figure 3-11. These curves portray a *Maxwell-Boltzmann distribution* of speeds. The equations for these curves can be derived from the kinetic theory of gases by

Figure 3-11

The distribution of speeds among molecules in nitrogen gas at three different temperatures. At higher temperatures the average speed is greater, there are fewer molecules that have precisely this average speed, and there is a broader distribution of speed among molecules.



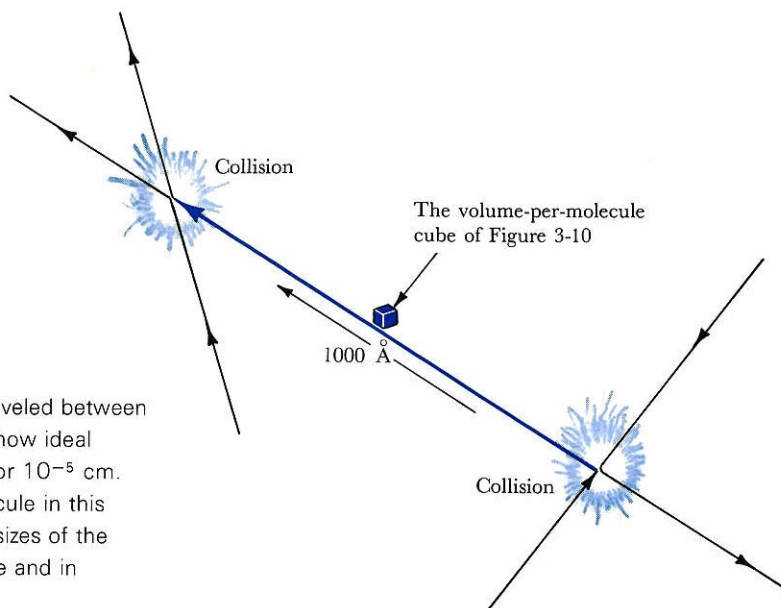
using statistical or probability arguments. At higher temperatures, the root-mean-square speed increases, as expected from equation 3-28. But Figure 3-11 shows that the distribution of speeds also becomes more diffuse. There is a greater range of speeds, and fewer molecules have a speed close to the average value.

From the size of a molecule, the speed with which it travels, and the number of other molecules per unit of volume around it, we can calculate the **mean free path** (the distance a molecule travels between two successive collisions) and the **collision frequency**. Molecules such as O_2 or N_2 travel an average of 1000 Å between collisions, and they experience approximately 5 billion collisions per second at STP (Figure 3-12).

Dalton's Law of Partial Pressures

If each molecule in a gas travels independently of every other except at moments of collisions, and if collisions are elastic, then in a mixture of different gases the total kinetic energy of all the different gases will be the sum of the kinetic energies of the individual gases:

$$E = E_1 + E_2 + E_3 + E_4 + \dots$$

**Figure 3-12**

The mean free path, or distance traveled between collisions, for gas molecules that show ideal behavior at STP, is about 1000 Å or 10^{-5} cm. We can imagine the size of a molecule in this drawing by comparing the relative sizes of the cube 33.4 Å on a side in this figure and in Figure 3-10.

Since each gas molecule moves independently, the pressure that each gas exerts on the walls of the container can be derived separately (equation 3-25). For example,

$$p_1 = \frac{2E_1}{3V} \quad p_2 = \frac{2E_2}{3V} \quad p_3 = \frac{2E_3}{3V} \quad (3-30)$$

This pressure exerted by one component of a gas mixture is called its **partial pressure**, p . Each of these equations can be rewritten to give kinetic energy in terms of pressure:

$$E_1 = \frac{3}{2}p_1V \quad E_2 = \frac{3}{2}p_2V \quad E_3 = \frac{3}{2}p_3V$$

Substituting in the energy expression and canceling the $\frac{3}{2}V$ terms from both sides of the equation produces

$$P = p_1 + p_2 + p_3 + p_4 + \cdots = \sum_j p_j \quad (3-31)$$

The special sign at the right is a **summation sign**, which is a shorthand way of writing the instructions: Sum all the terms of the type p_j for all the different values of j . It will be used frequently.

The *total pressure*, P , then, is the *sum of the partial pressures* of the individual components of the gas mixture, each considered as if it were the only gas present in the given volume. John Dalton (1766–1844) proposed his *law of partial pressures* during the gas investigations that eventually led him to the theory of atoms.

An important measure of concentrations in a mixture of gases (and in solutions and solids as well) is the **mole fraction**, X . The mole fraction of the j th component in a mixture of substances is defined as the number of moles (n) of the given substance divided by the total number of moles of all substances:

$$X_j = \frac{n_j}{n_1 + n_2 + n_3 + n_4 + \cdots} = \frac{n_j}{\sum_i n_i} \quad (3-32)$$

Another version of Dalton's law is the statement that the partial pressure of one component in a mixture of gases is its concentration in mole fraction times the total pressure. If there are n_j moles of gas j present in a mixture, the partial pressure of that gas is calculable from the ideal gas law:

$$p_j = n_j \frac{RT}{V} = \frac{n_j}{n} \times n \times \frac{RT}{V} \quad \left(n = n_1 + n_2 + n_3 + \cdots = \sum_i n_i \right)$$

Since $n_j/n = X_j$ is the mole fraction, and $nRT/V = P$ is the *total* pressure, Dalton's law becomes

$$p_j = X_j P \quad (3-33)$$

Example 15

A gas mixture at 100°C and 0.800 atm pressure contains 50% helium, He, and 50% xenon, Xe, by weight. What are the partial pressures of the individual gases?

