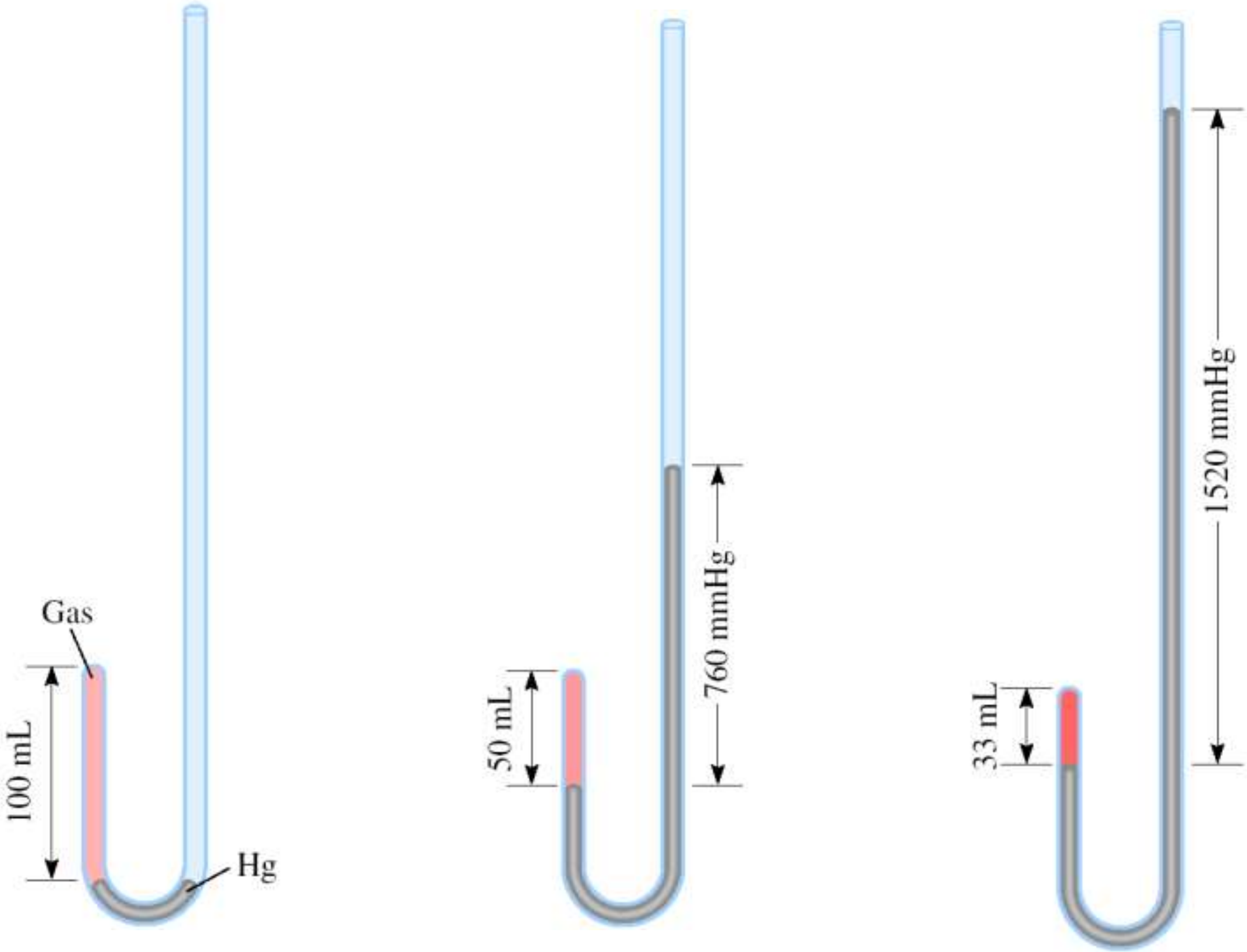
CHAPTER 5: GASES

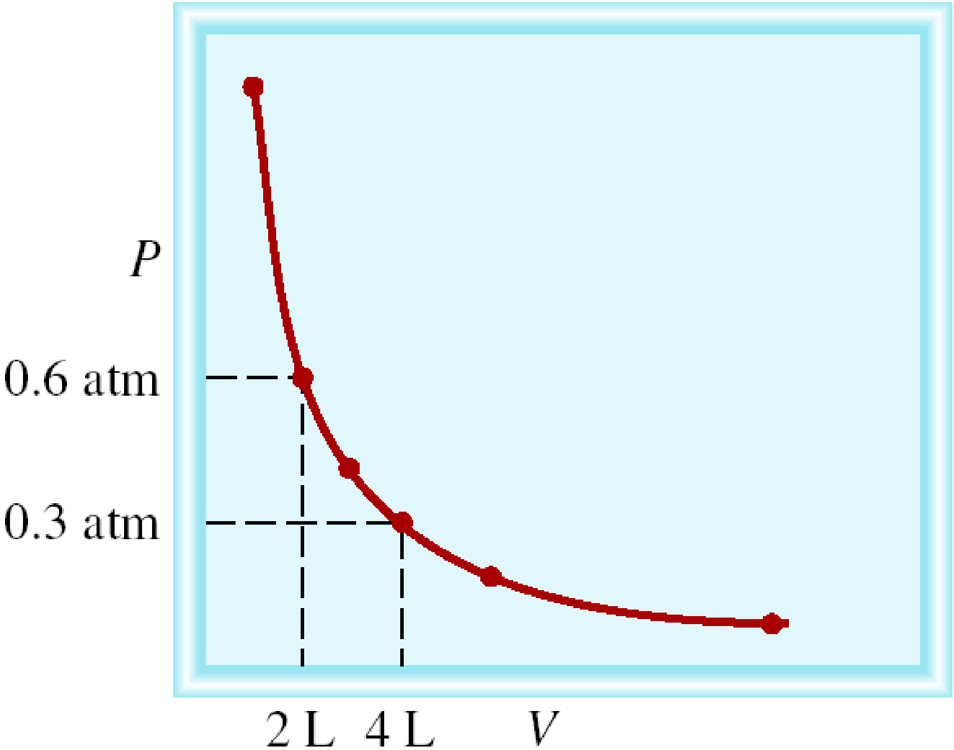
Chapter Outline

