Chemistry

Zumdahl, 7th edition

歐亞書局

CH5 Gases

The steaming fumaroles located in Bjarnarflag , lceland release a variety of gaes.

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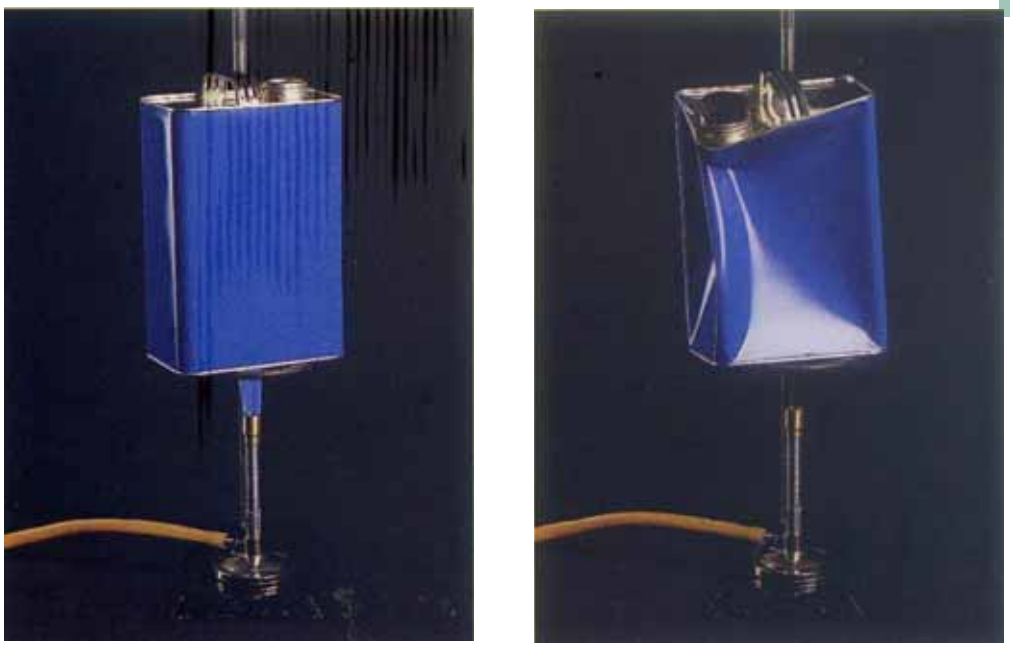
Introduction

- Matter exists in three distinct physical states: gas, liquid, and solid. Although relatively few substances exist in the gaseous state under typical conditions, gases are very important.

5.1 Pressure

- The gases most familiar to us form the earth's atmosphere.
- The pressure exerted by this gaseous mixture that we call air can be dramatically demonstrated by the experiment shown in Fig. 5.1.

Figure 5.1

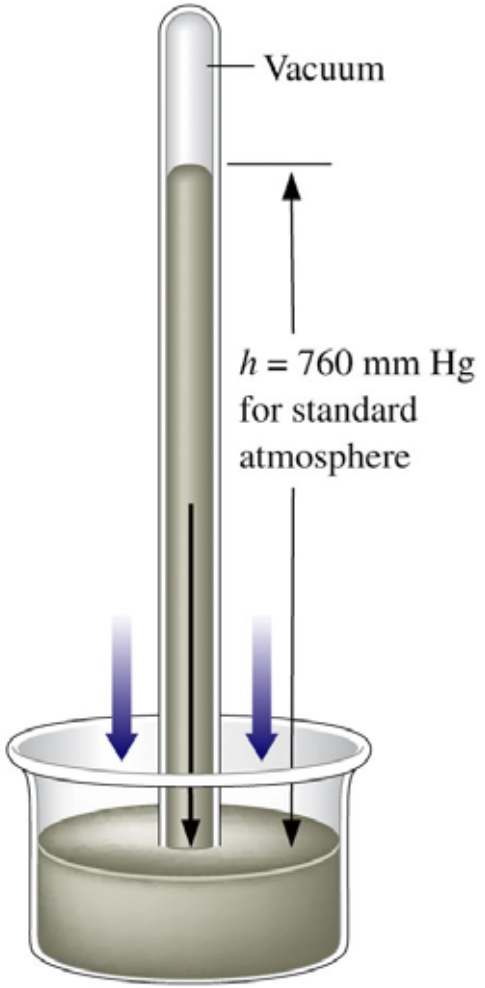


The pressure exerted by the gases in the atmosphere can be demonstrated by boiling water in a large metal can (a) and then turning off the heat and sealing the can. As the can cools, the water vapor condenses, lowering the gas pressure inside the can. This causes the can to crumple (b).

- A device to measure atmospheric pressure, the barometer, was invented in 1643 by an Italian scientist named Evangelista Torricelli (1608-1647), who had been a student of Galileo.
- Torricelli's barometer is constructed by filling a glass tube with liquid mercury and inverting it in a dish of mercury, as shown in Fig. 5.2.
- At sea level the height of this column of mercury averages 760 mm.

Figure 5.2

A torricellian barometer. The tube, completely filled with mercury, is inverted in a dish of mercury. Mercury flows out of the tube until the pressure of the column of mercury (shown by the black arrow) "standing on the surface" of the mercury in the dish is equal to the pressure of the air (shown by the purple arrows) on the rest of the surface of the mercury in the dish.



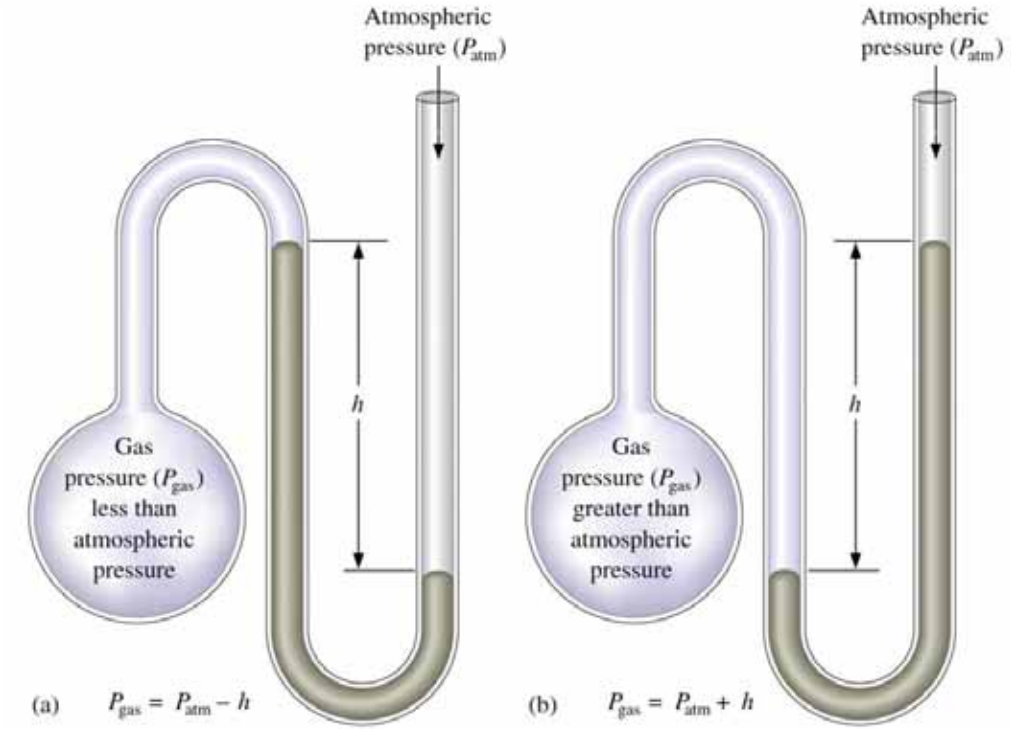
Units of Pressure

- Because instruments used for measuring pressure, such as the **manometer** (Fig. 5.3), often contain mercury, the most commonly used units for pressure are based on the height of the mercury column (in millimeters).
- The unit **mm Hg** (millimeter of mercury) is often called the torr in honor of Torricelli.
- A related unit for pressure is the **standard atmosphere** (abbreviated atm):

1 standard atmosphere = 1 atm = 760 mm Hg = 760 torr

Figure 5.3

A simple manometer, a device for measuring the pressure of a gas in a container. The pressure of the gas is given by *h* (the difference in mercury levels) in units of torr (equivalent to mm Hg). (a) Gas pressure = atmospheric pressure − *h*. (b) Gas pressure = atmospheric pressure + *h*.



- Pressure is defined as force per unit area,

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

- Thus the unit of pressure in the SI system is newtons per meter squared (N/m) and is called the **pascal** (Pa).

$$1 \text{ standard atmosphere} = 101{,}325 \text{ Pa}$$

- Thus 1 atmosphere is about 10^5 pascals.

$$1 \text{ atm} = 760 \text{ mm Hg}$$
$$= 760 \text{ torr}$$
$$= 101{,}325 \text{ Pa}$$
$$= 29.92 \text{ in Hg}$$
$$= 14.7 \text{ lb/in}$$

5.2 The Gas Laws of Boyle, Charles, and Avogadro

Boyle's Law

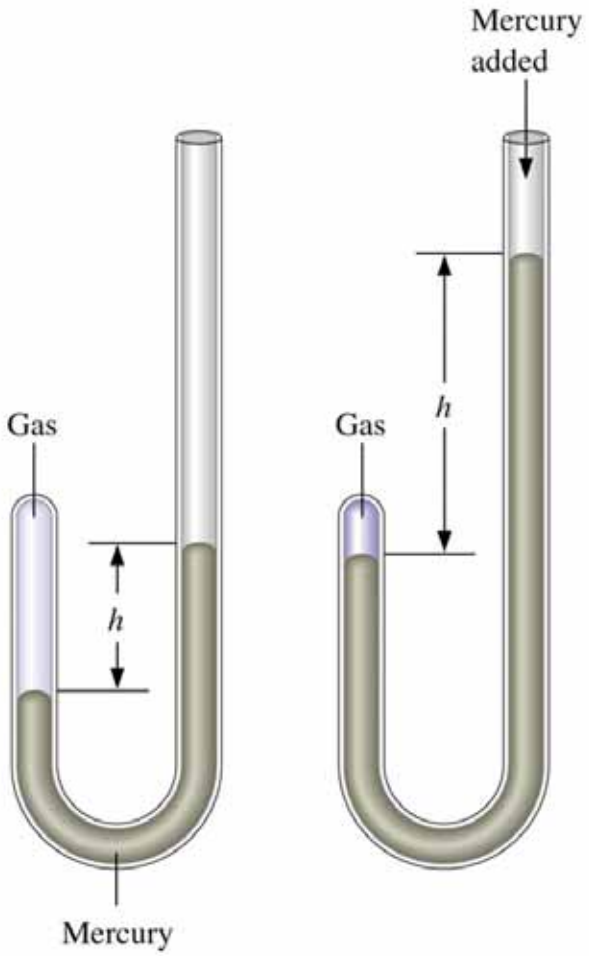
- The first quantitative experiments on gases were performed by an Irish chemist, Robert Boyie (1627-1691).
- Representative values from Boyle's experiments are given in Table 5.1.

$$PV = k$$

TABLE 5.1 Actual Data From Boyle's Experiment

Volume (in^3)	Pressure (in Hg)	Pressure × Volume (in Hg × in^3)
117.5	12.0	14.1×10^2
87.2	16.0	14.0×10^2
70.7	20.0	14.1×10^2
58.8	24.0	14.1×10^2
44.2	32.0	14.1×10^2
35.3	40.0	14.1×10^2
29.1	48.0	14.0×10^2

Figure 5.4



A J-tube similar to the one used by Boyle.

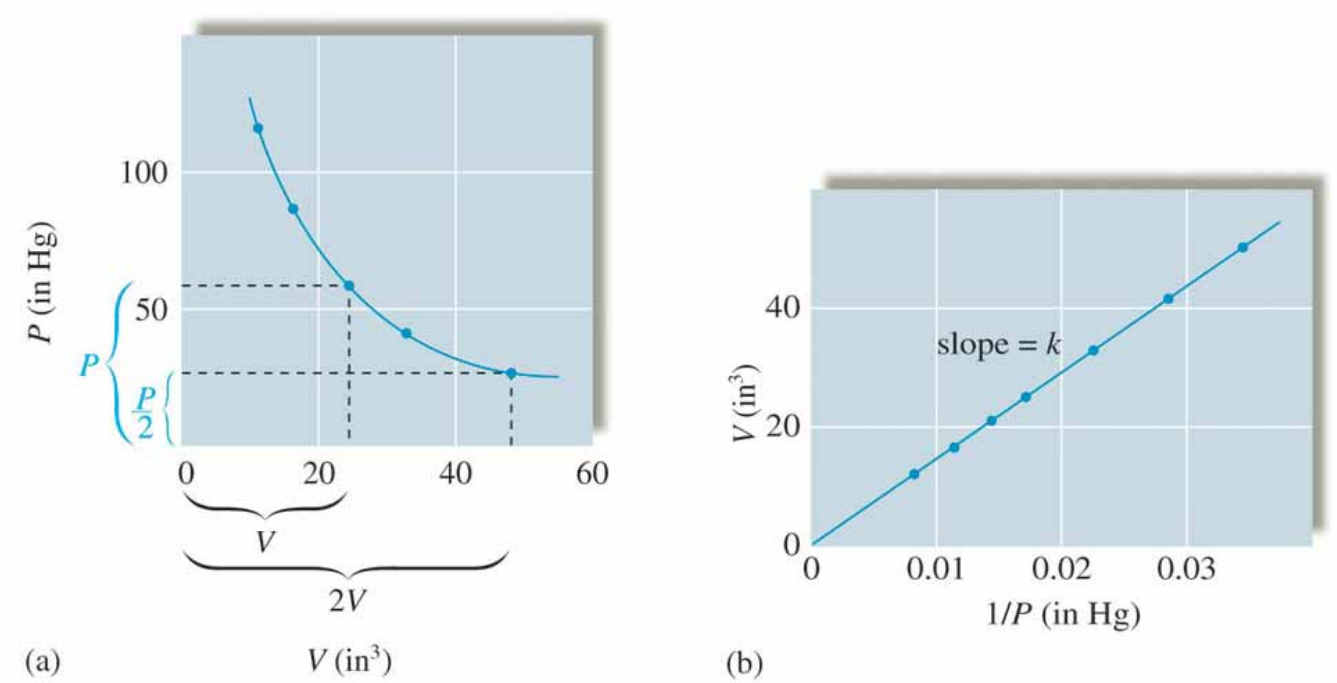
- Which is called **Boyle's law** and where *k* is a constant for a given sample of air at a specific temperature.
- The first type of plot, P versus V, firms a curve called a *hyperbola* shown in Fig. 5.5(a).

$$V = \frac{k}{p} = k \frac{1}{p}$$

$$y = mx + b$$

- where *m* represents the slope and *b* the intercept of the straight line.