Solution

First find the number of moles of helium and xenon in any given sample. A convenient sample choice is 100 g. Then the number of moles of each gas is

$$n_{\text{He}} = \frac{50.0 \text{ g}}{4.00 \text{ g mole}^{-1}} = 12.5 \text{ moles He}$$

$$n_{\text{Xe}} = \frac{50.0 \text{ g}}{131.3 \text{ g mole}^{-1}} = 0.381 \text{ mole Xe}$$

The next step is to calculate the mole fraction, X_j , of each component:

$$X_{\text{He}} = \frac{12.5}{12.5 + 0.381} = 0.970$$

$$X_{\text{Xe}} = \frac{0.381}{12.5 + 0.381} = 0.030$$

According to Dalton's law, the partial pressure of each component is ex-

pressed as $p_j = X_j P$. Thus, we have

$$p_{\text{He}} = 0.970 P = 0.970(0.800) = 0.776 \text{ atm}$$

$$p_{\text{Xe}} = 0.030 P = 0.030(0.800) = 0.024 \text{ atm}$$

Notice that no total volume was specified, and a convenient but arbitrary sample size was used for calculation purposes. Why is the answer independent of volume? Will the answer change if the temperature is changed?

Often gases are collected over liquids such as water or mercury, as in Figure 3-13. Dalton's law must be applied in such cases to account for partial evaporation of the liquid into the space occupied by the gas.

Example 16

Oxygen gas generated in an experiment is collected at 25°C in a bottle inverted in a trough of water (Figure 3-13). The external laboratory pressure is 1.000 atm. When the water level in the originally full bottle has fallen to the level in the trough, the volume of collected gas is 1750 ml. How many moles of oxygen gas have been collected?

Solution

If the water levels inside and outside the bottle are the same, then the total pressure inside the bottle equals 1.000 atm. But at 25°C the vapor pressure of water (or the pressure of water vapor in equilibrium with the liquid) is 23.8 mm Hg or 0.0313 atm, so the partial pressure of oxygen gas is only 1.000 – 0.031, or 0.969 atm. The mole fraction of oxygen gas in the bottle is 0.969 and not 1.000, and the partial pressure of oxygen also is 0.969 atm. The number of moles is

$$\begin{aligned} n &= \frac{PV}{RT} = \frac{0.969 \text{ atm} \times 1750 \text{ cm}^3}{82.054 \text{ cm}^3 \text{ atm K}^{-1} \text{ mole}^{-1} \times 298 \text{ K}} \\ &= 0.0694 \text{ mole} \end{aligned}$$

What would the answer have been had the pressure of water vapor been neglected?

Example 17

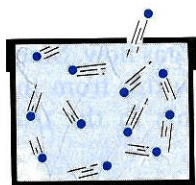
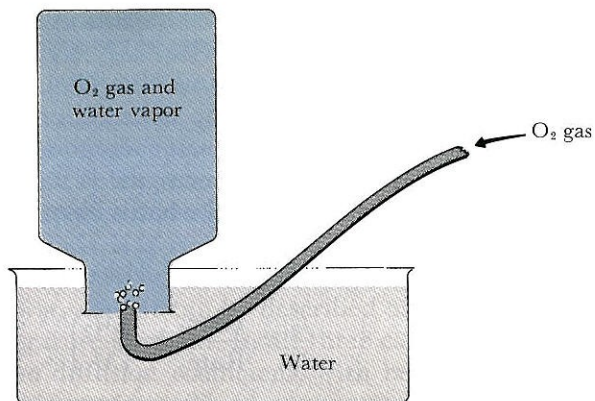
On a humid day at 43.3°C in Galveston, Texas, the vapor pressure of water is 0.087 atm. What is the water content of the atmosphere, expressed as a mole fraction? Assuming that dry air is 20 mole percent O₂ and 80 mole percent N₂, what is the water content in percent by weight?

Solution

The answers are 0.087 and 5.62%.

Figure 3-13

When oxygen gas is collected by displacing water from an inverted bottle, the presence of water vapor in the collecting bottle must be recognized when calculating the amount of oxygen collected. The correction is made easily by using Dalton's law of partial pressures.

**Figure 3-14**

Effusion is the flow of gas from a small hole in a container into an outside region of equal pressure. According to Graham's law, the rates of effusion of two gases at equal temperature are inversely proportional to the square roots of their molecular weights or, by kinetic molecular theory, proportional to their velocities.

Other Predictions of the Kinetic Molecular Theory

Derivations from the kinetic molecular theory that are not much more complicated in principle than the ones we have seen for the gas pressure furnish us with a host of other predictions about the behavior of gases. These predictions have been tested by many scientists and have encouraged confidence in the theory. A derivation of the probability of a molecule hitting a hole in the wall of a container leads to Graham's law of effusion, which predicts that the rate of leakage of a gas from a small hole in a tank will be inversely proportional to the square root of the molecular weight (Figure 3-14).

Thomas Graham (1805–1869) observed, in 1846, that the rates of effusion of gases are inversely proportional to the square roots of their densities. Since, by Avogadro's hypothesis, the density of a gas is proportional to its molecular weight, Graham's observation agrees with the kinetic theory, which predicts that the rate of escape is proportional to molecular velocity or inversely proportional to the square root of the molecular weight (equation 3-29):

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{v_2}{v_1} = \left(\frac{M_1}{M_2} \right)^{1/2} \quad (3-34)$$

However, the law begins to fail at high densities, in which molecules collide several times with one another as they escape through the hole. The law also fails when there are holes large enough so the gas has a hydrodynamic flow toward the hole, thereby leading to the formation of a jet of escaping gas. But so long as isolated molecules escape by going through the hole during their random motions through a stationary gas, the kinetic molecular theory prediction is exact.

Example 18

A given volume of oxygen gas effuses through a small orifice into a vacuum in 1 min. The same volume of an unknown gas takes 1 min and 34 sec to effuse at the same temperature. What is the approximate molecular weight of the unknown gas? If its empirical formula is CH, what is its molecular formula, and what is its molecular weight?

Solution

From equation 3-34 we can derive

$$\frac{t_2}{t_1} = \frac{\text{Rate}_1}{\text{Rate}_2} = \left(\frac{M_2}{M_1}\right)^{1/2}$$

the subscript 1 representing oxygen and the subscript 2 representing the unknown gas. Substituting the observed data, and rearranging the equation to solve for M_2 , we get

$$M_2 = 32.00 \text{ g mole}^{-1} \times \left(\frac{1.57}{1.00}\right)^2 = 78.9 \text{ g mole}^{-1}$$

This is an approximate value, subject to errors in measuring gas flow. Since the formula weight of the unknown gas is 13.02 g (we know this from the empirical formula, CH), there must be six formula weights in the true molecular weight. Since $6 \times 13.02 = 78.12$, the gas is C_6H_6 .

