Helpful review of the basis of the ideal gas law (pV = nRT)

III.

GENERAL CHARACTERISTICS OF GASES

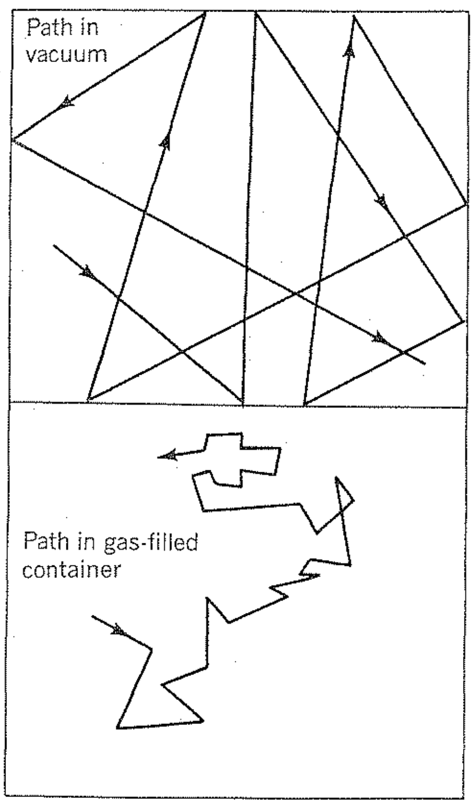
Inertia is that property possessed by a body in motion that tends to keep it in motion with the same direction and same velocity.

1 calorie = 4.18×10^7 ergs
The butter that you eat with your toast in the morning (2 pats) liberates about 4×10^{12} (1 trillion) ergs when it is completely used by your body. This is approximately the amount of kinetic energy possessed by a 10-pound ball traveling through space at 500 mi/hr.

4-1 Molecular Motion Suppose we remove all of the air from a stoppered flask by means of a vacuum pump and introduce a colored gas into the evacuated vessel. Immediately the colored material is observed to be uniformly distributed throughout the flask. This observation suggests that matter in the gaseous phase is in constant motion and shows that a gas fills all the space available to it. If the gas is then transferred to another vessel having a different volume and shape, the gas will occupy the second vessel completely. Thus, we may conclude that *gases do not have definite shapes or volumes.* Observation over long periods of time shows that the gas does not settle out. This may be interpreted to mean that the *gas molecules remain in motion.* Apparently there is no net loss of energy during collisions between molecules and *negligible attractive forces* between molecules. Their ability to maintain movement and to fill any available space suggests that gas molecules have a great deal of energy. The energy of motion is called ***kinetic energy.*** Experiments show that the kinetic energy possessed by a moving particle depends on the mass of the particle and its velocity. The quantitative relationship is

$$\text{K.E.} = \tfrac{1}{2}mv^2 \qquad 4\text{-}1$$

where m is the mass expressed in grams and v is the velocity usually expressed in cm/sec. Substituting grams for m and cm/sec for v in Equation 4-1 the unit of energy in the cgs system has the dimensions of cm^2/sec^2. This unit is called an ***erg.***



4-1 Mean free paths of molecules. A single molecule in a vacuum would follow a path similar to that shown above. In a gas-filled container, a molecule makes countless collisions. Thus, its mean free path is shorter in air than it is in a vacuum.

The effect of molecular motion can be seen by examining smoke from a burning match under a microscope. The tiny, solid quivering smoke particles are observed to move about haphazardly in a zigzag path. The particles do not show any appreciable tendency to settle to the bottom of the container. If the chamber is warmed, the particles are observed to move faster. This constant motion of very small, but visible, particles suggests that they are suspended in a medium of even smaller but faster-moving particles. Thus, as the tiny smoke particles float in the air, they are struck irregularly on all sides by the rapidly moving molecules of gas which compose the air. Since the collisions are random, the particles follow an erratic, zigzag path. It may be shown that at room temperature molecules of gases in the air travel at an average speed of about 1300 ft/sec, the speed of an ordinary rifle bullet. At higher temperatures, the average velocity and kinetic energy are greater.

4-2 Mean Free Path The rapid motion of gas molecules might lead us to predict that odors should be propagated instantly across a room and that a localized change in temperature, caused by the opening of a window, should be felt immediately at the opposite side of the room. Experience shows that this is not true. Gas molecules in a room are somewhat similar to a large number of billiard balls rolling around on a table. Molecules travel only a short distance before they collide with other particles and are deflected from their original paths. The average length of the free path between two successive collisions is known as the ***mean free path.*** The shorter the path, the more slowly any condition depending on molecular motion is propagated.