Figure 5.5

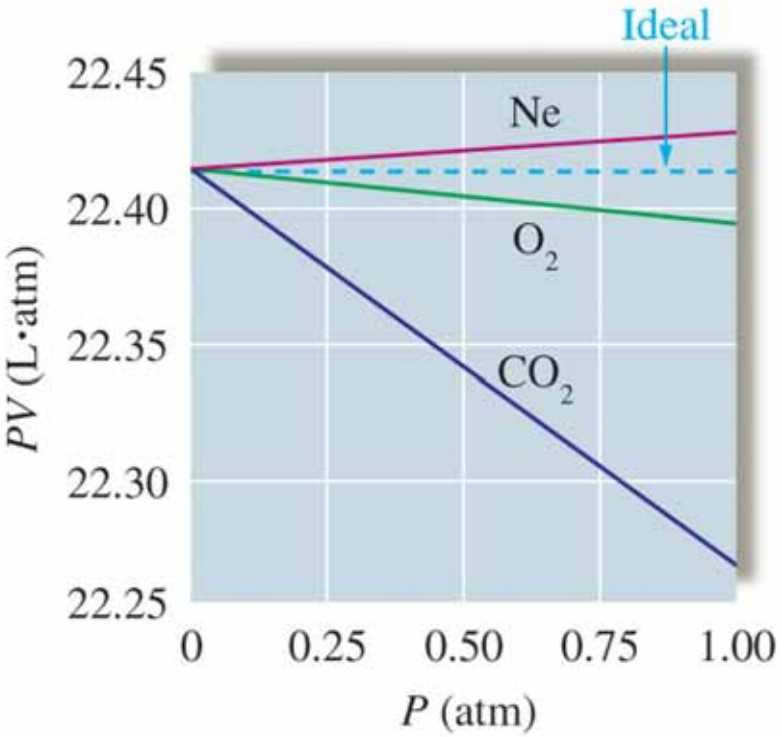


Plotting Boyle's data from Table 5.1. (a) A plot of P versus V shows that the volume doubles as the pressure is halved. (b) A lot of V versus 1/P gives a straight line. The slope of this line equals the value of the constant k.

- Results for several gases at pressures below 1 atm are shown in Fig. 5.6.
- *A gas that strictly obeys Boyle's law is called an* ***ideal gas***.
- One common use of Boyle's law is to predict the new volume of a gas when the pressure is changed (at constant temperature), or vice versa.

Figure 5.6

A plot of *PV* versus *P* for several gases at pressures below 1 atm. An ideal gas is expected to have a constant value of *PV*, as shown by the dotted line. Carbon dioxide shows the largest change in *PV*, and this change is actually quite small: *PV* changes from about 22.39 L · atm at 0.25 atm to 22.26 L · atm at 1.00 atm. Thus Boyle's law is a good approximation at these relatively low pressures.

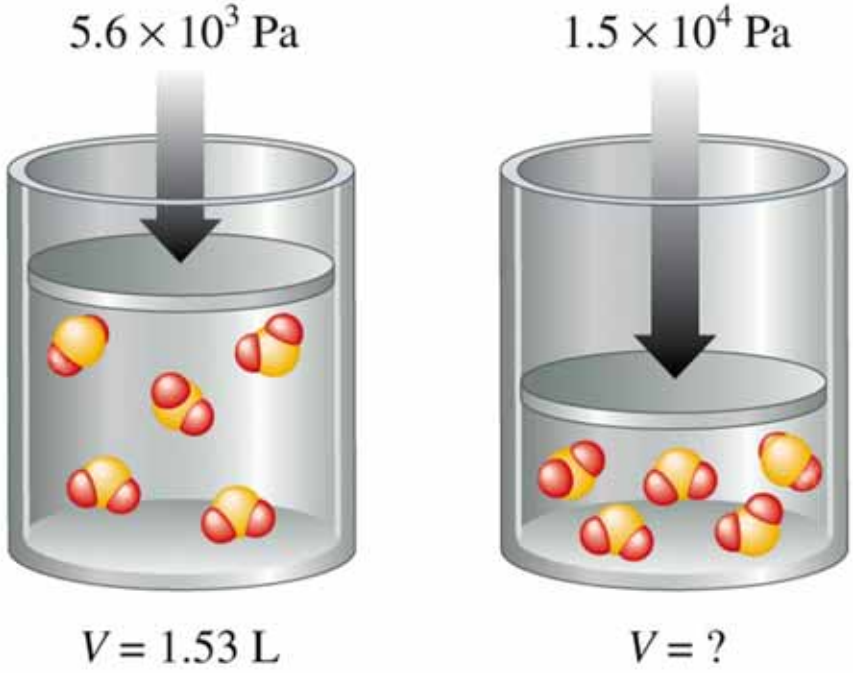


Sample Exercise 5.2 Boyle's law I

Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53-L sample of gaseous SO_2 at a pressure of 5.6×10^3 Pa. If the pressure is changed to 1.5×10^3 Pa at a constant temperature, what will be the new volume of the gas?

Sample Exercise 5.2

As pressure increases, the volume of SO_2 decreases.



Boyle's law also can be written as

$$P_1V_1 = P_2V_2$$

See Exercises 5.33

Sample Exercise 5.3

Boyle' law II

In a study to see how closely gaseous ammonia obeys Boyle's law, several volume measurements were made at various pressure, using 1.0 mol NH_3 gas at a temperature of 0℃. Using the results listed on the following page, calculate the Boyle's law constant for NH_3 at the various pressure.

Experiment	Pressure (atm)	Volume (L)
1	0.1300	172.1
2	0.2500	89.28
3	0.3000	74.35
4	0.5000	44.49
5	0.7500	29.55
6	1.000	22.08

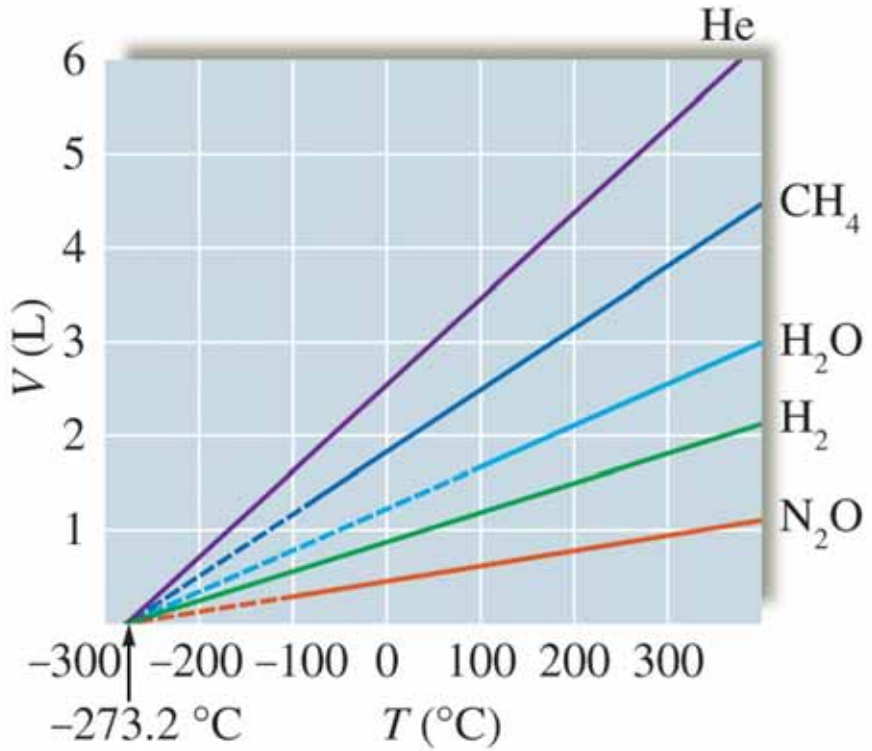
Charles's Law

- Jacques Charles (1746-1823), who was the first person to fill a balloon with hydrogen gas and who made the first solo balloon flight.
- Charles found in 1787 that the volume of a gas at constant pressure increases linearly with the temperature of gas.

A snowmaking machine, in which water is blown through nozzles compressed air. The mixture is cooled by expansion to form ice crystals of snow.

Figure 5.8

Plots of V versus T (℃) for several gases. The solid lines represent experimental measurements on gases. The dashed lines represent extrapolation of the data into regions where these gases would become liquids or solids. Note that the samples of the various gases contain different numbers of moles.



- Kelvin and Celsius scales:

$$K = ℃ + 273$$

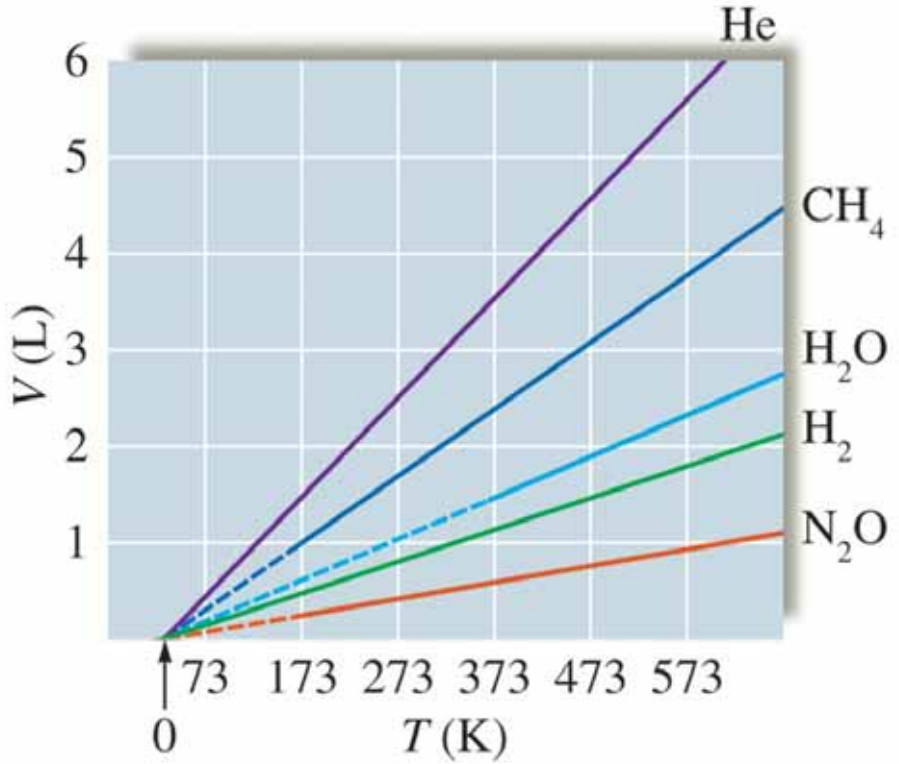
- When the volumes of the gases shown in Fig. 5.8 are plotted versus temperature on the Kelvin scale, the plots in Fig. 5.9 result.
- In this case, the volume of each gas is *directly proportional to temperature* and extrapolates to zero when the temperature is 0 K.

- This behavior is represented by the equation known as **Charles's law**,

$$V = bT$$

- Where T is in kelvins and b is a proportionality constant.
- 0 K is called **absolute zero**.

Figure 5.9



Plots of *V* versus *T* as in Fig. 5.8, except here the Kelvin scale is used for temperature.

Avogadro's Law

- Equal volumes of gases at the same temperature and pressure contain the same number of "particles."
- Avogadro's law is

$$V = an$$

- Where V is the volume of the gas, n is the number of moles of gas particles, and a is a proportionality constant.

- This equation states that *for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles of gas*.

5.3 The Ideal Gas Law

Boyle's law: $V = \frac{k}{p}$ (at constant T and n)

Charle's law: $V = bT$ (at constant P and n)

Avogadro's law: $V = an$ (at constant T and P)

$$V = R\frac{Tn}{p}$$

• Where R is the combined proportionality constant called the universal constant.

- When the pressure is expressed in atmospheres and the volume in liters, R has the value 0.082.0 L • atm/K• mol.
- The preceding equation can be rearranged to the more familiar form of the ideal gas law:

$$PV = nRT$$

- A particular state of a gas is described by its pressure, volume, temperature, and number of moles.

- Knowledge of any three of properties is enough to completely define the state of a gas, since the fourth property can then be determined from the equation for the ideal gas law.

Sample Exercise 5.6

Ideal Gas Law I

A sample of hydrogen gas (H_2) has a volume of 8.56 L at a temperature of 0℃ and a pressure of 1.5 atm. Calculate the moles of H_2 molecules present in this gas sample.