Example 19

Calculate the relative effusion rates of the two isotopic forms of uranium hexafluoride, $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$. All fluorine is ^{19}F .

Solution

The molecular weight of $^{238}\text{UF}_6$ is 352.0 amu, and that of $^{235}\text{UF}_6$ is 349.0 amu. The ratio of effusion rates then is

$$\frac{\text{Rate}(235)}{\text{Rate}(238)} = \left(\frac{352.0}{349.0}\right)^{1/2} = 1.0043$$

Although there is only 0.43% difference in effusion rates of the hexafluorides of the two isotopes of uranium, scientists used this difference to separate fissionable ^{235}U from ^{238}U during the construction of the first atomic bombs at the end of World War II. No other separation method proved workable at the time. The scientists used UF_6 because it is a gaseous compound of uranium, but the small separation ratio meant that the gas had to be passed through many thousands of porous barriers in the special gas diffusion plant at Oak Ridge, Tennessee, to achieve a useful degree of separation.

The kinetic molecular theory also allows us to predict gaseous diffusion, viscosity, and thermal conductivity, the three so-called transport properties. Each phenomenon can be treated mathematically as the diffusion of some molecular property down a gradient. In gaseous diffusion, mass diffuses from regions of high to low concentration, or down a concentration gradient. Viscosity of a fluid arises because slowly moving molecules diffuse into (and retard) rapidly moving fluid layers, and faster molecules diffuse into (and accelerate) the slow regions. This is a transport of momentum down a velocity gradient. Thermal conductivity is the scattering of rapidly moving molecules into regions of slower ones. It can be described as a transport of kinetic energy down a temperature gradient. In all three cases, the kinetic molecular theory predicts the diffusion coefficient, with best accuracy at low gas pressures and high temperatures. These are just the conditions for which the simple ideal gas law is most applicable.

In summary, the elementary kinetic molecular theory, as outlined here, provides a correct explanation for the behavior of ideal gases. It gives us confidence in the reality of molecules, and encourages us to look for molecular modifications of the simple theory that will account for deviations from ideal gas behavior.

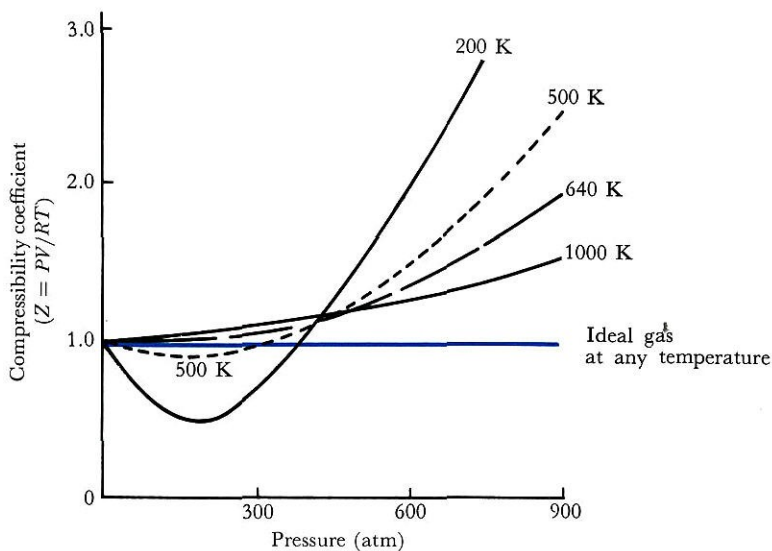
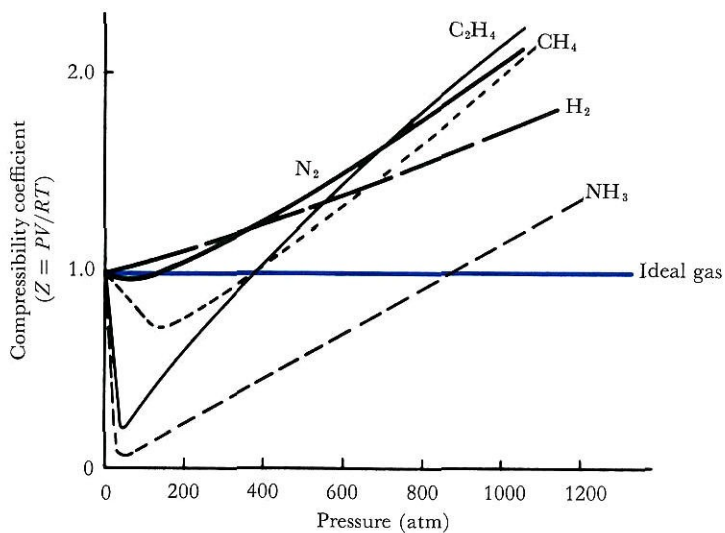
3-8 REAL GASES AND DEVIATIONS FROM THE IDEAL GAS LAW

If gases were ideal, the quotient PV/RT would always equal 1 for 1 mole of gas. Actually all real gases deviate, to some extent, from ideal behavior; the quantity $Z = PV/RT$, called the *compressibility coefficient*, is one measure of this deviation. Z is plotted against pressure for several gases at 273 K in Figure 3-15, and for one gas at several temperatures in Figure 3-16. We can interpret the behavior of real gases as a combination of intermolecular attractions (which are effective over comparatively long distances) and repulsions caused by the finite sizes of molecules (which become significant only when molecules are crowded together at high pressures). At low pressures—but still too high for ideal behavior—intermolecular attractions make the molar volume unexpectedly low, and the compressibility coefficient is less than 1. However, at sufficiently high pressures the crowding of molecules begins to predominate, and the molar volume of the gas is greater than it would be if the molecules were point masses. The higher the temperature (Figure 3-16), the less significant the intermolecular attraction will be in comparison with the kinetic energy of the moving molecules, and the lower will be the pressure at which the bulk factor dominates and Z rises above 1.