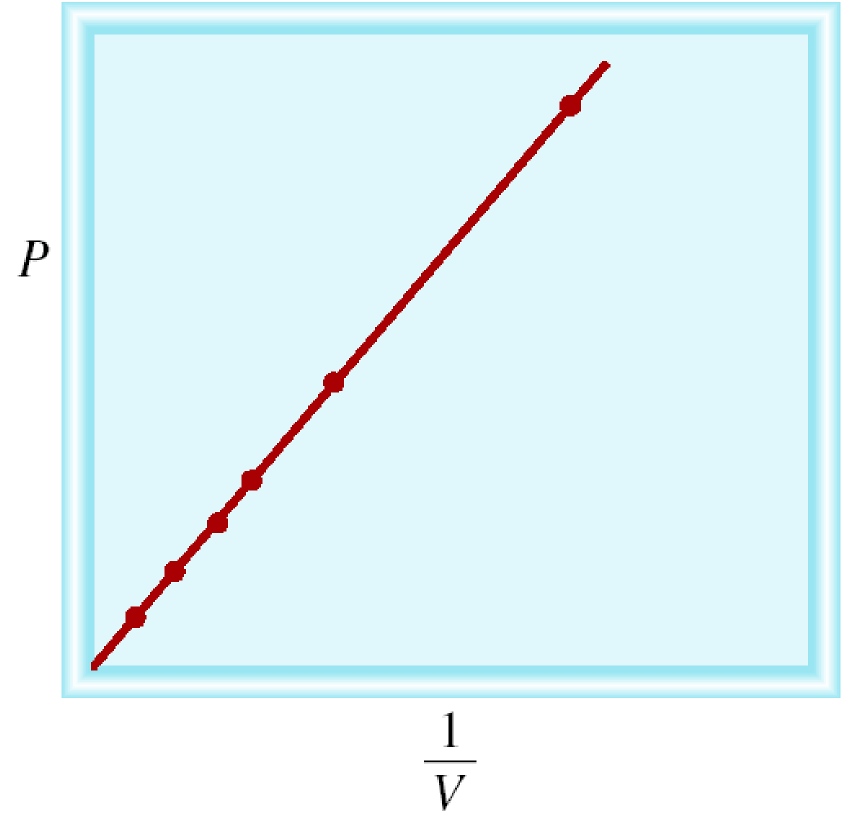
Apparatus for Studying the Relationship Between Pressure and Volume of a Gas