Solution

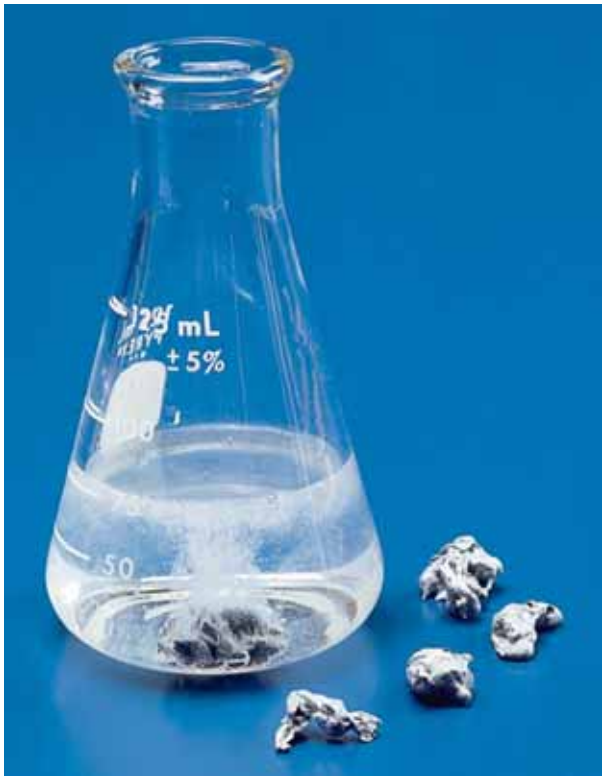
Solving the ideal gas law for n gives

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

In this case $P = 1.5$ atm, $V = 8.56$ L, $T = 0℃ + 273 = 273$ K, and $R = 0.08206$ L • atm/K• mol. Thus

Sample Exercise 5.6

$$n = \frac{(1.5\ \cancel{\text{atm}})(8.56\ \cancel{\text{L}})}{\left(0.08206\ \frac{\cancel{\text{L}} \cdot \cancel{\text{atm}}}{\cancel{\text{K}} \cdot \text{mol}}\right)(273\ \cancel{\text{K}})} = 0.57\ \text{mol}$$



The reaction of zinc with hydrochloric acid to produce bubble of hydrogen gas.

See Exercises 5.37 though 5.42

Sample Exercise 5.7

Ideal Gas Law II

Suppose we have a sample of ammonia gas with a volume of 7.0 mL at a pressure of 1.68 atm. The gas is compressed to a volume of 2.7 mL at a constant temperature. Use the ideal gas law to calculate the final pressure.

Solution

We always place the variables that change on one side of the equals sign and the constants on the other.

Sample Exercise 5.7

In this

$$PV = nRT$$

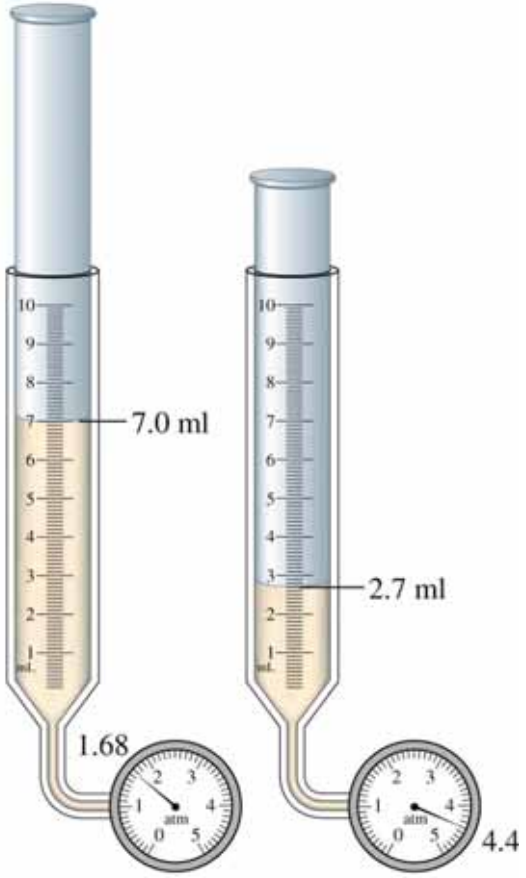
Change (↗ PV) Remain constant (↖ nRT)

Since n and T remain the same in this case, we can write $P_1V_1 = nRT$ and $P_2V_2 = nRT$.

$$P_1V_1 = nRT = P_2V_2 \quad \text{or} \quad P_1V_1 = P_2V_2$$

Reality Check: The volume decreased (at constant temperature), so the pressure should increase, as the result of the calculation indicates.

Sample Exercise 5.7



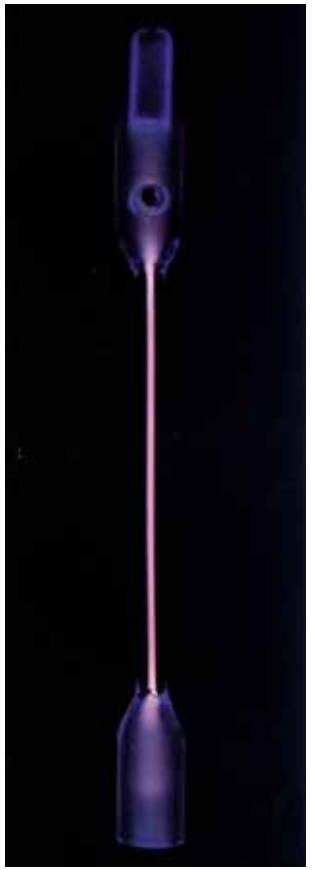
As pressure increases, the volume decreases.

See Exercises 5.37 though 5.42

Sample Exercise 5.10

Ideal Gas Law V

A sample containing 0.35 mol argon gas at a temperature of 13℃ and a pressure of 568 torr is heated to 56℃ and pressure of 897 torr. Calculate the change in volume that occurs.



Argon glowing in a discharge tube.

Solution

We use the ideal gas law to find the volume for each set of conditions:

Sample Exercise 5.10

State 1	State 2
$n_1 = 0.35$ mol	$n_2 = 0.35$ mol
$P_1 = 568\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.747\ \text{atm}$	$P_2 = 897\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 1.18\ \text{atm}$
$T_1 = 13°\text{C} + 273 = 286\ \text{K}$	$T_2 = 56°\text{C} + 273 = 329\ \text{K}$

See Exercises 5.49

5.4 Gas Stoichiometry

- Suppose we have 1 mole of an ideal gas at 0℃ (273.2K) and 1 atm.
- From the ideal gas law, the volume of the gas is given by

$$V = \frac{nRT}{P} = \frac{(1.000\ \cancel{\text{mol}})(0.08206\ \text{L}\cdot\cancel{\text{atm}}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(273.2\ \cancel{\text{K}})}{1.000\ \cancel{\text{atm}}}$$

$$= 22.42\ \text{L}$$

- This volume of 22.4 liters is the **molar volume** of an ideal gas (at 0℃ and 1 atm).
- The measured molar volumes of several gases are listed in Table 5.2.
- The conditions 0℃ and 1 atm, called **standard temperature and pressure** (abbreviated **STP**), are common reference conditions for the properties of gases.
- For example, the molar volume of an ideal gas is 22.42 liters at STP (see Fig 5.11).

TABLE 5.2 Molar Volumes for Various Gases at 0℃ and 1 atm

Gas	Molar Volume (L)
Oxygen (O_2)	22.397
Nitrogen (N_2)	22.402
Hydrogen (H_2)	22.433
Helium (He)	22.434
Argon (Ar)	22.397
Carbon dioxide (CO_2)	22.260
Ammonia (NH_3)	22.079

Figure 5.11

22.4 L of gas would just fit into this box.

Sample Exercise 5.11

Gas Stoichiometry I

A sample of nitrogen gas has a volume of 1.75 L at STP. How many moles of N_2 are present?

Solution

$$1.75\ \cancel{\text{L N}_2} \times \frac{1\ \text{mol N}_2}{22.42\ \cancel{\text{L N}_2}} = 7.81 \times 10^{-2}\ \text{mol N}_2$$

See Exercises 5.51 and 5.52

Sample Exercise 5.12

Gas Stoichiometry II

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate ($CaCO_3$). Calculate the volume of CO_2 at STP produced from the decomposition of 152 g $CaCO_3$ by the reaction

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

Solution

Thus the decomposition of 152 g $CaCO_3$ produces 34.1 L CO_2 at STP.

See Exercises 5.51 and 5.52

Molar Mass of Gas

- One very important use of the ideal gas law is in the calculation of the molar mass (molecular weight) of a gas from its measured density.

$$n = \frac{\text{Grams of gas}}{\text{molar mass}} = \frac{\text{mass}}{\text{molar mass}} = \frac{m}{\text{molar mass}}$$

- Substitution into the udeal gas equation gives.

$$P = \frac{nRT}{V} = \frac{(m/\text{molar mass})RT}{V} = \frac{m(RT)}{V(\text{molar mass})}$$

- However, m/V is the gas density d in units of grams per liter. Thus

$$P = \frac{dRT}{\text{molar mass}}$$

- or

$$\text{Molar mass} = \frac{dRT}{P} \qquad (5.1)$$

5.5 Dalton's Law of Partial Pressures

- In 1803 Dalton summarized his observations as follows: *For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.*
- This statement, known as Dalton's law of partial pressures, can be expressed as follows:

$$P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \cdots$$

- Where the subscripts refer to the individual gases (gas 1, gas 2,and so on).

- The symbols P_1, P_2, P_3, and so on represent each partial pressure.

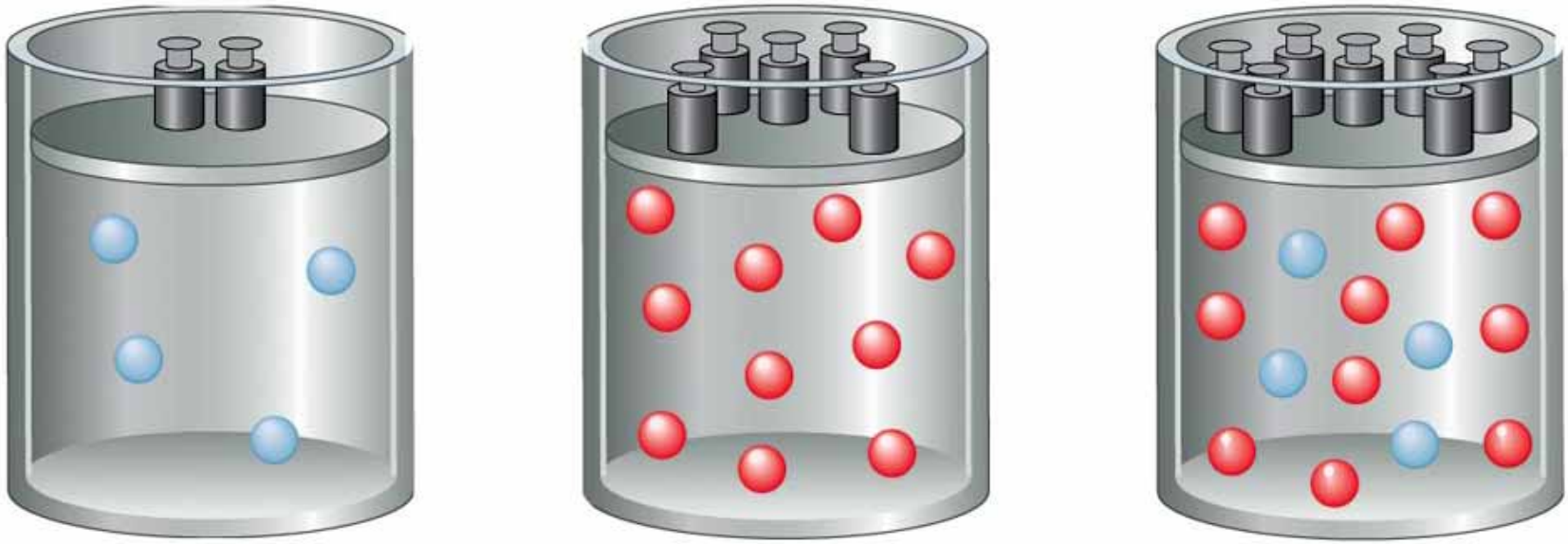
$$P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \cdots = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \cdots$$

$$= (n_1 + n_2 + n_3 + \cdots)\left(\frac{RT}{V}\right)$$

- Where n_{TOTAL} is the sum of the numbers of moles of the various gases.

- Thus, for a mixture of ideal gases, it is the total number of moles of particles that is important, not the identity or composition of the involved gas particles.
- This idea is illustrated in Fig. 5.12.

Figure 5.12



The partial pressure of each gas in a mixture of gases in a container depends on the number of moles of that gas. The total pressure is the sum of the partial pressures and depends on the total moles of gas particles present, no matter what they are.