An equation such as the ideal gas law, $PV = nRT$, is known as an **equation of state** because it describes the state of a system in terms of the measurable variables P , V , T , and n (Figure 3-17). Other equations of state that have been proposed describe the behavior of real gases better than the ideal gas

Figure 3-15

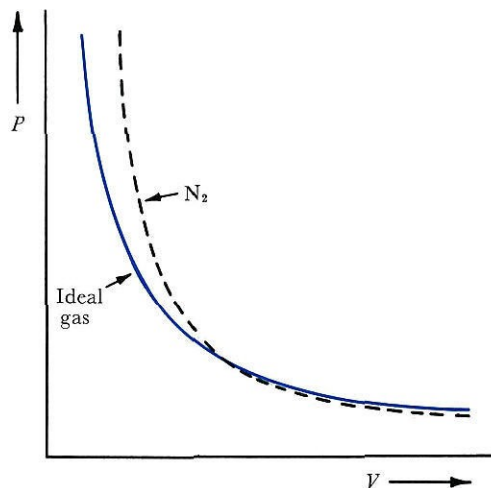
Deviations from the ideal gas law for several gases at 273 K, in terms of the compressibility factor $Z = PV/RT$. The dip of Z below 1.0 at low pressures is caused by intermolecular attractions; the rise above 1.0 at high pressures is produced by the shorter range intermolecular repulsions as the molecules, of finite bulk, are crowded closely together.

**Figure 3-16**

PV/RT for 1 mole of methane gas at several temperatures. Note that PV/RT is less than 1.0 at low pressures and greater than 1.0 at high pressures. Ideal gas behavior is approached at high temperatures.

Figure 3-17

Pressure—volume curves for nitrogen and an ideal gas at constant temperature. At low pressures, the molar volume of N_2 gas is less than that of an ideal gas because of intermolecular attraction. At high pressures, the nonzero volume of individual N_2 molecules makes the gas volume greater than ideal.

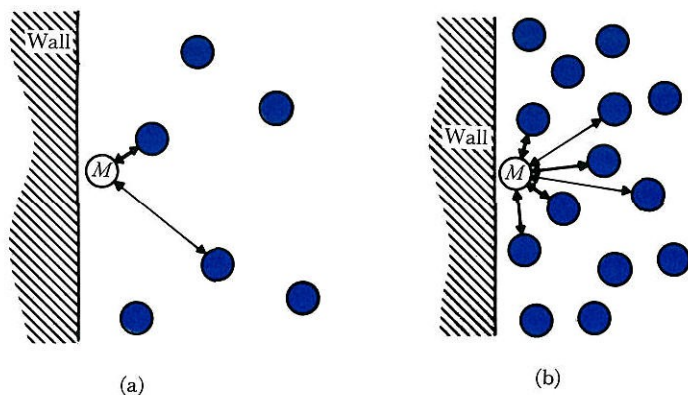


law. The best known of these equations is the one introduced, in 1873, by Johannes van der Waals. Van der Waals assumed that, even for a real gas, there is an ideal pressure, P^* , and an ideal volume, V^* , that would apply to the ideal expression $P^*V^* = nRT$; but because of the imperfections of the gas, these were not the same as the measured pressure, P , and measured volume, V . The ideal volume, he reasoned, should be less than the measured volume because the individual molecules have a finite volume instead of being point masses, and the portion of the container's volume that is occupied by other molecules is unavailable to any given molecule. Therefore, the "ideal" volume should be less than the measured volume by a constant, b , that is related to molecular size by $V^* = V - b$.

Moreover, a gas molecule subject to attractions from other gas molecules strikes the walls with less force than it would if these attractions were absent. For as the molecule approaches the wall, there are more gas molecules behind it in the bulk of the gas than there are between it and the wall (Figure 3-18). The number of collisions with the wall in a given time is proportional to the density of the gas, and each collision is softened by a back-attraction factor, which itself is proportional to the density of molecules doing the attracting. Therefore, the correction factor to P is proportional to the square of the gas density, or inversely proportional to the square of the volume: $P^* = P + a/V^2$, where a is related to the attractions between molecules. The complete van der Waals equation is

$$\left(P + \frac{a}{V^2}\right)(\bar{V} - b) = RT$$

Here \bar{V} is the *volume per mole*, or: $\bar{V} \equiv V/n$. The equation is simpler when written this way. Similarly, the ideal gas law can be written $P\bar{V} = RT$ as easily as $PV = nRT$. The constants a and b are chosen empirically to provide

**Figure 3-18**

Reduction of pressure of a real gas as a result of intermolecular attractions. (a) Gas at low density. (b) Gas at high density. A molecule M in a high-density gas hits the wall with a smaller impact than in a low-density gas because the attractions of its nearest neighbors reduce the force of its impact.

Table 3-2**Measures of Molecular Size Obtained from the Kinetic Theory**

Gas	Van der Waals constants		Spherical molecular diameters, d (Å)		
	a (liter ² atm mole ⁻²)	b (cm ³ mole ⁻¹)	From van der Waals ^a	From gas viscosity	From density of liquid or solid ^b
Hg	8.09	17.0	2.38	3.60	3.26
He	0.0341	23.70	2.48	2.00	—
H ₂	0.2444	26.61	2.76	2.18	—
H ₂ O	5.464	30.49	2.88	2.72	3.48
O ₂	1.360	31.83	2.90	2.96	3.75
N ₂	1.390	39.12	3.14	3.16	4.00
CO ₂	3.592	42.67	3.24	4.60	4.54

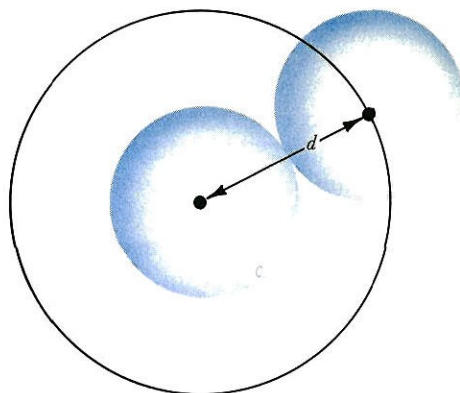
^aThis is a bad approximation of d for all gases except Hg and He.