As *P* (h) increases *V* decreases

Boyle's Law





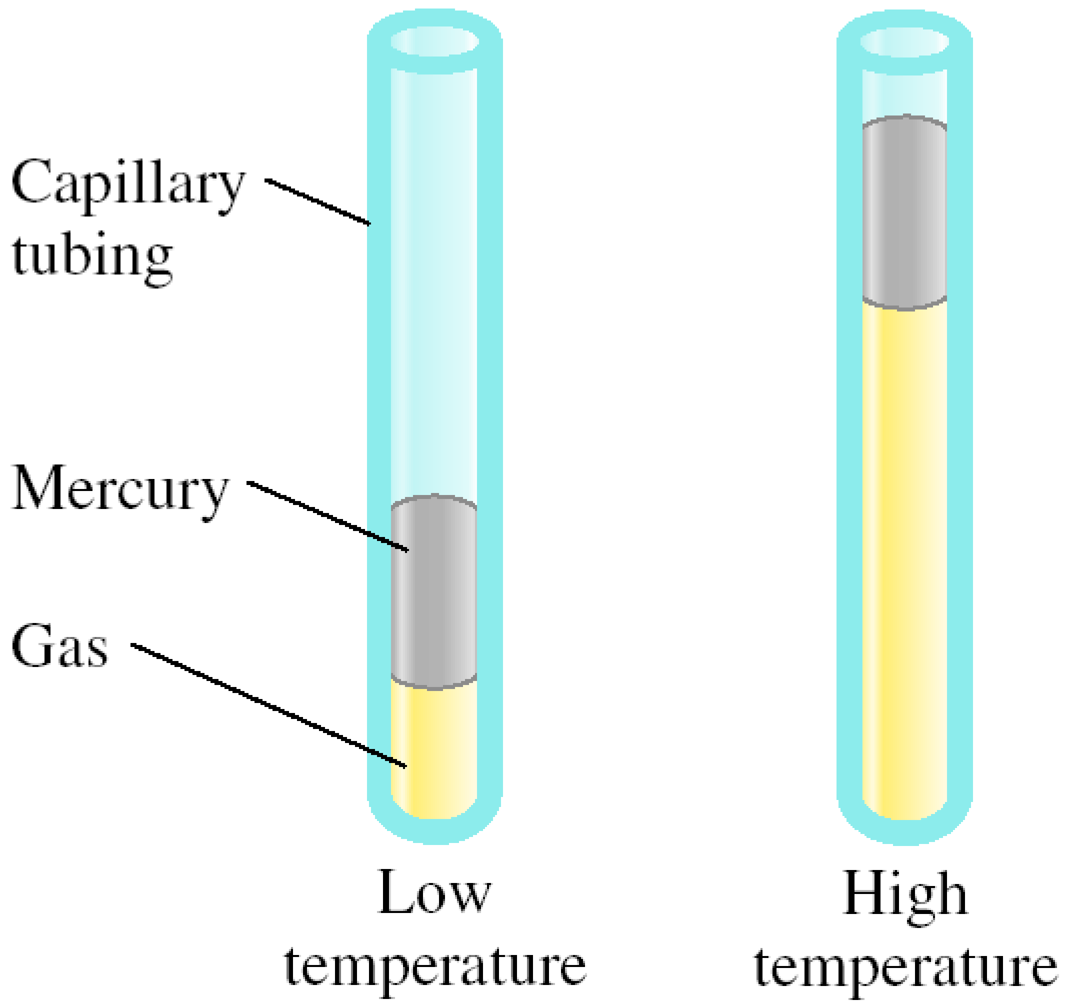
$P \propto 1/V$

$P \times V = \text{constant}$

$P_1 \times V_1 = P_2 \times V_2$

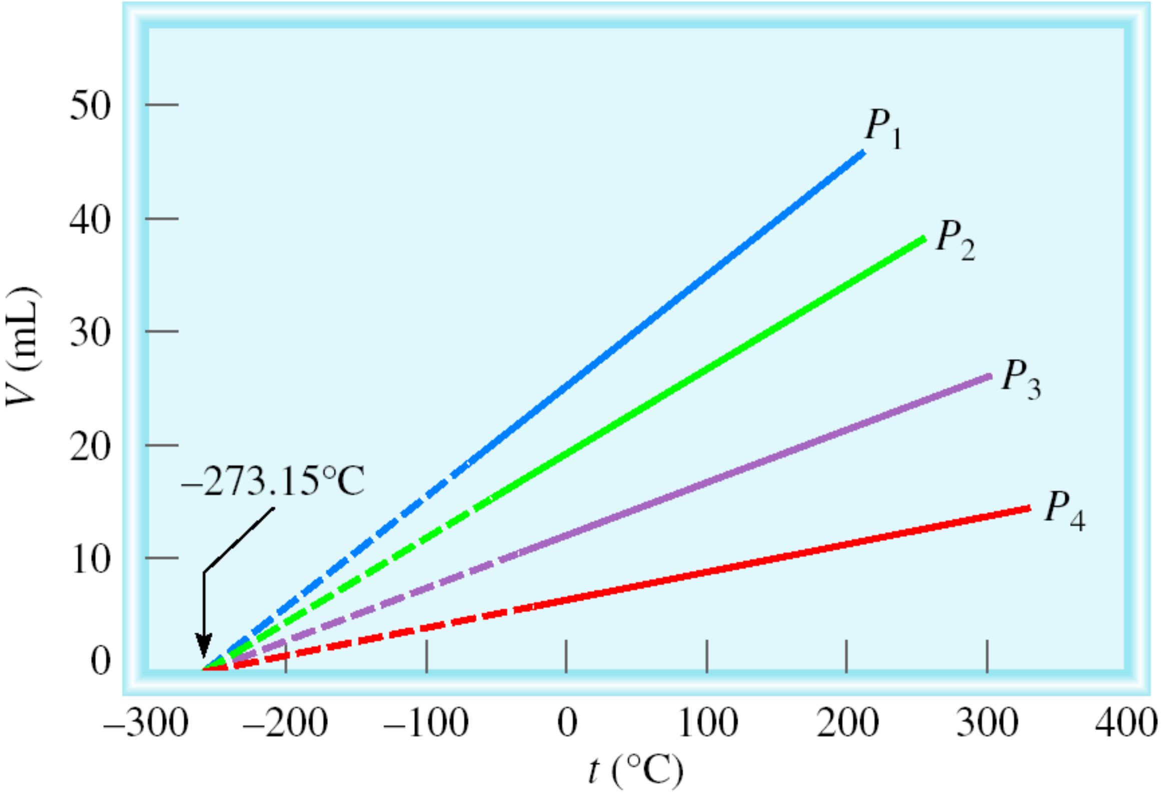
Constant temperature
Constant amount of gas