- **mole fraction**: *the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.*
- The mole fraction χ_1 is

$$\chi_1 = \frac{n_1}{n_{\text{TOTAL}}} = \frac{n_1}{n_1 + n_2 + n_3 + \cdots}$$

• From the ideal gas equation we know that the number of moles of a gas is directly proportional to the pressure of the gas ,since

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

$$n_1 = P\left(\frac{V}{RT}\right), \qquad n_2 = P\left(\frac{V}{RT}\right)$$

$$\chi_1 = \frac{n_1}{n_{\text{TOTAL}}} = \frac{\overbrace{P_1(V/RT)}^{n_1}}{\underbrace{P_1(V/RT)}_{n_1} + \underbrace{P_2(V/RT)}_{n_2} + \underbrace{P_3(V/RT)}_{n_3} + \cdots}$$

$$= \frac{P_1}{P_{\text{TOTAL}}}$$

The mole fraction of each component in a mixture of ideal gases is directly related to its partial pressure:

$$\chi_1 = \frac{n_2}{n_{\text{TOTAL}}} = \frac{P_2}{P_{\text{TOTAL}}}$$

• The expression for the mole fraction,

$$\chi_1 = \frac{P_1}{P_{\text{TOTAL}}}$$

• Can be rearranged to give

$$P_1 = \chi_1 \times P_{\text{TOTAL}}$$

- Can be rearranged to give

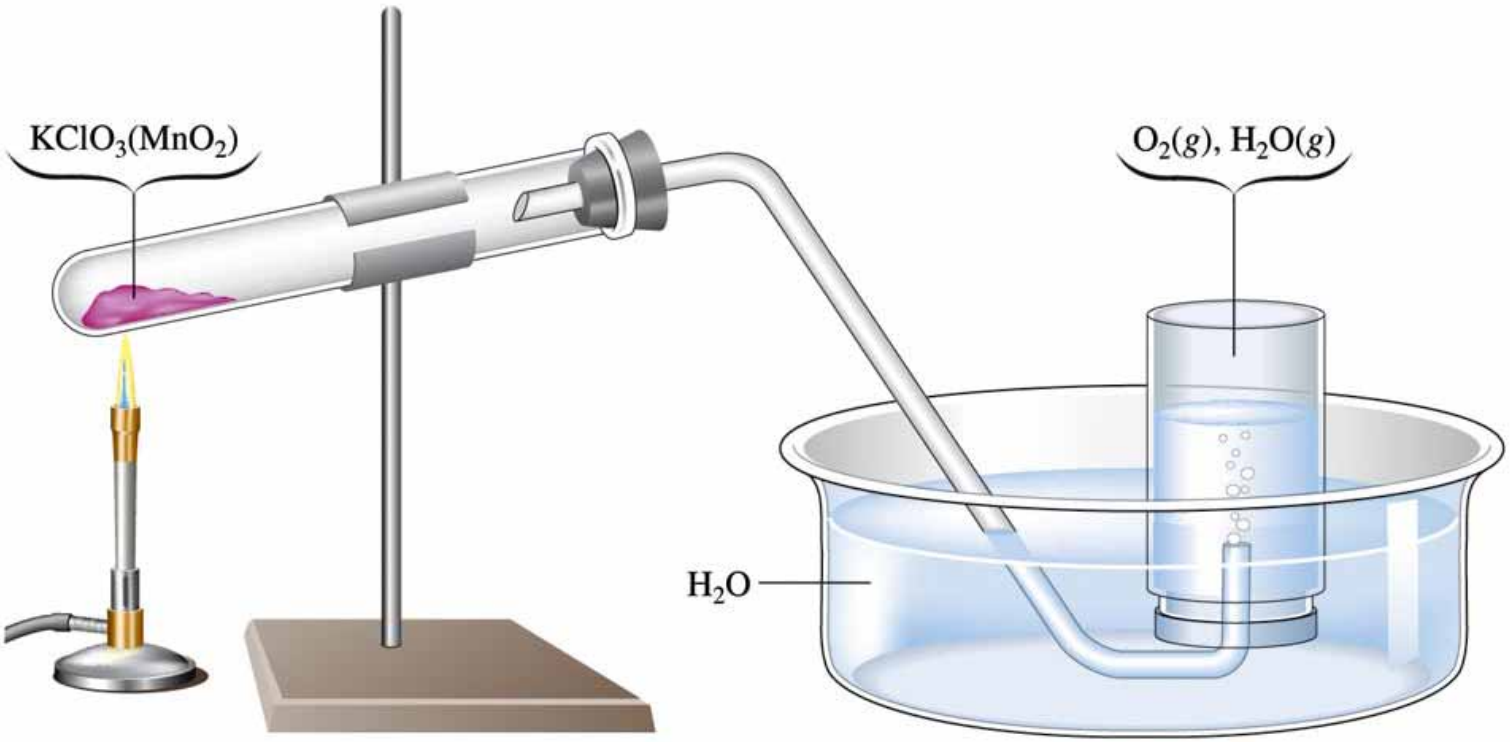
$$P_1 = \chi_1 \times P_{\text{TOTAL}}$$

• That is, *the partial pressure of a particular component of a gaseous mixture is the mole fraction of that component times the total pressure.*

Collecting a Gas over Water

- Fig. 5.13 shows the collection of oxygen gas produced by the decomposition of solid potassium chlorate.
- This pressure, which depends on temperature, is called the *vapor pressure of water*.

Figure 5.13



The production of oxygen by thermal decomposition of $KClO_3$. The MnO_2 is mixed with the $KClO_3$ to make the reaction faster.

Sample Exercise 5.18

Gas Collection over Water

A sample of solid potassium chlorate ($KClO_3$) was heated in a test tube (see Fig. 5.13) and decomposed by the following reaction:

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

The oxygen produced was collected by displacement of water at 22℃ at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22℃ is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of $KClO_3$ in the sample that was decomposed.

Sample Exercise 5.18

Solution

First we find the partial pressure of O_2 from Dalton's law of partial pressure:

$$P_{TOTAL} = P_{O_2} + P_{H_2O} = P_{O_2} + 21 \text{ torr} = 754 \text{ torr}$$

Thus

$$P_{O_2} = 754 \text{ torr} - 21 \text{ torr} = 733 \text{ torr}$$

A mole ratio of 2 mol $KClO_3$/3 mol O_2. the moles of $KClO_3$ can be calculated as follows:

Sample Exercise 5.18

Thus

$$n_{O_2} = \frac{(0.964\ \cancel{atm})(0.650\ \cancel{L})}{(0.08206\ \cancel{L} \cdot \cancel{atm}/\cancel{K} \cdot mol)(295\ \cancel{K})} = 2.59 \times 10^{-2}\ mol$$

A mole ratio of 2 mol $KClO_3$/3 mol O_2. The moles of $KClO_3$ can be calculated as follows:

$$2.59 \times 10^{-2}\ \cancel{mol\ O_2} \times \frac{2\ mol\ KClO_3}{3\ \cancel{mol\ O_2}} = 1.73 \times 10^{-2}\ mol\ KClO_3$$

$$= 2.12\ g\ KClO_3$$

See Exercises 5.71 through 5.73

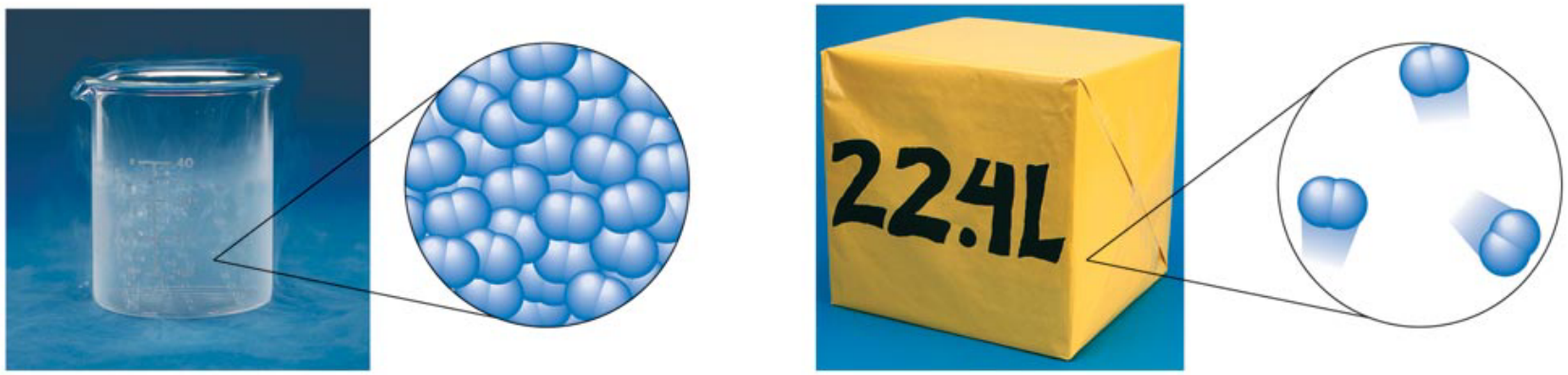
5.6 The Kinetic Molecular Theory of Gases

- **kinetic molecular theory (KMT)**, a simple model that attempts to explain the properties of an ideal gas.
- The postulates of the kinetic molecular theory as they relate to the particles of an ideal gas can be stated as follows:

1. The particles are so small compared with the distances between them that *the volume of the individual particles can be assumed to be negligible* (zero). See Fig. 5.14.

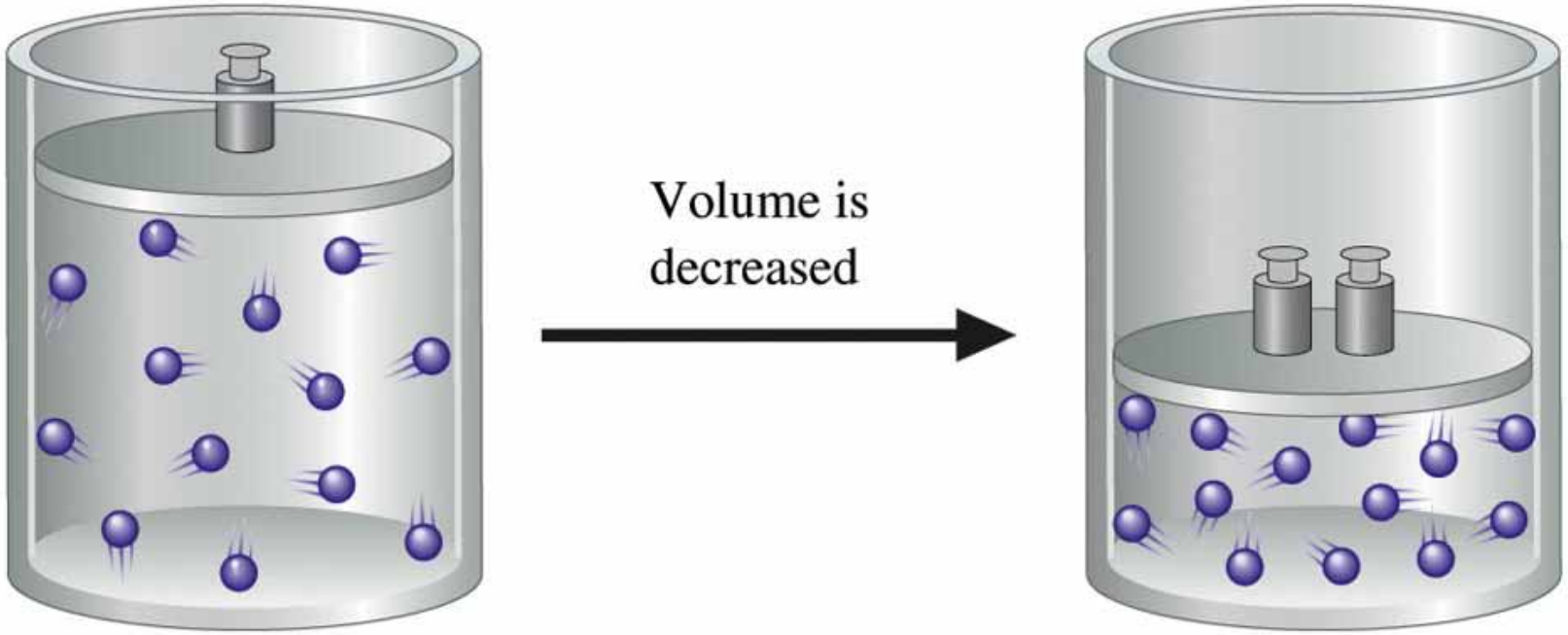
2. The particles are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.
3. The particles are assumed to exert no forces on each other; they are assumed neither to attract nor to repel each other.
4. The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.

Figure 5.14



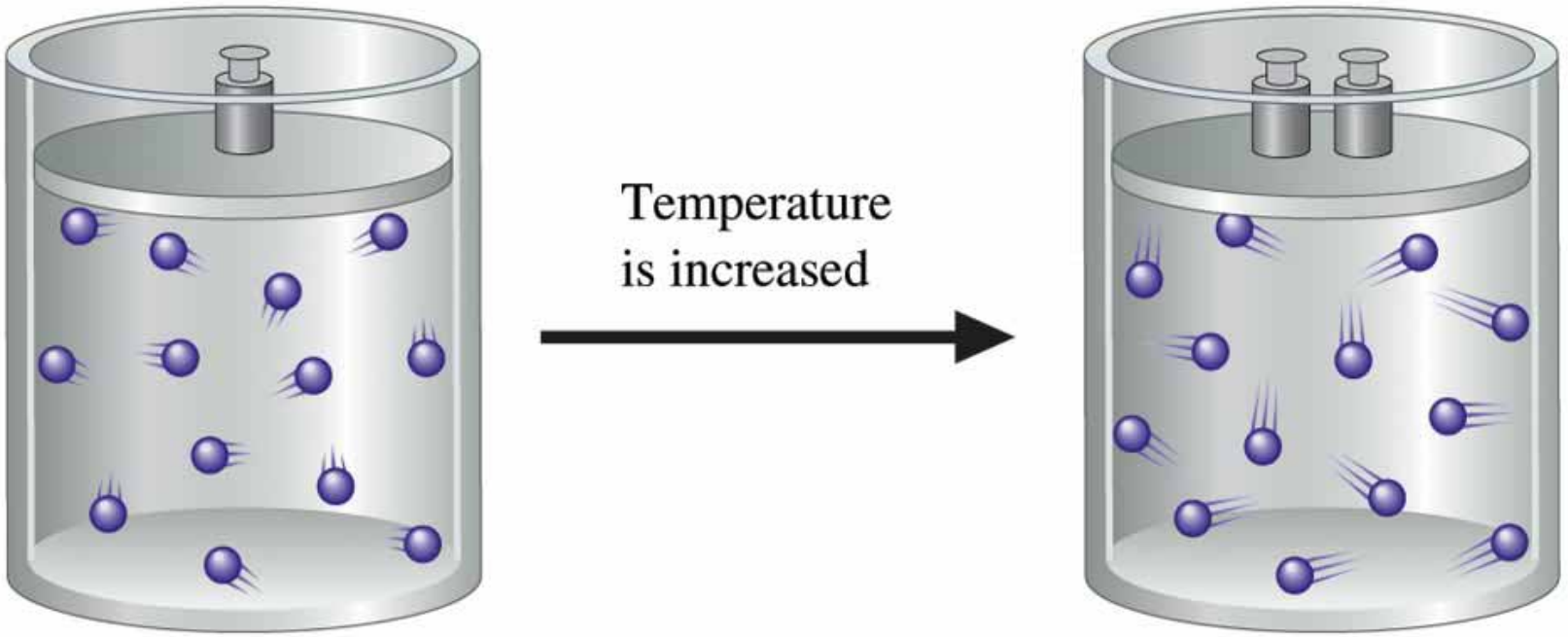
(a) One mole of $N_2(l)$ has a volume of approximately 35 mL and a density of 0.81 g/mL. (b) One mole of $N_2(g)$ has a volume of 22.4 L (STP) and a density of 1.2×10^{-3} g/mL. Thus the ratio of the volumes of gaseous N_2 and liquid N_2 is 22.4/0.035 = 640 and the spacing of the molecules is 9 times farther apart in $N_2(g)$.