^bWe are assuming that the molecules are spheres, which when most closely packed fill 74% of the space available. If M is the molecular weight, N is Avogadro's number, and D is the density, the molecular volume is

$$V_m = \frac{\pi}{6} d^3 = 0.74 \frac{M}{ND}$$

Figure 3-19

This center of no other molecule can come closer than a molecular diameter to the center of a given molecule. The volume around each molecule from which other molecules are excluded then is $\frac{4}{3}\pi d^3$, or eight times the molecular volume of $\frac{\pi}{6}d^3$.



the best relationship of the equation to the actual PVT behavior of a gas. Even so, the molecular size calculated from this purely experimental b agrees well with the ones obtained by other means (Table 3-2), and gives us confidence that we have the right explanation for deviations from ideality.

Experimentally obtained values of a and b for several gases are given in Table 3-2, along with several calculations of molecular diameters. We might suppose that the constant b is simply the excluded volume per mole, V_m (as in Figure 3-19): $b = 8NV_m = \frac{4}{3}\pi Nd^3$. However, collision is a two-molecule process and this calculation overcounts the excluded volume by a factor of 2. The molecular diameters in Table 3-2 were obtained from the b values by having b equal to $4NV_m$, in which $V_m = \pi d^3/6$ is the volume of one molecule.

The van der Waals equation is applicable over a much wider range of temperatures and pressures than is the ideal gas law; it is even compatible with the condensation of a gas to a liquid.

Summary

We have seen four experimentally derived principles or laws of gas behavior, which all gases obey approximately, especially under conditions of low pressure and high temperature.

1. Avogadro's law: At fixed pressure and temperature, the volume of any gas is proportional to the number of moles present.

2. Boyle's law: At constant temperature, the volume of a sample of gas is inversely proportional to the pressure on the gas.

3. Charles' law: At constant pressure, the volume of a sample of gas is proportional to the temperature of the gas on the absolute, or Kelvin, scale.

4. **Gay-Lussac's law:** At constant volume, the pressure exhibited by a sample of gas is proportional to the temperature of the gas on the absolute scale.

Although real gases only approximate this behavior, we can define an **ideal gas** as one that follows the preceding laws exactly under all conditions. All the foregoing observations can be combined in one expression, the **ideal gas law**:

$$PV = nRT$$

If P is pressure in atmospheres, V is volume in liters, T is the absolute Kelvin temperature, and n is the number of moles, then the proportionality constant R , known as the gas constant, has the value

$$R = 0.08205 \text{ liter atm K}^{-1} \text{ mole}^{-1}$$

In practical calculations, the ideal gas law is often most useful in one of the various ratio forms given in equations 3-9 through 3-12.

Standard temperature and pressure, or STP, is defined as 273.15 K (0°C) and exactly 1 atm. Gas properties are frequently converted to STP conditions for comparison purposes, even for gases such as H₂O that liquefy at STP. One mole of any ideal gas at STP has a volume of 22.414 liters, and this is called a **standard molar volume**.

The **kinetic molecular theory of gases** successfully explains the behavior of ideal gases with a minimum of starting assumptions, and also provides a framework for understanding the deviations of real gases from ideal gas behavior. In its simplest form, the kinetic theory assumes that a gas is made up of noninteracting point molecules in a state of constant motion, colliding elastically with one another and with the walls of a container. In extending the theory to cover real gases, we recognize that molecules have finite volume and exert attractive forces on one another.

In the kinetic theory, pressure is simply the result of collision of molecules with the container walls, and transfer of momentum. The product of pressure and volume is equal to two-thirds the kinetic energy of motion of the molecules (equation 3-25). Combining this fact with the observed ideal gas law, we come to the important conclusion that the kinetic energy of motion of the molecules is directly proportional to absolute temperature (equation 3-26), or that *temperature is simply a consequence of molecular motion*.

Comparing the densities of substances in the gaseous and condensed phases, we find that the average space available to a gas molecule at STP is roughly three orders of magnitude (or 10^3) greater than the volume of the molecule itself. The **root-mean-square (rms) speed** of a molecule is inversely proportional to the square root of its molecular weight (equation 3-27), and this speed is on the order of several thousand miles per hour at STP. The heavier the molecule, the more slowly it moves.

The actual molecular velocities in a gas vary in a distribution around this rms value, with some velocities nearly zero and others very much

faster than average. Velocities of individual molecules vary as the molecules collide with one another and rebound. Nevertheless, the *distribution* of molecular speeds remains constant at constant temperature. An ideal gas at STP has a **mean free path**, or average distance between collisions, on the order of 1000 \AA , and a collision rate of around 5×10^9 collisions sec^{-1} .

Dalton's law of partial pressures says that each component of a gas mixture behaves as if it were the only gas present. The **mole fraction**, X_j , is the number of moles of gas j present divided by the total number of moles of all gases. The partial pressure of gas j is the mole fraction of j times the total pressure: $p_j = X_j P$. The sum of partial pressures of all components is the total pressure.

The kinetic theory of gases predicts that the rate of effusion of a gas through a small orifice will be inversely proportional to the square root of molecular velocity (equation 3-34), and this prediction is borne out by experiment. The theory is also successful in accounting quantitatively for diffusion of gases, viscosity, and conductivity of heat.

Real gases deviate from ideal behavior because molecules are not volumeless, shapeless points, and because real molecules attract one another. Molecular attractions become impossible to neglect when the molecules are moving more slowly, at low temperatures; molecular volumes become significant when the gas is compressed. Hence the gases approximate ideal behavior most closely at high temperature and low pressure.