Variation in Gas Volume with Temperature at Constant Pressure



As *T* increases $\quad$ *V* increases

Variation of Gas Volume with Temperature at Constant Pressure



Charles's & Gay-Lussac's Law

$V \alpha T$

V = constant x T

$V_1/T_1 = V_2/T_2$

Temperature **must** be in Kelvin

T (K) = t (^{0}C) + 273.15

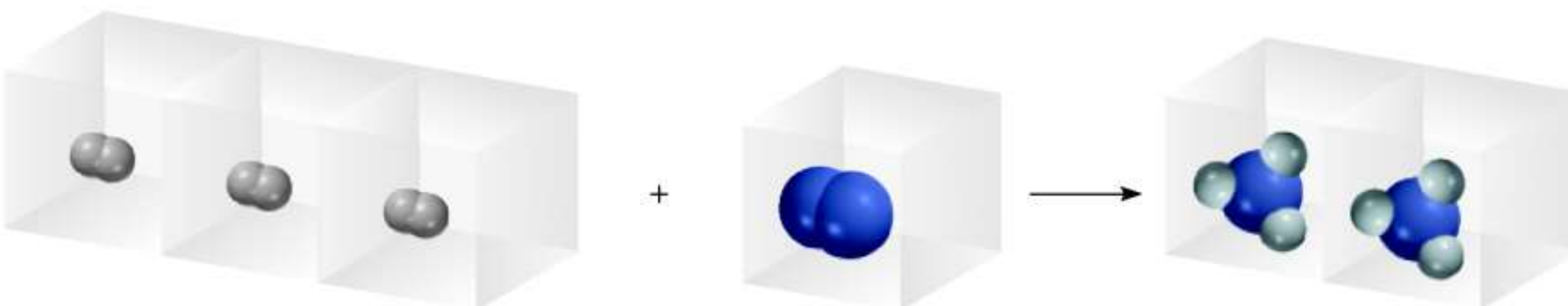
Avogadro's Law

$V \propto$ number of moles (n)

V = constant x n

Constant temperature
Constant pressure

$$V_1 / n_1 = V_2 / n_2$$

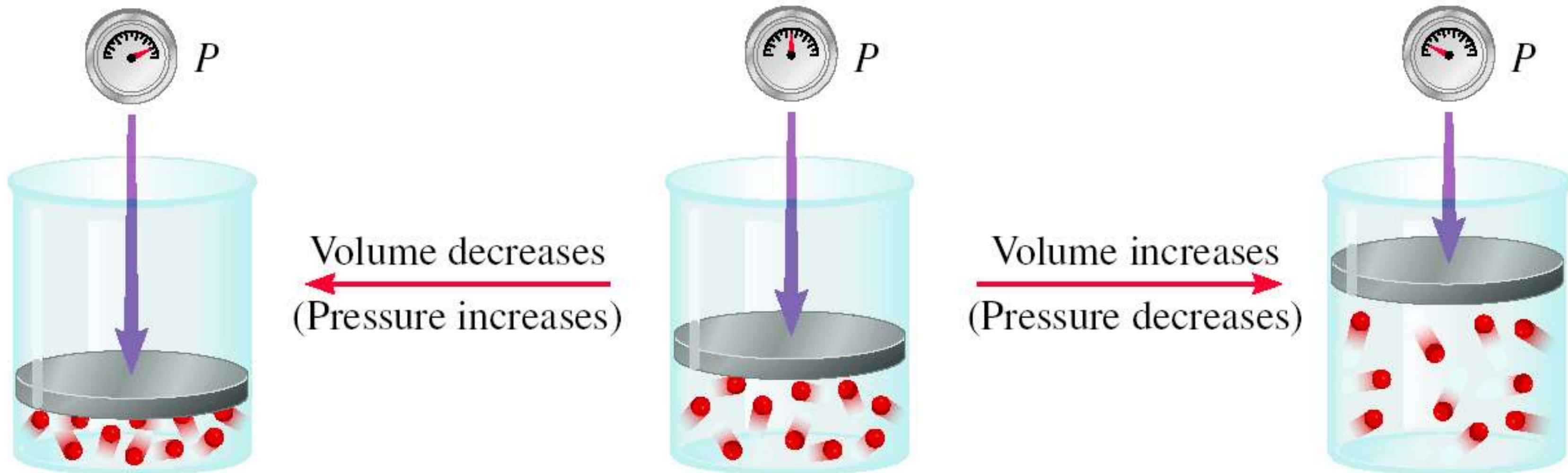


$3H_2(g)$	+	$N_2(g)$	$\longrightarrow$	$2NH_3(g)$
3 molecules	+	1 molecule	$\longrightarrow$	2 molecules
3 moles	+	1 mole	$\longrightarrow$	2 moles
3 volumes	+	1 volume	$\longrightarrow$	2 volumes