Pressure and Volume (Boyle's Law)



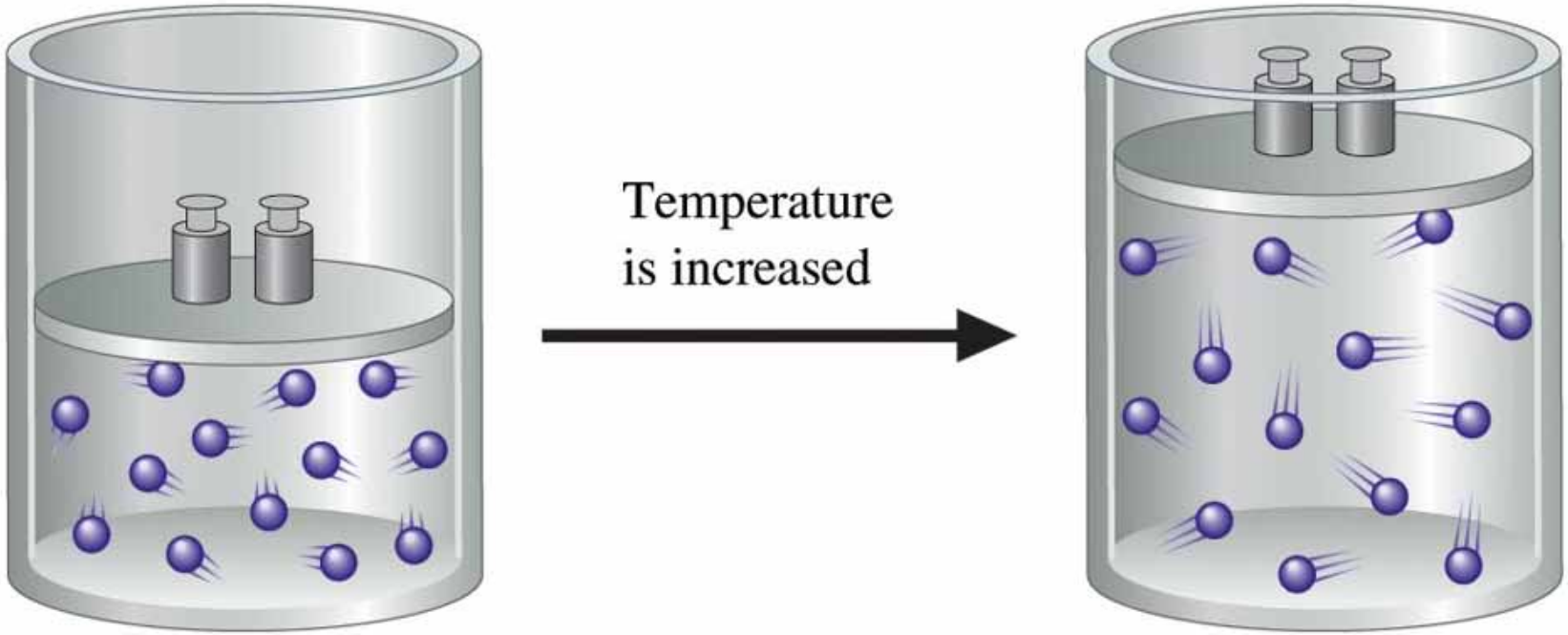
The effects of decreasing the volume of a sample of gas at constant temperature.

Figure 5.16



The effects of increasing the temperature of a sample of gas at constant volume.

Volume and Temperature (Charles's Law)



The effects of increasing the temperature of a sample of gas constant pressure.

Volume and Number of Moles (Avogadro's Law)

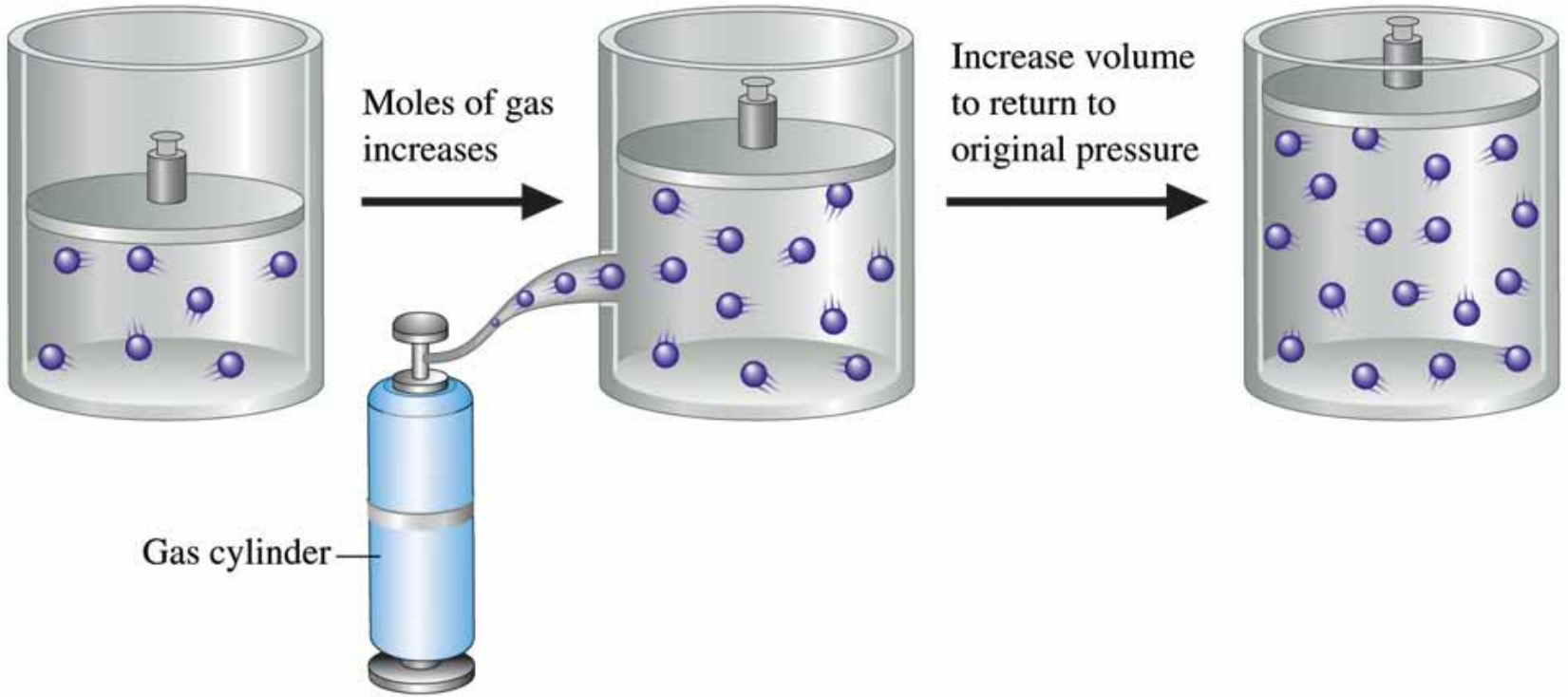
The ideal gas law predicts that the volume of a gas at a constant temperature and pressure depends directly on the number of gas particles present:

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

($\frac{RT}{P}$: Constant)

• It is important to recognize that the volume of a gas (at constant P and T) depends only on the number of gas particles present.

Figure 5.18



The effects of increasing the number of moles of gas particles at constant temperature and pressure.

Mixture of Gases (Dalton's Law)

- The observation that the total pressure exerted by a mixture of gases is the sum of the pressures of the individual gases is expected because the KMT assumes that all gas particles are independent of each other and that the volumes of the individual particles are unimportant.
- Thus the identities of the gas particles do not matter.

Deriving the Ideal Gas Law

- By applying the principles of physics to the assumptions of the KMT, we can in effect derive the ideal gas law.

$$P = \frac{2}{3}\left[\frac{nN_A(\frac{1}{2}m\overline{u^2})}{V}\right]$$

- where P is the pressure of the gas, n is the number of moles of gas, N_A is Avogadro's number, m is the mass of each particle, $\overline{u^2}$ is the average of the square of the velocities of the particles, and V is the volume of the container.

$$(\mathrm{KE})_{\mathrm{avg}} = N_A(\tfrac{1}{2}m\overline{u^2})$$

$$P = \frac{2}{3}\left[\frac{n(\mathrm{KE})_{\mathrm{avg}}}{V}\right] \quad \text{or} \quad \frac{PV}{n} = \frac{2}{3}(\mathrm{KE})_{\mathrm{avg}}$$

- The fourth postulate of the kinetic molecular theory is that the average kinetic energy of the particles in the gas sample is directly proportional to the temperature in Kelvins.

- sine $(KE)_{avg} \propto T$

$$\frac{PV}{n} = \frac{2}{3}(KE)_{avg} \propto T \quad \text{or} \quad \frac{PV}{n} \propto T$$

- Note that this expression has been derived from the assumptions of the kinetic molecular theory.

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

$$\frac{PV}{n} \propto T$$ Form theory

(a) A balloon filled with air at room temperature. (b) The balloon is dipped into liquid nitrogen at 77 K. (c) The balloon collapses as the molecules inside slow down due to the decreased temperature. Slower molecules produce a lower pressure.

The Meaning of Temperature

- The exact relationship between temperature and average kinetic energy can be obtained by combining the equations:

$$\frac{PV}{n} = RT = \frac{2}{3}(\mathrm{KE})_{\mathrm{avg}}$$

$$(\mathrm{KE})_{\mathrm{avg}} = \frac{3}{2}RT$$

- The meaning of the Kelvin temperature of a gas: The Kelvin temperature is an index of the random motions of the particles of a gas, with higher temperature meaning greater motion.

Root Mean Square Velocity

- The square root of $\overline{u^2}$ is called the **root mean square velocity** and is symbolized by u_{rms}:

$$u_{rms} = \sqrt{\overline{u^2}}$$

$$(KE)_{avg} = N_A(\tfrac{1}{2}m\overline{u^2}) \quad \text{and} \quad (KE)_{avg} = \frac{3}{2}RT$$

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

$$\sqrt{\overline{u^2}} = u_{\text{rms}} = \sqrt{\frac{3RT}{N_A m}}$$

- R = 0.08206 L•atm/K•mol

Sample Exercise 5.19

Root Mean Square Velocity

Calculate the root mean square velocity for the atoms in a sample of helium gas at 25℃.

Solution

The formula for root mean square velocity is

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

$T = 25℃ + 273 = 298$ K, $R = 8.3145$ J/K• mol, and

$$M = 4.00\frac{\text{g}}{\text{mol}} \times \frac{1\text{ kg}}{1000\text{ g}} = 4.00 \times 10^{-3}\text{ kg/mol}$$

Sample Exercise 5.19

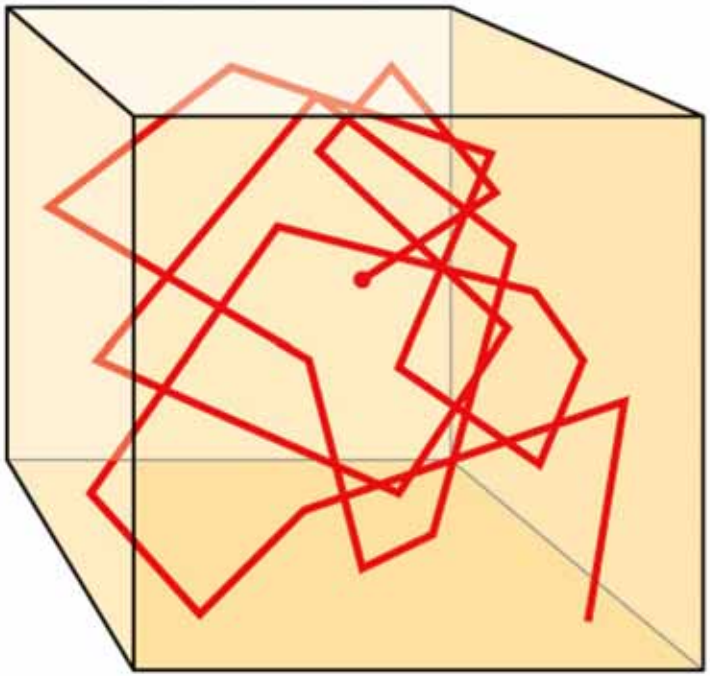
Thus

$$u_{rms} = 1.36 \times 10^3 \text{ m/s}$$

See Exercises 5.79 through 5.80

- If the path of a particular gas particle could be monitored, it would look very erratic, something like that shown in Fig. 5.19.
- The average distance a particle travels between collisions in a particular gas sample is called the mean free path.
- The actual distribution of molecular velocities for oxygen gas at STP is shown in Fig. 5.20.
- This figure shows the relative number of gas molecules having each particular velocity.

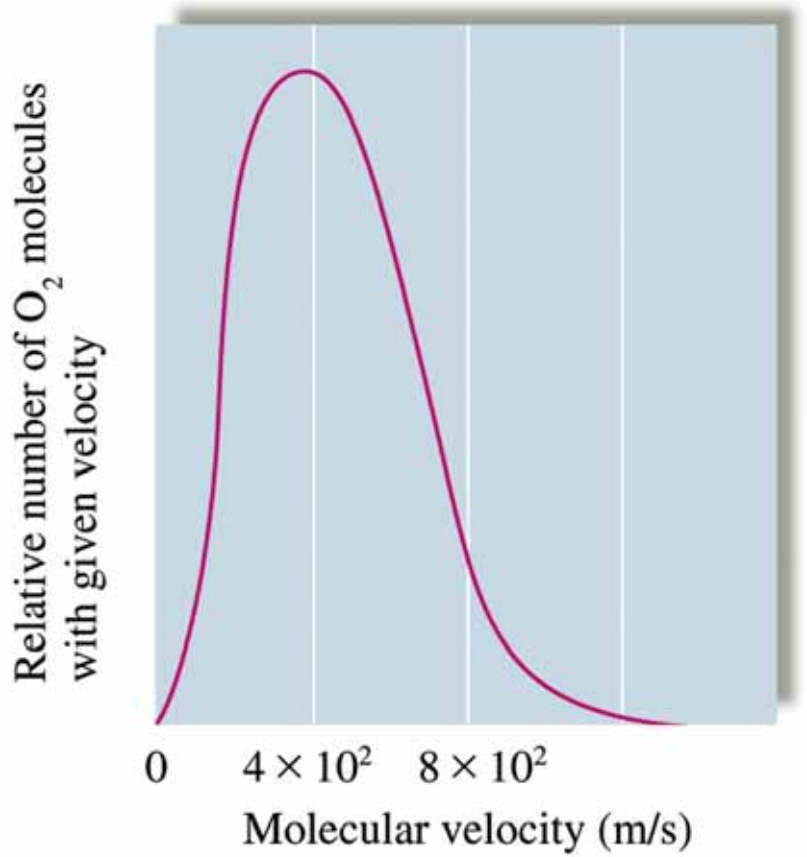
Figure 5.19



Path of one particle in a gas. Any given particle will continuously change its course as a result of collisions with other particles, as well as with the walls of the container.