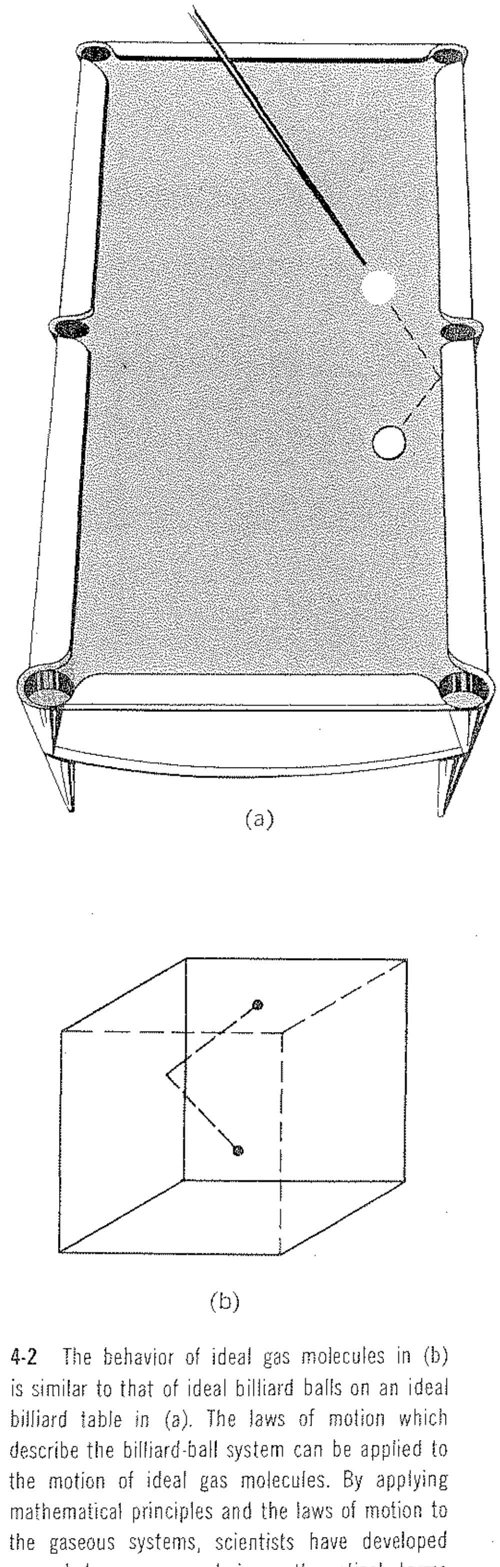
The mean free path depends on both the *concentration of the molecules* and on their *size*. The greater the number of molecules per unit volume and the greater their size, the shorter is the mean free path.

4-3 Gas Pressure and Compressibility Another characteristic of gases may be observed by blowing up a balloon. As the gas is introduced, the balloon expands, becomes firmer, and finally bursts. This observation may be explained by assuming that *gases exert pressure* on the inner walls of their containers. How can this be explained in terms of our concept of the molecular motion of gases? Sometimes it is possible to relate the behavior of a submicroscopic system to that of a well-understood macroscopic system. Thus, the pressure of a gas on the walls of its container may be explained in terms of the behavior of *ideal* billiard balls on an *ideal* table.