Summary of Gas Laws

Boyle's Law

Increasing or decreasing the volume of a gas
at a constant temperature

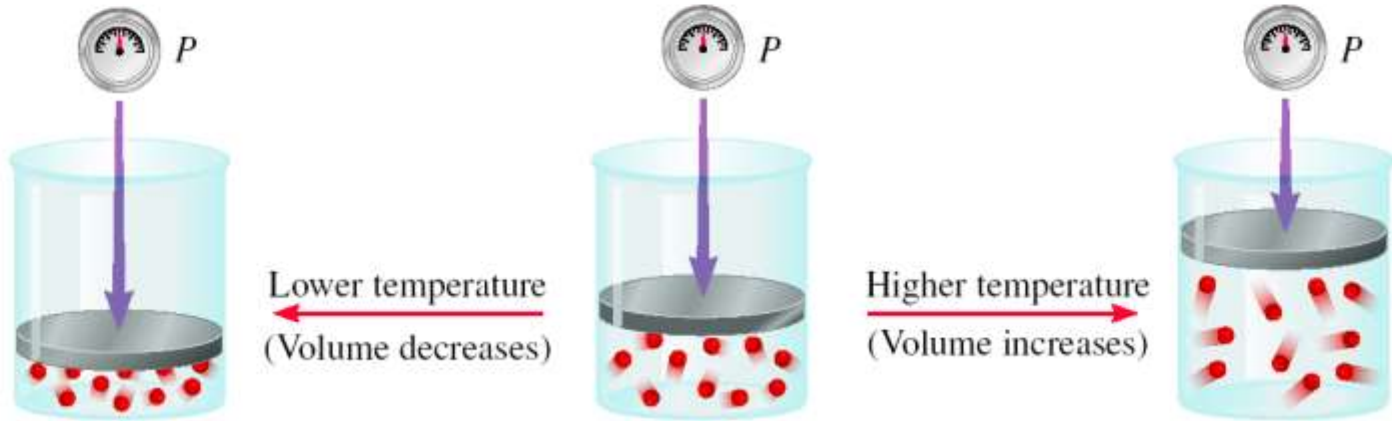


Boyle's Law

$$P = (nRT)\frac{1}{V} \quad nRT \text{ is constant}$$

Charles's Law

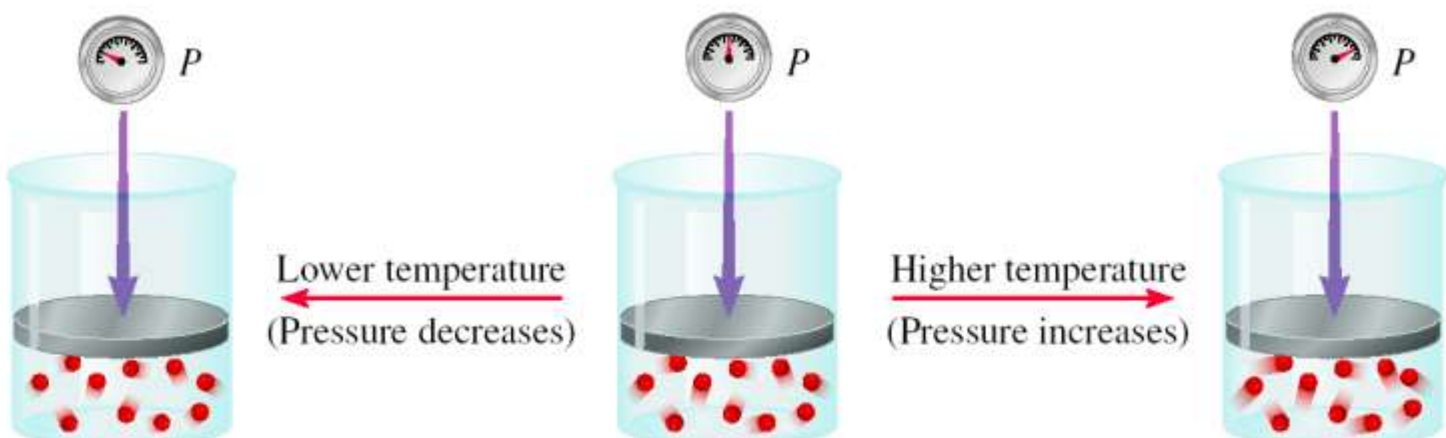
Heating or cooling a gas at constant pressure