Van der Waals modified the ideal gas law to take both of the preceding factors into account. The van der Waals equation, $(P + a/\bar{V}^2)(\bar{V} - b) = RT$ for 1 mole of gas, has an experimental constant, b , that is related to molecular volume, and another constant, a , that is related to molecular attractions or "stickiness." From the van der Waals constant b we can obtain approximate molecular diameters, and these values agree roughly with estimates of diameters obtained from densities of solids or from gas viscosities.

Self-Study Questions

1. Why should gases obey simpler laws than those governing liquids or solids?
2. Early hydraulic engineers found that no suction pump could lift water more than approximately 34 ft. Can you explain this phenomenon from the information in this chapter?
3. How did Boyle design his experiment to test the "spring of the air" theory?
4. Why is a plot of experimental data that produces a straight line useful or desirable?
5. How is an absolute scale of temperature defined in terms of gas behavior?

6. Under what conditions does Boyle's law apply? When is Charles' law applicable? How are these laws derived from the complete ideal gas law?
7. What does STP signify, and why is it useful?
8. What molecular explanation can you give for the deviation of real gases from ideal gas behavior? Under what conditions will real gases most resemble ideal behavior?
9. What experimental evidence is there that each of the three assumptions of the kinetic molecular theory of gases is valid?
10. What can we say that the product, PV , for an ideal gas is proportional to the kinetic energy, E_k ?
11. Why can we say that the temperature is proportional to the square of the speed of the molecules (actually to the mean square speed)?
12. If the molecules in a liter of hydrogen gas and those in a liter of oxygen gas are moving with the same mean square speed, which gas is hotter?
13. What fraction of a typical gas is occupied by the volume of the molecules of which it is composed? What direct physical measurements can tell you this?
14. Why is the gas volume of 22.414 liters significant?
15. How does the speed of sound in air at sea level compare with the root-mean-square speed of the molecules in the air?
16. Which would you expect to be greater, the average speed or the root-mean-square speed? Can you explain your answers by using the definitions of the two speeds?
17. What does Dalton's law of partial pressure indicate about the behavior of gases in a mixture?
18. Why does the compressibility coefficient of a real gas deviate above and below 1.00 as it does?
19. How is a measure of molecular size obtained from the van der Waals equation?

Problems

Atmospheric pressure

1. One atmosphere of pressure will push a column of mercury to a height of 760 mm when the cross-sectional area of the column is 1.00 cm^2 . What would be the height of the column of mercury supported by the atmosphere if its cross-sectional area were 0.500 cm^2 ? How high would the mercury column be if the area were 2 cm^2 ?

2. Standard atmospheric pressure is quoted by the U.S. Weather Bureau as 29.92 in. How can pressure have units of inches? Show how this measure is related to other units of pressure discussed in this chapter.

Boyle's law

3. A gas at an initial pressure of 0.921 atm is allowed to expand at constant temperature until the pressure falls to 0.197

atm. What is the ratio of final volume to initial volume?

- An ideal gas occupies 76.0 liters at 1.00 atm pressure. What pressure will reduce the volume to 10.0 liters, if $T = \text{constant}$?
- A sample of neon gas occupies 75.0 ml at 1.00 atm pressure. If the temperature is unchanged, what volume will it occupy at (a) 5.00 atm, (b) 0.100 atm, and (c) 1000 Pa?
- An experiment is being carried out at 75°C in a 5.00-liter flask that contains an evacuated glass bulb of 400 cm^3 volume. If the bulb breaks, what will be the new pressure in the flask, assuming no temperature change?

Charles' law

- If a sample of gas at 25°C occupies 2.34 liters, what will be its volume at 400°C if the pressure is unchanged?
- A sample of gas is heated from 25°C to 50°C at constant pressure. Will the gas volume double? Why, or why not? What will be the ratio of final volume to initial volume?

Ideal gas law

- At STP, 10.3 g of a gas occupies 453 in.^3 . What is the volume of this sample at 1.25 atm and 100°C ?
- The temperature of a 0.0100-g sample of chlorine gas, Cl_2 , in a 10-ml sealed glass container is increased, in an oven, from 20°C to 250°C . What is the initial pressure at 20°C ? What is the pressure at 250°C ?

Molecules

- How many molecules of an ideal gas are there in 1.000 ml of the gas if the

temperature is -80°C and the pressure 1.000 Pa?

- What pressure will be exerted by 5.0×10^{13} molecules of an ideal gas in 1.000 ml at 0°C ? Express your answer in atmospheres and in pascals.

Partial pressures

- A 2.00-liter flask at 27°C contains 4.40 g of carbon dioxide and 1.00 g of nitrogen gas. What is the pressure inside the flask? What are the partial pressures of each of the two components? (Express pressures in atmospheres.)
- One liter each of oxygen, nitrogen, and hydrogen gas, all originally at 1.00 atm pressure, are forced into a single 2.00-liter container. What is the resulting pressure if temperature is unchanged? What are the partial pressures of the components?
- A gas mixture contains half argon and half helium by weight, with a total pressure of 1.11 atm. What is the partial pressure of each gas in the mixture?
- A mixture of gases contains 0.5 mole of oxygen, 0.1 mole of hydrogen, and 0.8 mole of nitrogen. The total pressure is 0.80 atm. What is the partial pressure of each gas?
- The concentration of carbon monoxide, CO, in cigarette smoke is 20,000 parts per million (ppm) by volume. Calculate the partial pressure of carbon monoxide in 1 liter of cigarette smoke which exerts a total pressure of 1.00 atm.
- A mixture of 3.86 g of CCl_4 (carbon tetrachloride) and 1.92 g of C_2H_4 (ethylene) at 450°C exerts how many atmospheres of pressure inside a 30-ml metal bomb? How much pressure is contributed by ethylene?

Gas density

19. What is the density of XeF_6 gas at STP in grams per liter? What will be its density at 25°C and 1.30 atm?
20. The density of a gas at STP is 1.62 g liter^{-1} . What will be its density at 302 K and 0.950 atm?