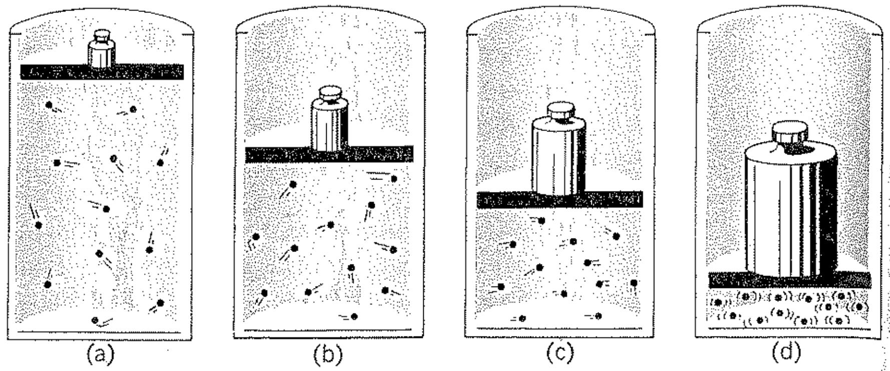
The motion of a billiard ball can be described by assuming that an ideal table has perfectly elastic cushions so that the speed of the ball is not decreased when it rebounds from a cushion. That is, when a ball pushes on a cushion and rebounds with no loss of energy, the collision is said to be a *perfectly elastic collision.* If there were no friction with the table top or air resistance, the ball, once struck, would travel indefinitely in a zigzag path. If several balls were placed on the table and set in motion, they would behave similarly. If the balls were *perfectly elastic,* there would be *no loss of energy* when two of them collided. Their directions would change but *inertia* would keep the balls in motion forever. An increase in the number of balls results in a greater number of collisions and more frequent pushes on the cushion. The principles and mathematics of the billiard-ball system mentioned above are well understood. Since the behavior of gas molecules is similar to that of the ideal billiard-ball system, the same mathematics may be used to describe the pressure exerted by gas molecules. In this manner, the ideal billiard-ball system serves as a model for our understanding of the behavior of gases.

Scientists visualize a gas as a collection of molecules moving around in a container, making perfectly elastic collisions with the walls. Even the smallest sample of gas contains countless molecules. Therefore, a vast number of collisions and "pushes" on the walls of the container occur each second. The sum of all the "pushes" on a given area accounts for the *pressure* of the gas. For example, blowing up a balloon increases the number of gas molecules within the balloon and, consequently, the number of collisions. An increased number of collisions results in more outward "pushes" on the wall, causing the expansion of the balloon.

Experiments such as that illustrated in Fig. 4-3 show that an



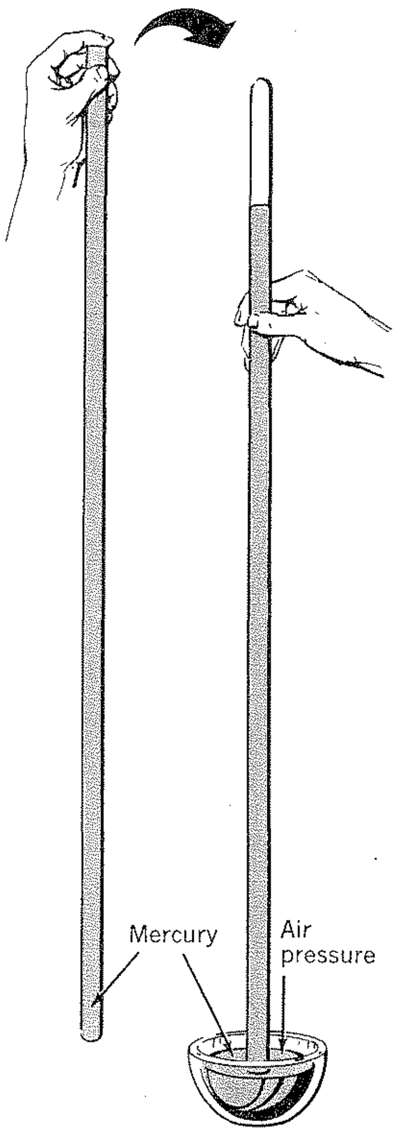
4-2 The behavior of ideal gas molecules in (b) is similar to that of ideal billiard balls on an ideal billiard table in (a). The laws of motion which describe the billiard-ball system can be applied to the motion of ideal gas molecules. By applying mathematical principles and the laws of motion to the gaseous systems, scientists have developed general laws expressed in mathematical terms which accurately describe the behavior of ideal gases.



4-3 As mass is added to the piston, the pressure on the gas increases, and its volume correspondingly decreases.

increase in the external pressure exerted on a gas produces a large decrease in volume. In other words, *gases are highly compressible.* If you have ever owned a bicycle and have used a hand-pump to fill a tire with air, you yourself have demonstrated the compressibility of gases. When you pushed down on the pump, you pushed the molecules together (compressed the gas). Compressing a gas decreases the distances between molecules. It may be shown at room temperature and pressure, that a confined gas is more than 99 percent empty space. Thus, the molecules themselves occupy relatively small space. This vast distance between molecules accounts for the relative ease of compression and the extent to which gases may be compressed. When a gas is compressed, the number of molecules striking a unit area of wall per second is greater than that before compression. The result is greater pressure. Let us now define the concept of pressure more rigorously and identify pressure units commonly used in chemistry.