Charles's Law

$V = \left(\frac{nR}{P}\right) T \quad \frac{nR}{P}$ is constant

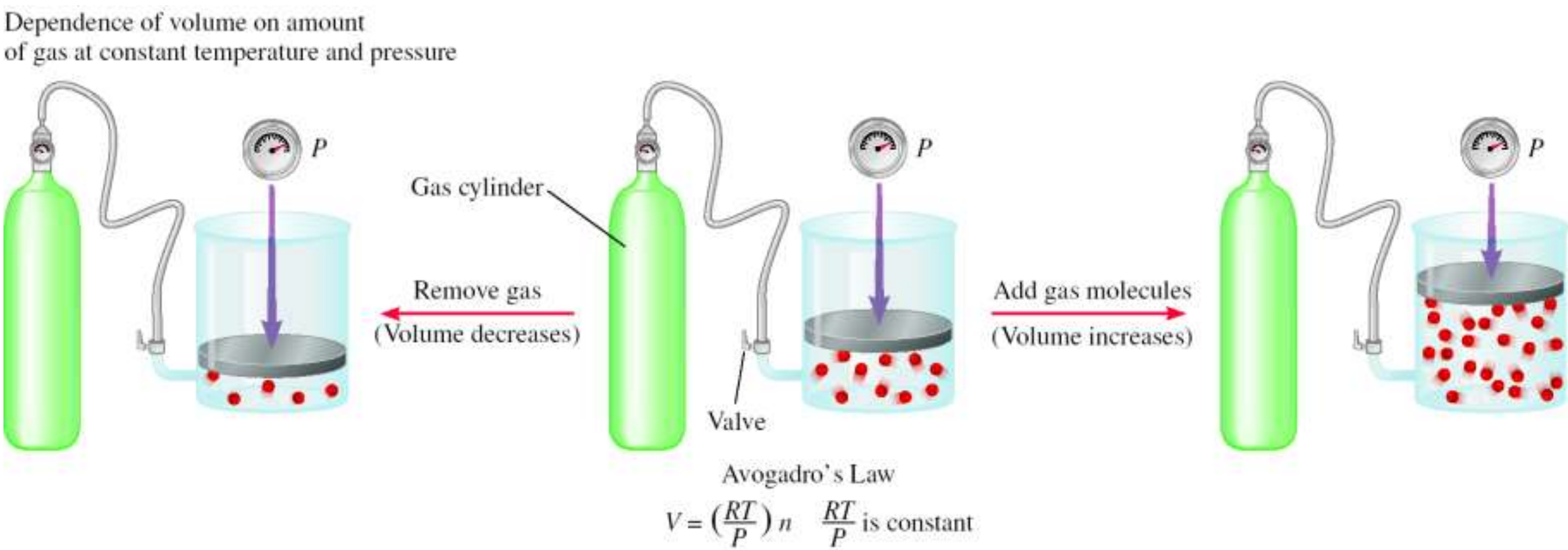
Heating or cooling a gas at constant volume



Charles's Law

$P = \left(\frac{nR}{V}\right) T \quad \frac{nR}{V}$ is constant

Avogadro's Law



Ideal Gas Equation

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

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

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

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

$$V = \text{constant} \times \frac{nT}{P} = R\frac{nT}{P}$$

R is the **gas constant**

$$\boxed{PV = nRT}$$

The conditions 0 ^{0}C and 1 atm are called **standard temperature and pressure (STP).**

Experiments show that at STP, 1 mole of an ideal gas occupies 22.414 L.

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{(1\ \text{atm})(22.414\text{L})}{(1\ \text{mol})(273.15\ \text{K})}$$

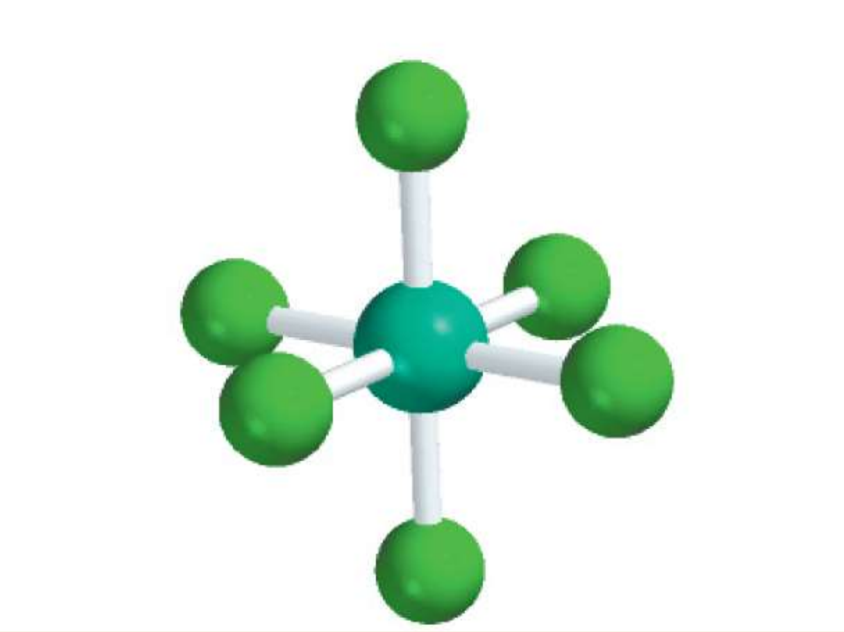
$$R = 0.082057\ \text{L} \bullet \text{atm} / (\text{mol} \bullet \text{K})$$

Example 5.2

Sulfur hexafluoride (SF_6) is a colorless and odorless gas.