Figure 5.20

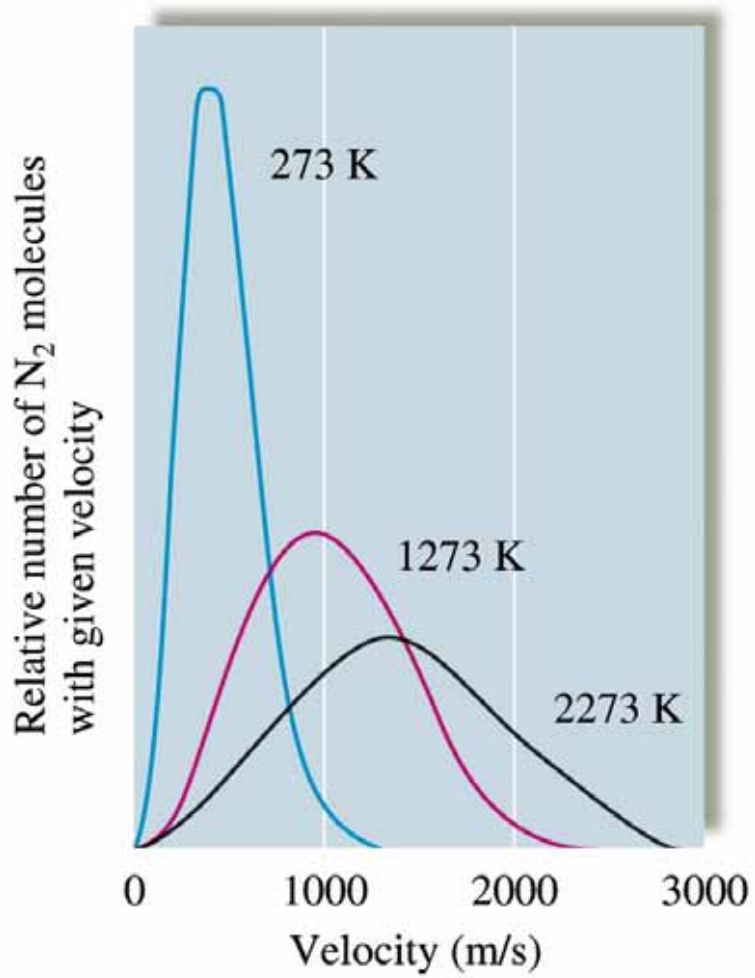
A plot of the relative number of O_2 molecules that have a given velocity at STP.



- Figure 5.21 shows the velocity distribution for nitrogen gas at three temperatures.
- Note that as the temperature is increased, the curve peak moves toward higher values and the range of velocities becomes much larger.

Figure 5.21

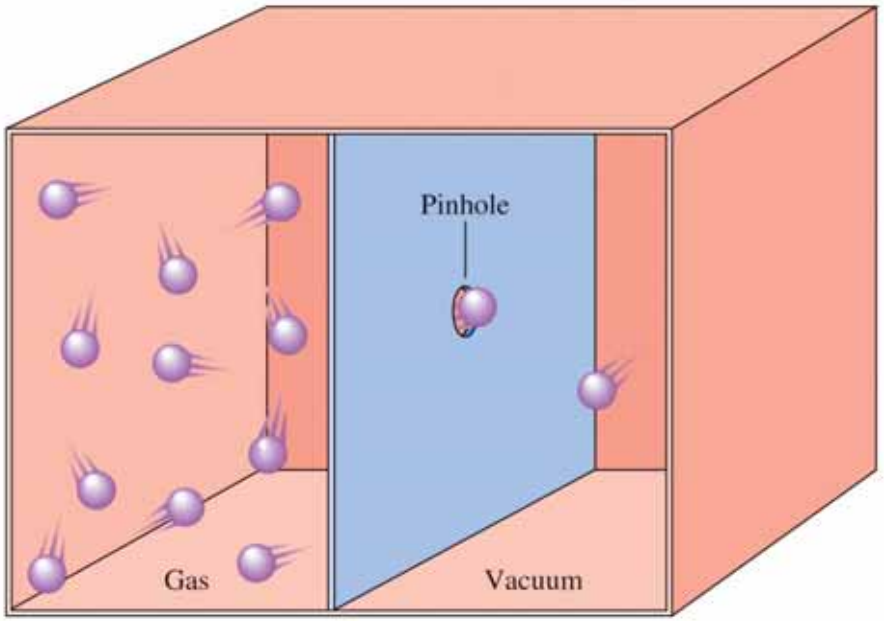
A plot of the relative number of N2molecules that have a given velocity at three temperatures. Note that as the temperature increases, both the average velocity and the spread of velocities increase.



5.7 Effusion and Diffusion

- Diffusion is the term used to describe the mixing of gases.
- Effusion is the term used to describe the passage of a gas through a tiny orifice into evacuated chamber, as shown in Fig. 5.22.
- The rate of effusion measures the speed at which the gas is transferred into the chamber.

Figure 5.22



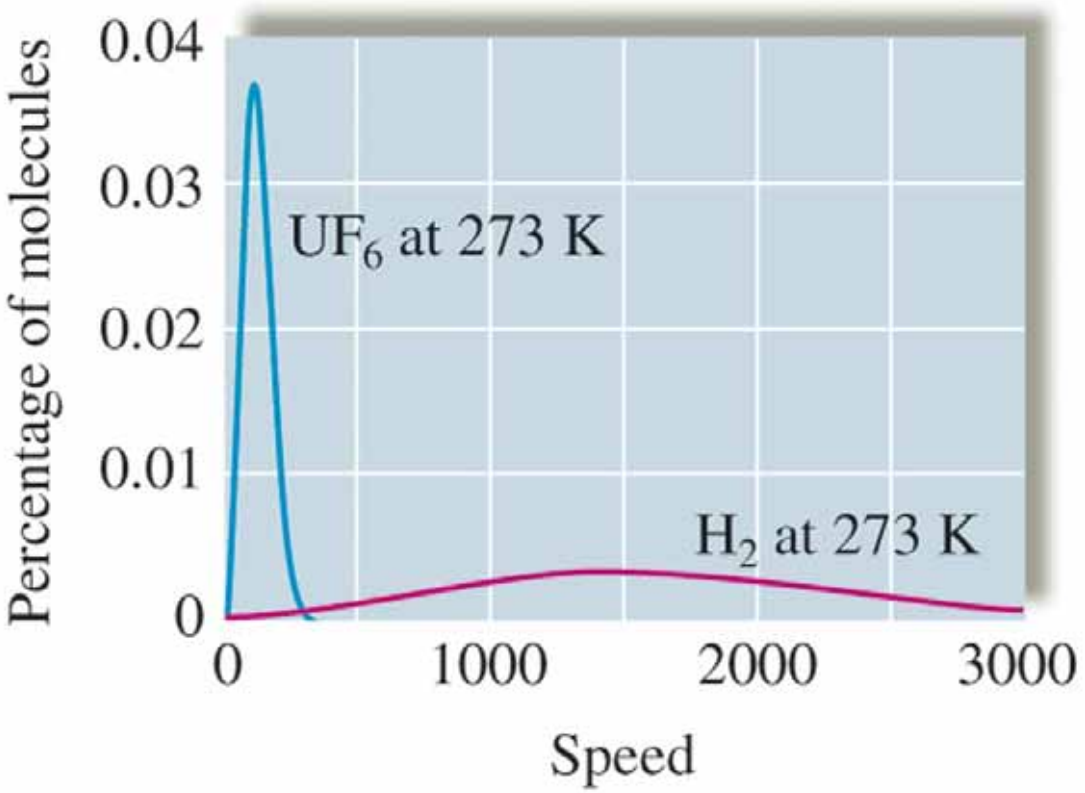
The effusion of a gas into an evacuated chamber. The rate of effusion (the rate at which the gas is transferred across the barrier through the pin hole) is inversely proportional to the square root of the mass of the gas molecules.

Effusion

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

- Where M_1 and M_2 represent the molar masses of the gases.
- This equation is called **Graham's law of effusion**.

Figure 5.23



Relative molecular speed distribution of H_2 and UF_6.

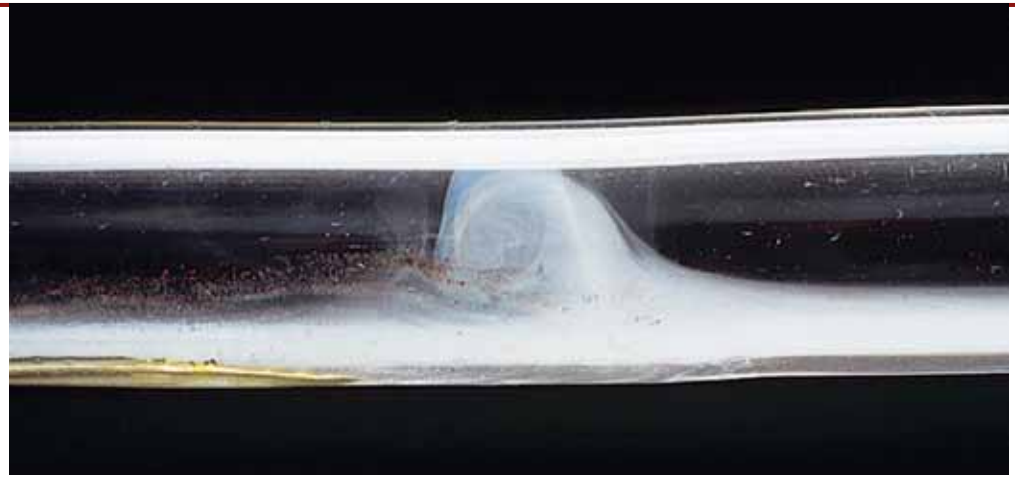
Diffusion

- Diffusion is frequently illustrated by the lecture demonstration represented in Fig. 5.24.
- A white ring of ammonium chloride (NH_4Cl) forms where the NH_3 and HCl molecules meet several minutes later:

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

White solid

Figure 5.24



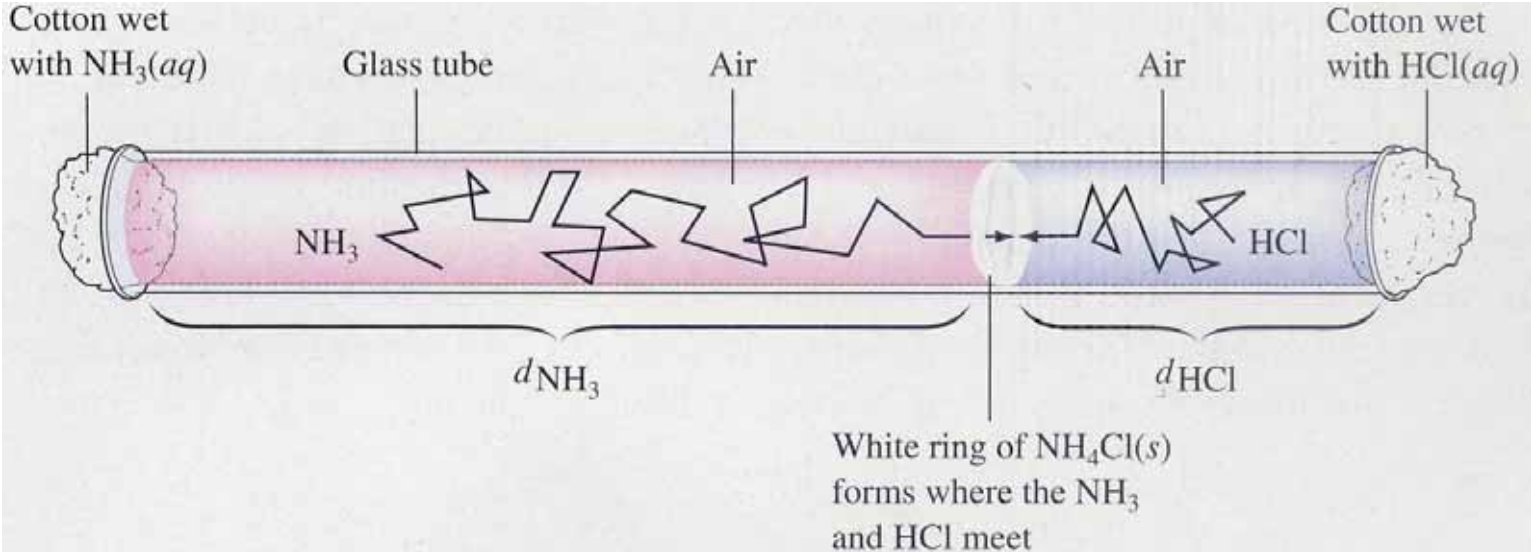

Cotton wet
with $NH_3(aq)$
Glass tube
Air
Air
Cotton wet
with $HCl(aq)$
NH_3
HCl
d_{NH_3}
d_{HCl}
White ring of $NH_4Cl(s)$
forms where the NH_3
and HCl meet

Figure 5.24

(above right) When HCl(*g*) and NH_3(*g*) meet in the tube, a white ring of NH4Cl(*s*) forms. (above left) A demonstration of the relative diffusion rates of NH_3 and HCl molecules through air. Two cotton plugs, one dipped in HCl(*aq*) and one dipped in NH_3(*aq*), are simultaneously inserted into the ends of the tube. Gaseous NH_3 and HCl vaporizing from the cotton plugs diffuse toward each other and, where they meet, react to form NH_4Cl(*s*).