Pressure is *the force per unit area* which (in this case) gas molecules exert on the walls of their container. Gas pressure is usually measured in chemistry laboratories by means of the Torricellian-type barometer, shown in Fig. 4-4. This type of apparatus was first constructed by Evangelista Torricelli (1608–1647) around the year 1640. To reproduce Torricelli's experiment, take a glass tube of about $\frac{1}{4}$ in. in diameter and about 3 ft. long, sealed at one end, and fill it with mercury. Place your finger over the open end, invert, and submerge the closed end in a dish containing mercury. Remove your finger and note that the column of mercury drops to a height of about 760 mm above the mercury in the dish.



4-4 The downward pressure of the atmosphere on the surface of the mercury is transmitted through the mercury reservoir and exerts an upward force in the barometer tube which is just balanced by the downward force of the mass of the mercury in the tube.

The empty space above the mercury column contains a little mercury vapor but is essentially free of other molecules. The height of the mercury column depends on the force per unit area exerted by the atmosphere on the mercury in the dish. At sea level, the force per unit area exerted by a column of air extending to the "top" of the atmosphere is approximately equal to the force per unit area exerted by a column of mercury 760 mm in height. This quantity is known as ***one standard atmosphere of pressure*** when the mercury is at 0°C.

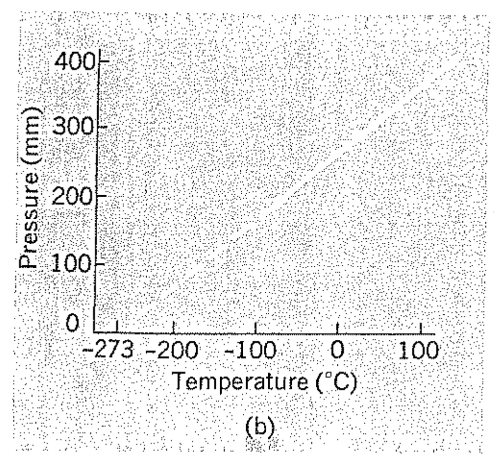
4-11 Combined Gas Law In many instances, a sample of gas is subjected to simultaneous changes in temperature and pressure. To determine the overall change in volume, it is necessary to consider the effect of both temperature and pressure changes. That is, we must find the volume resulting from the temperature change, and then determine the effect of the pressure change on this new volume. This calculation is illustrated below.

Suppose we have a 68.0-ml sample of carbon dioxide gas at 30.0°C and 725 torr. Let us find the volume of this sample at STP. We shall first calculate what volume this sample occupies at 273°K and 725 torr. Since a decrease in temperature decreases the volume, the new volume is

$$68 \text{ ml} \times \frac{273°\text{K}}{303°\text{K}} = 61.3 \text{ ml}$$

This 61.3-ml sample is at 273°K and 725 torr. Next we calculate the effect of increasing the pressure to 760 torr. Since an increase in pressure decreases the volume, the final volume is

$$61.3 \text{ ml} \times \frac{725 \text{ torr}}{760 \text{ torr}} = 58.5 \text{ ml}$$



4-17 (a) An apparatus used to obtain pressure-temperature data. (b) The pressure-temperature graph for an ideal gas. What does the graph reveal about the relationship between the variables *P* and *T*?

The one-step solution is

$$68.0\ \text{ml} \times \frac{273°\text{K}}{303°\text{K}} \times \frac{725\ \text{torr}}{760\ \text{torr}} = 58.5\ \text{ml}$$

In solving this problem, we use a combination of Boyle's and Charles' Laws. It can be shown experimentally that for a constant mass of gas, PV/T = a constant. The value of the constant depends on the mass or the number of moles of gas. This so-called Combined Gas Law is sometimes mathematically expressed as

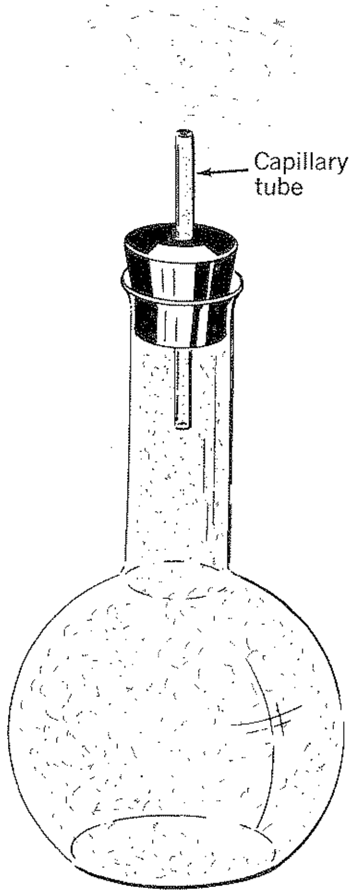
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{4-7}$$

Thus, the answer to the preceding problem could have been obtained by substituting the itemized data in Equation 4-7.