Due to its lack of chemical reactivity, it is used as an insulator in electronic equipment.

Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C.



SF_6

Example 5.2

Strategy

The problem gives the amount of the gas and its volume and temperature.

Is the gas undergoing a change in any of its properties?

What equation should we use to solve for the pressure?

What temperature unit should we use?

Example 5.2

Solution Because no changes in gas properties occur, we can use the ideal gas equation to calculate the pressure.

Rearranging Equation (5.8), we write

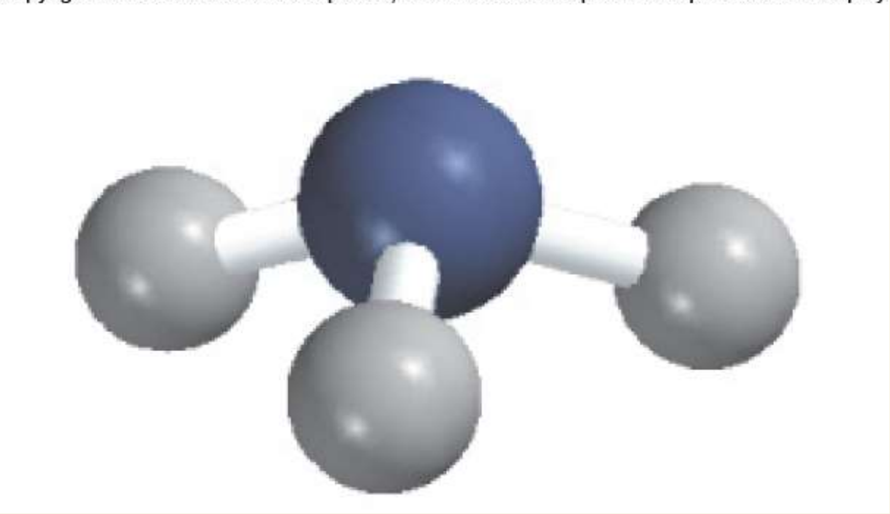
$$P = \frac{nRT}{V}$$

$$= \frac{(1.82\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(69.5 + 273)\text{K}}{5.43\ \text{L}}$$

$$= 9.42\ \text{atm}$$

Example 5.3

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



NH_3

Example 5.3

Strategy

What is the volume of one mole of an ideal gas at STP?

How many moles are there in 7.40 g of NH_3?

Solution

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

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

Example 5.3

So the volume of NH_3 is given by

$$V = 7.40\ \cancel{g\ NH_3} \times \frac{1\ \cancel{mol\ NH_3}}{17.03\ \cancel{g\ NH_3}} \times \frac{22.41\ L}{1\ \cancel{mol\ NH_3}}$$