5.8 Real Gases

- Plots of *PV*/*nRT* versus *P* are shown for several gases in Fig. 5.25.
- For an ideal gas, *PV*/*nRT* equals 1 under all conditions, but notice that for real gases, *PV*/*nRT* approaches 1 only at very low pressures (typically below 1 atm).
- To illustrate the effect of temperature, *PV*/*nRT* is plotted versus *P* for nitrogen gas at several temperatures in Fig. 5.26.

Figure 5.25

Plots of *PV*/*nRT* versus P for several gases (200 K). Note the significant deviations from ideal behavior (*PV*/*nRT* = 1). The behavior is close to ideal only at low pressures (less than 1 atm).

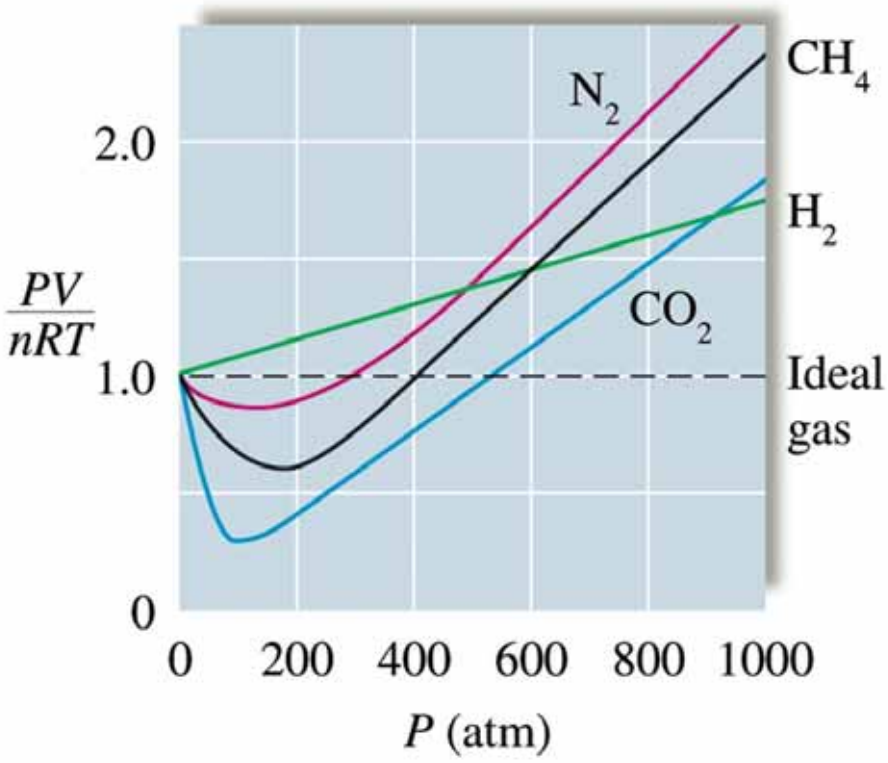
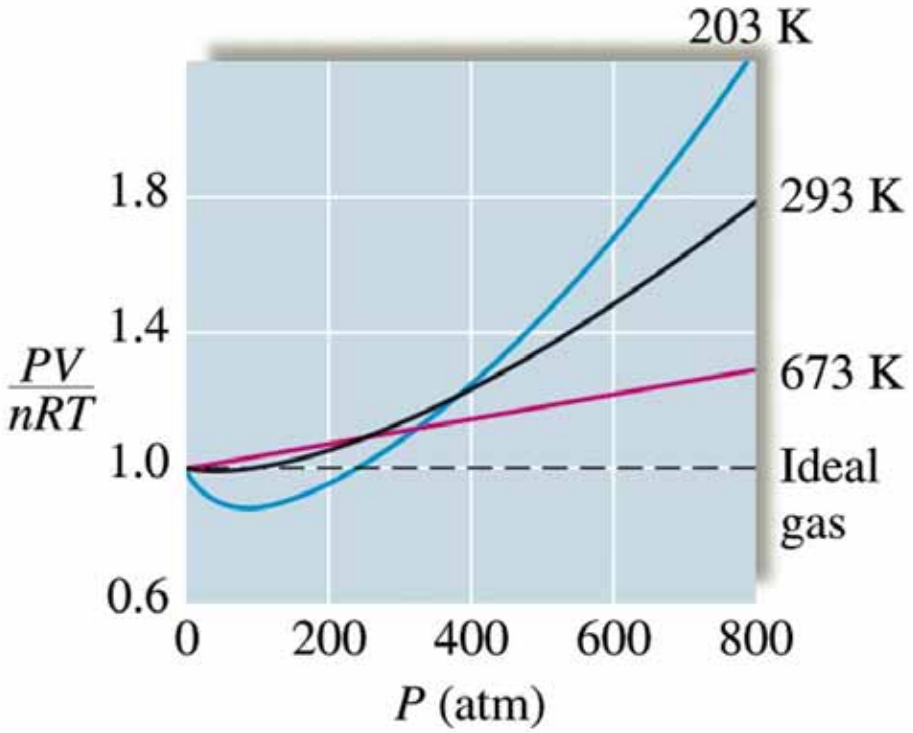


Figure 5.26

Plots of *PV*/*nRT* versus *P* for nitrogen gas at three temperatures. Note that although nonideal behavior is evident in each case, the deviations are small at the higher temperatures.



- The most important conclusion to be drawn from these figures is that a real gas typically exhibits behavior that is closest to ideal behavior at *low pressure* and *high temperatures*.
- The first person to do important work in this area was Johannes van der Waals (1837-1923), a physics professor at the University of Amsterdam who in 1910 received a Nobel Prize for his work.

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

- The volume *actually available* to a given gas molecule is given by difference $V - nb$.

$$P' = \frac{nRT}{V - nb}$$

$$P_{obs} = (P' - \text{correction factor})$$

$$= \left(\frac{nRT}{V - nb} - \text{correction factor} \right)$$

- When gas particles come close together, attractive forces occur, which cause the particles to hit the wall very slightly less often than they would in the absence of these interactions (see Fig. 5.27).
- In a gas sample containing N particles, there are N-1 partners available for each particle, as shown in Fig. 5.28.

$$P_{obs} = P' - a\left(\frac{n}{V}\right)^2$$

Figure 5.27

(a) Gas at low concentration—relatively few interactions between particles. The indicated gas particle exerts a pressure on the wall close to that predicted for an ideal gas.

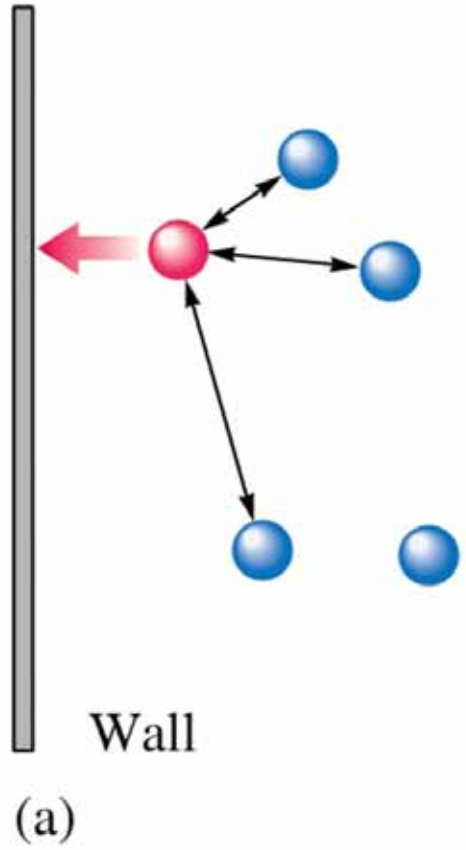
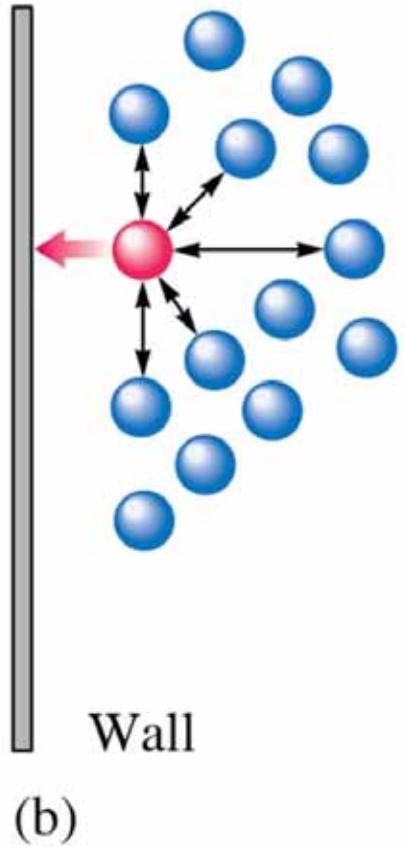
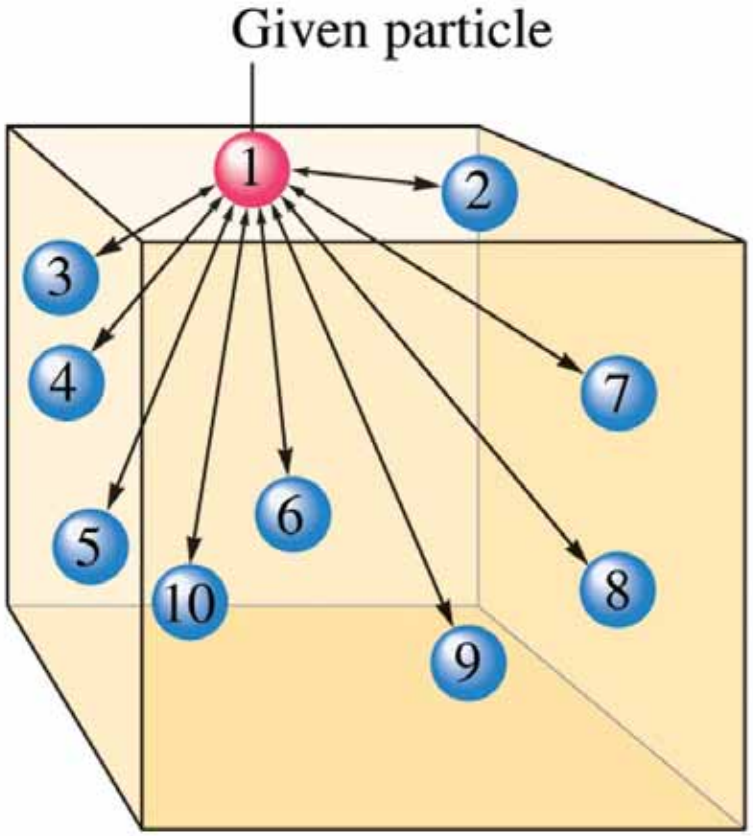


Figure 5.27



(b) Gas at high concentration—many more interactions between particles. The indicated gas particle exerts a much lower pressure on the wall than would be expected in the absence of interactions.

Figure 5.28



Gas sample with ten particles

Figure 5.28

Illustration of pairwise interactions among gas particles. In a sample with 10 particle, each particle has 9 possible partners, to give 10(9)/2 = 45 distinct pairs. The factor of ½ arises because when particle 1 is the particle of interest we count ①••• ② pair, and when particle ② is the particle of interest we count the ② ••• ① pair. However, ① ••• ② and ② ••• ① are the same pair that we have counted twice. Therefore, we must divide by 2 to get the actual number of pairs.

- Where a is a proportionality constant (which includes the factor of ½ from $N^2/2$).

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

Observed pressure

Volume of the container

Volume correction

Volume correction

- This equation can be rearranged to give the **van der Waals equation**:

$$\underbrace{\left[P_{\text{obs}} + a\left(\frac{n}{V}\right)^2\right]}_{\text{Corrected pressure}} \times \underbrace{(V - nb)}_{\text{Corrected volume}} = nRT$$

P_{ideal} V_{ideal}

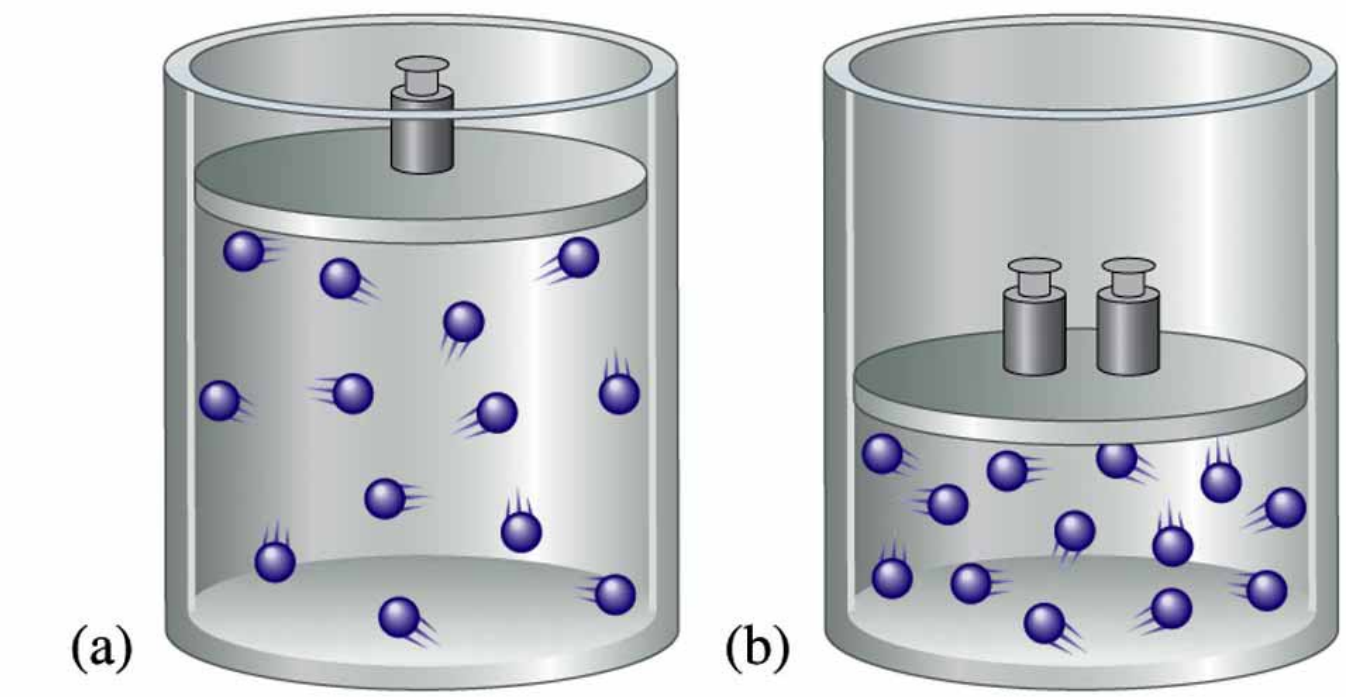
- The values of the weighting factors a and b are determined for a given gas by fitting experimental behavior.