FOLLOW-UP PROBLEM

A gas occupies 68.0 ml at standard temperature and pressure. What volume will it occupy at 30.0°C and 725 torr?

Ans. 79.0 ml.



4-18 As the temperature is increased and the outside pressure reduced, molecules escape through the capillary tube until the pressure within the flask equals that outside the flask.

4-12 Variation in Moles of Gas with Changes in Pressure and Temperature Earlier we remarked that the value of the PV constant depends on the temperature and the number of molecules of gas. The number of molecules may be expressed in terms of the *mass of gas* or the *moles of gas*. Let us examine a system with a fixed volume in which the number of molecules (mass or moles) of gas may vary with changes in temperature and pressure.

Consider a 5.00-liter flask equipped with a rubber stopper containing a fine capillary tube. At STP this flask holds 7.10 g of oxygen. What changes take place in the mass of oxygen when we heat this flask to 120°C and reduce the pressure outside the flask to 700 torr?

As the flask is warmed, a pressure increase would occur inside the flask if it were not open to the atmosphere. Since there is an opening through the capillary tube, we would expect some of the molecules to escape. In addition, the decrease in external pressure from 760 torr to 700 torr would also cause molecules to escape through the capillary tube, since the pressure inside and outside the flask tend to equalize (Fig. 4-18).

Experiments show that the original mass of 7.10 g of oxygen would be diminished to 4.50 g as a result of the temperature and pressure changes. The mass of oxygen present in the final state of the system can be calculated thus:

$$7.10\ \text{g} \times \frac{273°\text{K}}{293°\text{K}} \times \frac{700\ \text{torr}}{760\ \text{torr}} = 4.50\ \text{g}$$

If the mass had been expressed in moles, the same principles and procedures would apply. They indicate that **at constant volume and**

temperature, the pressure is directly proportional to the number of moles (*n*) of gas. This may be expressed mathematically as

$$P = n \times \text{Constant}$$

Where the constant depends on the volume and temperature. Similarly, the experiment above shows an *inverse relationship between Kelvin temperature and number of moles at constant volume* and may be expressed as

$$T = C/n \quad \text{or} \quad nT = C$$

where C is a constant that depends on pressure and volume.

FOLLOW-UP PROBLEM

An apparatus similar to that described above contains 2.25 g of methane (CH_4) at 120°C and 700 torr. (a) What mass of this gas does the flask hold at STP? (b) How many moles of methane does the flask hold at STP? **Ans. (a) 3.51 g, (b) 0.219 mole.**

4-13 The Equation of State for Gases The equation of state for gases shows how the variables which determine the state of the system are related. The four variables, pressure (P), volume (V), Kelvin temperature (T), and number of moles (n) are related by a general equation which may be derived from the individual gas laws or from the Kinetic Molecular Theory.

We shall give a simplified derivation based on the individual gas laws. The following is a summary of relationships derived from experimental observations.

1. At constant temperature, the volume of a fixed mass (number of moles) of gas is inversely proportional to the pressure. This relationship may be expressed mathematically as

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

where $\propto$ is a symbol for proportionality.

2. At constant pressure, the volume of a fixed mass of gas is directly proportional to its Kelvin temperature, T. That is,

$$V \propto T$$

3. From Avogadro's Principle that equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules (or moles), it follows that at constant temperature and pressure, the volume of a gas is directly proportional to the number of molecules. We can express this relationship as

$$V \propto n$$

where n is the number of moles of gas.