Molecular weight

21. If 0.750 g of a gas occupies 4.62 liters at 0.976 atm and 20°C , what is the molecular weight of the gas? What might the gas be?
22. A 1.12-liter sample of a gas weighs 0.400 g when measured at 0°C and 0.500 atm. The gas is 25.0% hydrogen by weight and 75.0% carbon. What is the molecular weight of the gas? What are its empirical formula and molecular formula?

Molecular formula

23. A 250-ml sample of a compound with the empirical formula CH_2 weighs 0.395 g at 0.921 atm and 27°C . What are the molecular weight and formula of the compound?
24. A sample of 0.524 g of a compound fills a volume of 129 ml at 25°C and 0.991 atm. Chemical analysis shows that it is 23.5% carbon, 2.0% hydrogen, and 74.5% fluorine by weight. What are its molecular weight and molecular formula?

Empirical formula

25. A 0.490-g sample of a compound is heated through the successive evolution of the following gases, all at 1.00 atm pressure: 280 ml of water vapor at

182°C , 112 ml of ammonia vapor at 273°C , 0.0225 g of water at 400°C , and 0.200 g of SO_3 at 700°C . At the end of the heating, 0.090 g of FeO remains. Deduce the empirical formula for the compound.

Molecular proportions

26. Both solid LiH and CaH_2 react with water to produce hydrogen gas and the corresponding hydroxide, LiOH or $\text{Ca}(\text{OH})_2$. A 0.850 g sample of a mixture of LiH and CaH_2 produces 1.200 liters of H_2 at STP. What percentage of the starting mixture was LiH? (Give both a mole percent and a percent by weight.)

Vapor pressure

27. One liter of dry air at 1.00 atm and 86°C is placed in contact with 1.00 ml of liquid water at the same temperature. The volume of the gas phase remains constant throughout the experiment. The vapor pressure of water at this temperature is 0.593 atm and its density is 0.970 g ml^{-1} . When equilibrium has been established,
- What is the partial pressure of air in the vessel?
 - What is the partial pressure of water vapor in the vessel?
 - What is the total pressure in the vessel?
 - How many moles of water will have evaporated?
 - What volume of liquid water, if any, will remain?
28. One gram of methane, CH_4 , is burned to produce CO_2 gas and liquid H_2O . At 25°C , the pressure exerted by the products is 0.987 atm. The vapor pressure of water at 25°C is 0.0313 atm. Calculate

the volume of dry CO_2 produced in the reaction.

Energy and temperature

29. Calculate the kinetic energy per mole of ideal gas molecules at a temperature of 25°C . If you use the value of the gas constant $R = 0.08205$ liter atm K^{-1} mole $^{-1}$, the kinetic energy will be in units of liter atm, which is unorthodox but perfectly acceptable. The calculation is easier with $R = 8.3144$ J K^{-1} mole $^{-1}$. How does this kinetic energy per mole compare in magnitude with the energy of a chemical bond, which typically is on the order of 350 kJ mole $^{-1}$? What would happen if kinetic energy of motion and bond energy were more similar in magnitude?
30. Calculate the kinetic energy per mole at 300°C for the following gas molecules, assuming ideal behavior: (a) H_2 , (b) CH_4 , (c) HBr . Why is this problem simpler than it looks? Calculate the rms velocities of the three molecules at 300°C , and compare their relative magnitudes. What general principle can you draw from them? Why is the second half of this problem more complex than the first?

Molecular volumes

31. Liquid benzene, C_6H_6 , has a density of 0.879 g ml $^{-1}$. If benzene vapor behaves as an ideal gas, what will the vapor density be at STP? Calculate the volume per molecule, in cubic angstroms, for the liquid and gaseous states. By what factor does the volume per molecule increase when the liquid evaporates?
32. At its normal boiling point of -164°C , liquid methane, CH_4 , has a density of

0.466 g ml $^{-1}$. If methane vapor behaved as an ideal gas at that temperature, what would be its density at 1 atm pressure? What are the volumes per molecule for liquid and for gas?

Molecular speeds

33. What is the rms speed of oxygen molecules at 25°C ? To what temperature must the gas be raised to increase the speed by a factor of 10 while maintaining a constant volume? By what factor would the pressure increase during this temperature increase at constant volume?
34. The speed of sound waves in an ideal gas is given by the formula

$$\text{Speed of sound} = c = \sqrt{\frac{\gamma RT}{M}}$$

This is remarkably like the equation for the rms speed of the molecules themselves, except that γ is a constant that has the theoretical value of $5/3$ for monatomic gases such as He and Ne, and a value near 1.41 for diatomic gases such as N_2 and O_2 . Calculate the speed of sound in pure nitrogen gas at 1.00 atm and 25°C , and compare this speed with the rms speed of the nitrogen molecules themselves.

35. Earth's atmosphere is approximately 80% nitrogen gas and 20% oxygen. The speed of sound in air can be calculated by using an average molecular weight in the expression given in the preceding problem. Calculate the speed of sound in air at 1.00 atm pressure and 25°C . Will sound travel faster, or slower, than this in helium gas? What will the speed of sound be in air at 35,000 ft, where the temperature is -40°C ?
36. How does the speed of sound in a gas

at 25°C and 1.00 atm pressure compare with that in the same gas at 25°C and 50.0 atm pressure? How do the rms molecular speeds compare? Does your answer seem sensible?

Dalton's law

37. One liter of hydrogen gas is collected over water at 10°C and 1.053 atm. The vapor pressure of water at this temperature is 0.0121 atm. If the hydrogen then is separated from the water and dried at constant temperature, what will be the new volume of the dry hydrogen gas? If the water vapor that was removed from the hydrogen is stored at 100°C and 0.0159 atm, what will be its volume?
38. Ultraviolet light from the sun converts some of the oxygen, O_2 , in the upper atmosphere to ozone, O_3 . If a sample at constant temperature and volume is irradiated until 5% of the O_2 is converted to O_3 , what will the final pressure be, assuming an initial pressure of 0.526 atm?