- That is, a and b are varied until the best fit of the observed pressure is obtained under all conditions. The values of a and b for various gases are given in Table 5.3.
- For a gas at high pressure, the volume of the particles becomes significant so that the volume available to the gas is significantly less than the container volume.
- These cases are illustrated in Fig. 5.29.
- At high temperatures the particles are moving so rapidly that the effects of interparticle interactions are not very important.

TABLE 5.3 Values of the van der Waals Constants for Some Common Gases

Gas	$a\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.0341	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
NH_3	4.17	0.0371
H_2O	5.46	0.0305

Figure 5.29



The volume taken up by the gas particles themselves is less important at (a) large container volume (low pressure) than at (b) small container volume (high pressure).

5.9 Characteristics of Several Real Gases

- We can understand gas behavior more completely if we examine the characteristics of several common gases.
- Note from Figure 5.25 that the gases H_2, N_2, CH_4, and CO_2 show different behavior when the compressibility (PV/nRT) is plotted versus P.
- H_2 molecules have very low attractive forces for each other. This idea is borne out by looking at the van der Waals a value for H2 in Table 5.3.

$$P_{\text{ideal}} = P_{\text{observed}} + a\left(\frac{n}{V}\right)^2$$

- The importance of intermolecular interactions increases in this order:

$$H_2 < N_2 < CH_4 < CO_2$$

- This order is reflected by the relative a values for these gases in table 5.3.

5.10 Chemistry in the Atmosphere

- The most important gases to us are those in the **atmosphere** that surrounds the earth's surface.
- The average composition of the earth's atmosphere near sea level, with the water vapor removed, is shown in Table 5.4.
- Because of gravitational effects, the composition of the earth's atmosphere is not constant.

TABLE 5.4 Atmospheric Composition Near Sea Level (Dry Air)*

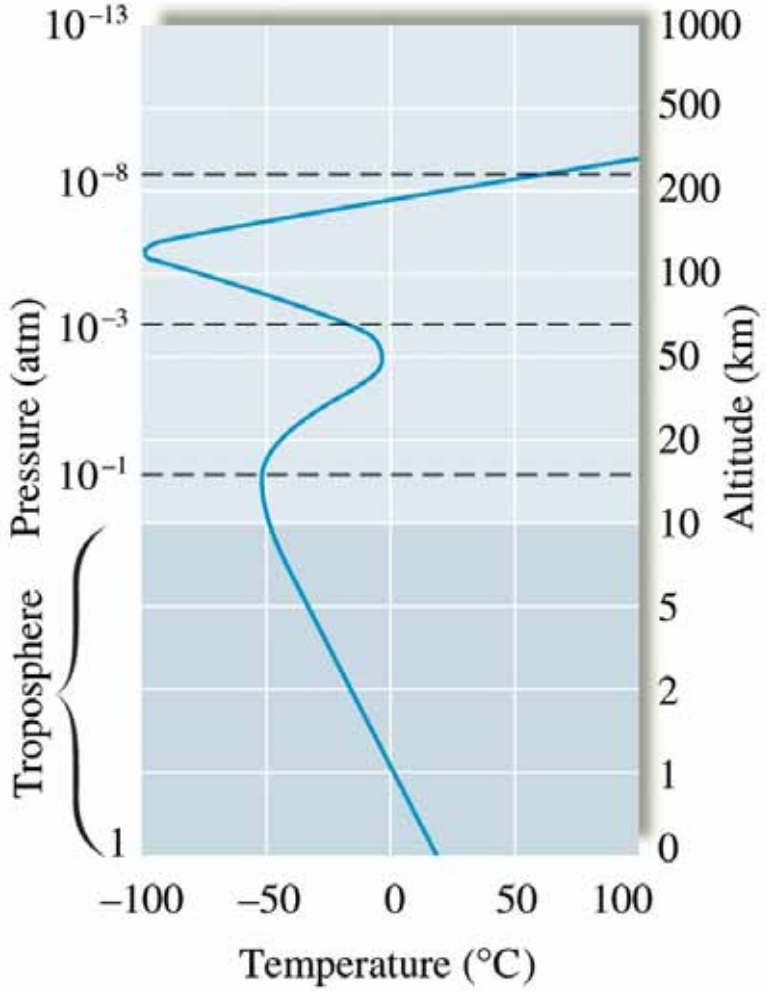
Component	Mole Fraction
N_2	0.78084
O_2	0.20948
Ar	0.00934
CO_2	0.000345
Ne	0.00001818
He	0.00000524
CH_4	0.00000168
Kr	0.00000114
H_2	0.0000005
NO	0.0000005
Xe	0.000000087

*The atmosphere contains various amounts of water vapor depending on conditions.

- Heavier molecules tend to be near the earth's surface, and light molecules tend to migrate to higher altitudes, with some eventually escaping into space.
- The atmosphere is a highly complex and dynamic system, but for convenience we divide it into several layers based on the way the temperature changes with altitude. (The lowest layer, called the troposphere, is shown on Fig. 5.30.)

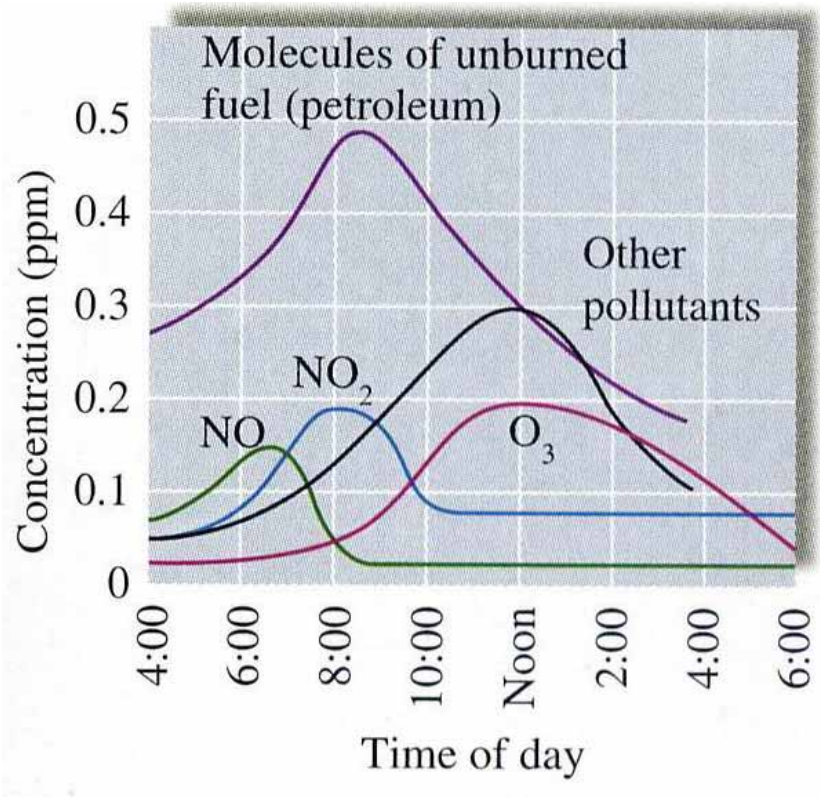
Figure 5.30

The variation of temperature (blue) and pressure (dashed lines) with altitude. Note that the pressure steadily decreases with altitude, but the temperature increases and decreases.



- In particular, the ozone in the upper atmosphere helps prevent high-energy ultraviolet radiation from penetrating to the earth.
- Severe **air pollution** is found around many large cities.
- The two main sources of pollution are transportation and the production of electricity.

Figure 5.31



Concentration (in molecules per million molecules of “air”) for some smog components versus time of day.

$$NO_2(g) \xrightarrow{\text{Radiant energy}} NO(g) + O(g)$$

- Ozone is also very reactive and can react directly with other pollutants,

$$O^* + H_2O \longrightarrow 2OH$$

$$OH + NO_2 \longrightarrow HNO_3$$

The damaging effects of acid rain can be seen by comparing these photos of a decorative statue on the Field Museum in Chicago. The first photo was taken about 1920, the second in 1990.

- The end product of this whole process is often referred to as **photochemical smog**, so called because light is required to initiate some of the reactions.

$$NO_2(g) \longrightarrow NO(g) + O(g)$$

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

$$\overline{\tfrac{3}{2}O_2(g) \longrightarrow O_3(g)}$$

- Note that the NO_2 molecules assist in the formation of ozone without being themselves used up.
- The ozone formed then leads to the formation of OH and other pollutants.
- We can observe this process by analyzing polluted air at various times during a day (see Fig. 5.31).
- The other major source of pollution results from burning coal to produce electricity.

- Much of the coal found in the Midwest contains significant quantities of sulfur, which,

$$\text{S (in coal)} + O_2(g) \longrightarrow SO_3(g)$$

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

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

- Sulfuric acid is very corrosive to both living things and building materials.

- Another result of this type of pollution is **acid rain**.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

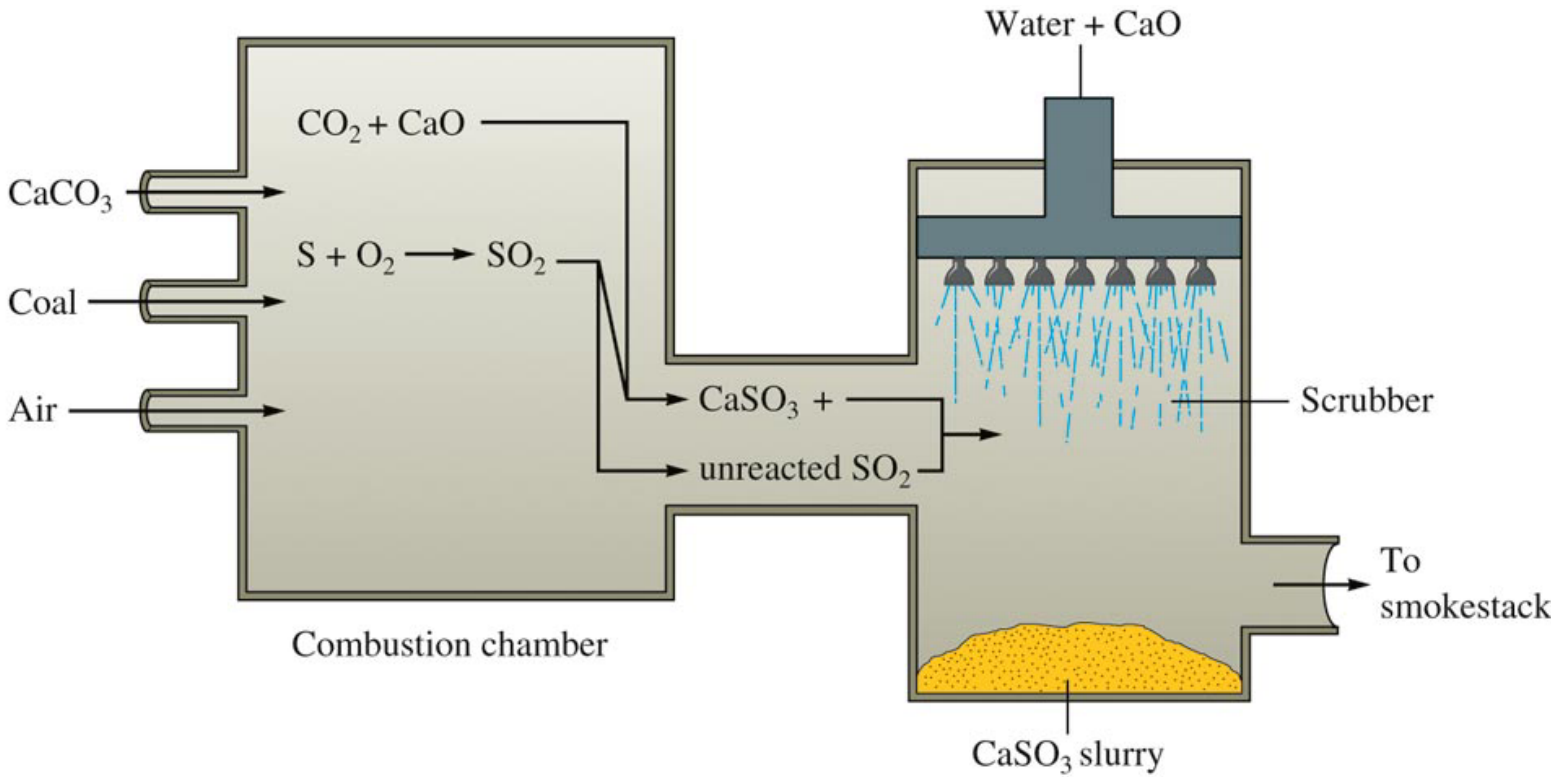
$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

- As shown in Fig. 5.33.

Figure 5.32

An environmental officer in Wales tests the pH of water.

Figure 5.33



A schematic diagram of the process for scrubbing sulfur dioxide from stack gases in power plants.