Mathematically, it is true that a quantity which is proportional to each of three separate quantities is proportional to their product. Therefore

$$V \propto \frac{1}{P} \times T \times n$$

It is also mathematically true that a proportion may be changed to an equality by inserting a constant. It follows that

$$\mathbf{V = a\ constant \times \frac{1}{P} \times T \times n}$$

which can be rearranged to give

$$\mathbf{PV = n \times constant \times T}$$

This constant, known as the gas constant, is symbolized by the letter R which has the same value for all gases whose behavior approaches that of an ideal gas. Substituting R in the preceding equation yields

$$\mathbf{PV = nRT} \qquad 4\text{-}8$$

Equation 4-8 is known as the ***Ideal Gas Equation.*** In this equation, R is called the ***universal gas constant.*** The value of R depends on the dimensions used for pressure, volume, and temperature. To evaluate R, it is necessary to have available simultaneous values for n, P, T, and V. A convenient set of values are standard conditions of temperature and pressure, 1 mole of gas, and the volume of a mole of gas at STP. The molar volume of the ideal gas is obtained from measurements made on real gases at high temperatures and low pressures, since under these conditions they behave closely to an ideal manner. The calculation of 22.414 liters/mole is then made by extrapolating the volume to STP by using Boyle's and Charles' Laws.

Solving Equation 4-8 for R and substituting standard condition values of P, V, and T for 1 mole of gas yields

$$\mathbf{R = \frac{22.4\ \ell \times 1\ atm}{1\ mole \times 273°K} = 0.082\ \ell\ atm/mole\ °K}$$

The value of 0.082 ℓ atm/mole °K may be used to solve problems with the Ideal Gas Law provided you express volume in liters, pressure in atm, n in moles, and temperature in °K.

Note that the individual gas laws and relationships between pairs of variables can be deduced from the Ideal Gas Equation. For example, if we wish to determine the pressure-volume relationship (Boyle's Law), we observe that n and T are constant. Since R is also constant, then PV = constant and the two factors (P, V) are inversely proportional to each other. Use the Ideal Gas Equation and derive a law mathematically (a) when P is constant, and (b) when V is constant.

TABLE 4-4
MOLAR VOLUMES OF COMMON GASES

Gas	Molecular Mass	Molar Volume (liters, S.T.P.)
Hydrogen	2.016	22.430
Helium	4.003	22.426
Ideal gas	—	22.414
Oxygen	32.00	22.392
Methane	16.043	22.360
Chlorine	70.914	22.063
Sulfur dioxide	64.066	21.888

Example 4-3
Sixteen grams of oxygen gas is introduced into an evacuated 10.0-l flask at 77.0°C. What is the pressure in atmospheres in the container?

Solution

1. In this problem, only one state of the system is given. The Ideal Gas Equation, PV = nRT, may therefore be used. However, in order to use the value of 0.0820 for *R*, it is first necessary to express the mass in moles and the temperature in °K.

$$n = 16.0 \text{ g} \times 1 \text{ mole}/32.0 \text{ g} = 0.500 \text{ mole}$$
$$RT = 77.0°C + 273 \times 350°K$$
$$V = 10.0\ \ell$$

2. Substituting these values in PV = nRT and solving for P yields

$$P = \frac{0.500 \text{ mole} \times 0.082\ \ell \text{ atm} \times 350°K}{10.0\ \ell \text{ mole } °K} = 1.43 \text{ atm.}$$

Pressure measurements in many laboratories are expressed in torr rather than in atmospheres. Thus, it is often convenient to express the general gas constant as

$$R = \frac{62.3 \text{ l torr}}{°K \text{ mole}}$$

or

$$R = \frac{6.23 \times 10^4 \text{ ml torr}}{°K \text{ mole}}$$

FOLLOW-UP PROBLEM

Fifty-six grams of nitrogen is introduced into an evacuated 20.0-liter flask at −73.0°C. What is the pressure (a) in atmospheres and (b) in torr in the container?

Ans. (a) 1.64 atm, (b) 1.25 × 10^3 torr.

Equation 4-8 can be modified to show a relationship unique to gases between density and molecular mass. The number of moles of substance may be expressed as

$$\mathbf{n = g/molecular\ mass\ (m.m.)}$$

Substituting this value in Equation 4-8 gives

$$\mathbf{PV = gRT/m.m.}$$

Rearranging gives

$$\mathbf{P = \frac{g}{V}\frac{RT}{m.m.}}$$

Substituting density, ρ, for *g/V*, we obtain

$$\mathbf{P = \rho RT/m.m.} \quad 4\text{-}9$$

Thus, the molecular mass of a gas may be determined experimentally by measuring its density. Equation 4-9 reveals that density and pressure are directly proportional where as density and Kelvin temperature are inversely proportional.