Graham's law

39. A sample of an unknown gas is shown by analysis to contain only sulfur and oxygen. The gas requires 28.3 sec to effuse through an orifice into a vacuum, whereas an identical number of O_2 molecules passes through the same orifice in

20.0 sec. Determine the molecular weight and formula of the gas.

40. In the same time required for 6 liters of carbon dioxide to effuse through a porous barrier, only 5 liters of an unknown gas will pass through. Estimate the molecular weight of the unknown gas.

Van der Waals gas

41. What is the volume per mole of an ideal gas at STP, or 1 atm pressure and 273.15 K? The van der Waals equation is a better description of the behavior of real gases. What pressure does this equation predict for a mole of O_2 kept at the volume that you just calculated for an ideal gas, and at 273.15 K? What is the percent difference between the ideal and van der Waals pressure predictions?
42. Use the van der Waals equation to calculate the molar volume of carbon dioxide at STP. [Note: To avoid solving a cubic equation, you can use the method of successive approximations. Solve for \bar{V} in the term $(\bar{V} - b)$, using the ideal gas value of the molar volume in the denominator of the a/\bar{V}^2 term. Then, if you are not happy with your approximate answer, you can repeat the process, using the approximate answer in the denominator of a/\bar{V}^2 , and continue until the answers cease changing from one cycle to the next.]

Postscript to Gas Laws and Atomic Theory

When the dust has settled after a new discovery, it is all too easy to forget how much controversy and effort went into its development. Thomas Thomson (1773–1852) was Regius Professor of Chemistry at the University of Glasgow, and was the man to whom John Dalton turned for help in

publicizing his new theory of atoms. In 1830, Thomson published his *History of Chemistry*, which is particularly interesting because many of the participants in the atomic revolution in chemistry were alive, active, and friends of Thomson. In the last chapter of his *History*, Thomson describes the circumstances of the birth of the atomic theory:

“In the year 1804, on the 26th of August, I spent a day or two at Manchester, and was much with Mr. Dalton. At that time he explained to me his notions respecting the composition of bodies. I wrote down at the time the opinions which he offered . . . [A brief account of the atomic theory followed.]

Mr. Dalton informed me that the atomic theory first occurred to him during his investigation of olefiant gas [acetylene, C_2H_2] and carburetted hydrogen gas [ethylene, C_2H_4], at that time imperfectly understood, and the constitution of which was first fully developed by Mr. Dalton himself. It was obvious from the experiments which he made upon them, that the constituents of both were carbon and hydrogen, and nothing else. He found further, that if we reckon the carbon in each the same, then carburetted hydrogen gas contains exactly twice as much hydrogen as olefiant gas does. This determined him to state the ratios of these constituents in numbers, and to consider the olefiant gas as a compound of one atom of carbon and one atom of hydrogen; and carburetted hydrogen of one atom of carbon and two atoms of hydrogen. The idea thus conceived was applied to carbonic oxide, water, ammonia, etc.; and numbers representing the atomic weights of oxygen, azote, etc., deduced from the best analytical experiments which chemistry then possessed. Let not the reader suppose that this was an easy task. Chemistry at that time did not possess a single analysis which could be considered as even approaching to accuracy. . . .

In the third edition of my *System of Chemistry*, published in 1807, I introduced a short sketch of Mr. Dalton's theory, and thus made it known to the chemical world. . . . These facts gradually drew the attention of chemists to Mr. Dalton's views. There were, however, some of our most eminent chemists who were very hostile to the atomic theory. The most conspicuous of these was Sir Humphry Davy. In the autumn of 1807 I had a long conversation with him at the Royal Institution, but could not convince him that there was any truth in the hypothesis. A few days after, I dined with him at the Royal Society Club, at the Crown and Anchor, in the Strand. Dr. Wollaston was present at the dinner. After dinner every member of the club left the tavern, except Dr. Wollaston, Mr. Davy, and myself, who stayed behind and had tea. We sat about an hour and a half together, and our whole conversation was about the atomic theory. Dr. Wollaston was a convert as well as myself; and we tried to convince Davy of the inaccuracy of his opinions; but, so far from being convinced, he went away, if possible, more prejudiced against it than ever. Soon after, Davy met Mr. David Gilbert, the late distinguished president of the Royal Society; and he amused him with a caricature description of the atomic theory,

which he exhibited in so ridiculous a light, that Mr. Gilbert was astonished how a man of sense or science could be taken in with such a tissue of absurdities. . . . [Wollaston finally convinced Gilbert after a long recital of the chemical evidence.]

Mr. Gilbert went away a convert to the truth of the atomic theory; and he had the merit of convincing Davy that his former opinions on the subject were wrong. What arguments he employed I do not know; but they must have been convincing ones, for Davy ever after became a strenuous supporter of the atomic theory. The only alteration which he made was to substitute *proportion* for Dalton's word, *atom*. Dr. Wollaston substituted for it the term *equivalent*. The object of these substitutions was to avoid all theoretical announcements. But, in fact, these terms, *proportion*, *equivalent*, are neither of them so convenient as the term *atom*; and unless we adopt the hypothesis with which Dalton set out, namely, that the ultimate particles of bodies are *atoms* incapable of further division, and that chemical combination consists in the union of these atoms with each other, we lose all the new light which the atomic theory throws upon chemistry, and bring our notions back to the obscurity of the days of Bergman and of Berthollet. ”

Suggested Reading

- J. Hildebrand, *An Introduction to Molecular Kinetic Theory*, Van Nostrand Reinhold, New York, 1963.
- T. L. Hill, *Lectures on Matter and Equilibrium*, W. A. Benjamin, Menlo Park, Calif., 1966. Written at the honors freshman level. The first four chapters, on states of matter, gases, and intermolecular forces, are particularly useful.
- W. Kauzmann, *Kinetic Theory of Gases*, W. A. Benjamin, Menlo Park, Calif., 1966. Thorough, clear. Chapters 1 and 2, on equations of state of gases, are especially relevant. Chapter 4 continues the discussion of the distribution of molecular velocities, but requires calculus.