$$= 9.74\ L$$

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

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

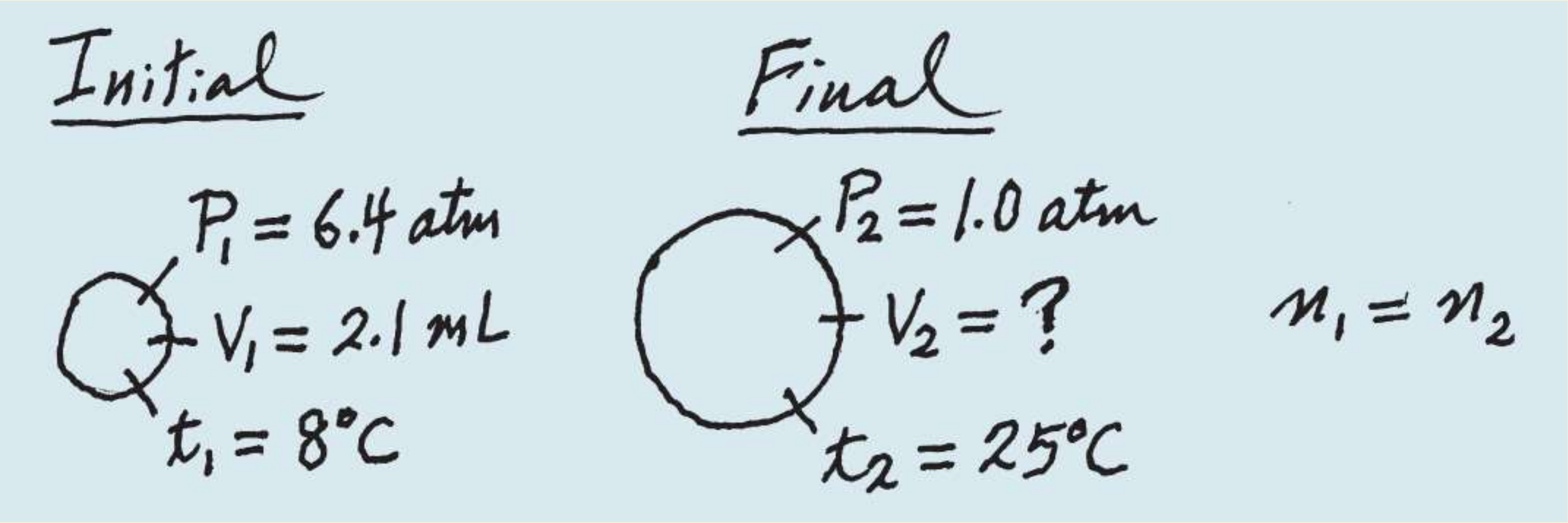
Example 5.4

A small bubble rises from the bottom of a lake, where the temperature and pressure are 8°C and 6.4 atm, to the water's surface, where the temperature is 25°C and the pressure is 1.0 atm.

Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL.

Example 5.4

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



What temperature unit should be used in the calculation?

Example 5.4

Solution According to Equation (5.9)

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

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

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

which is Equation (5.10).

Example 5.4

The given information is summarized:

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

Rearranging Equation (5.10) gives

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

$$= 2.1 \text{ mL} \times \frac{6.4 \text{ atm}}{1.0 \text{ atm}} \times \frac{298 \text{ K}}{281 \text{ K}}$$

$$= 14 \text{ mL}$$

Example 5.4

Check We see that the final volume involves multiplying the initial volume by a ratio of pressures (P_1/P_2) and a ratio of temperatures (T_2/T_1).

Recall that volume is inversely proportional to pressure, and volume is directly proportional to temperature.

Because the pressure decreases and temperature increases as the bubble rises, we expect the bubble's volume to increase.

In fact, here the change in pressure plays a greater role in the volume change.

Density (d) Calculations

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

m is the mass of the gas in g

$\mathcal{M}$ is the molar mass of the gas

Molar Mass ($\mathcal{M}$) of a Gaseous Substance

$$\mathcal{M} = \frac{dRT}{P}$$

d is the density of the gas in g/L

Example 5.5

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

Calculate the molar mass of the compound and determine its molecular formula.

Example 5.5

Strategy

Because Equations (5.11) and (5.12) are rearrangements of each other, we can calculate the molar mass of a gas if we know its density, temperature, and pressure.

The molecular formula of the compound must be consistent with its molar mass. What temperature unit should we use?

Example 5.5

Solution From Equation (5.12)

$$\mathscr{M} = \frac{dRT}{P}$$

$$= \frac{(7.71 \text{ g/L})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(36 + 273) \text{ K}}{2.88 \text{ atm}}$$

$$= 67.9 \text{ g/mol}$$

Alternatively, we can solve for the molar mass by writing

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

From the given density we know there are 7.71 g of the gas in 1 L.

Example 5.5

The number of moles of the gas in this volume can be obtained from the ideal gas equation

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

$$= \frac{(2.88 \text{ atm})\,(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})\,(309 \text{ K})}$$

$$= 0.1135 \text{ mol}$$

Therefore, the molar mass is given by

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

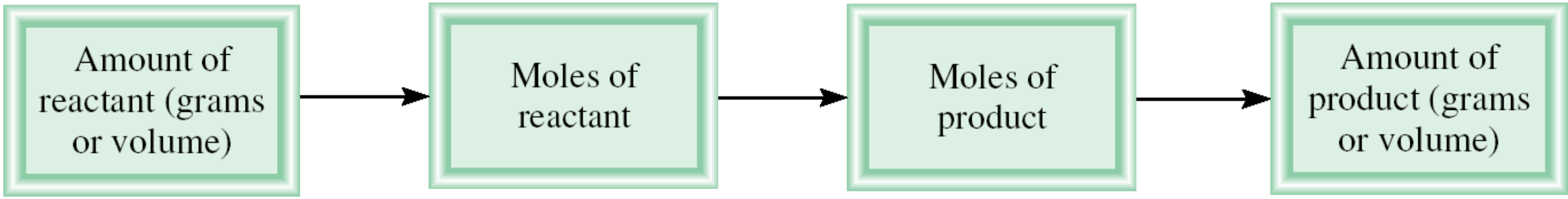
Example 5.5

We can determine the molecular formula of the compound by trial and error, using only the knowledge of the molar masses of chlorine (35.45 g) and oxygen (16.00 g).

We know that a compound containing one Cl atom and one O atom would have a molar mass of 51.45 g, which is too low, while the molar mass of a compound made up of two Cl atoms and one O atom is 86.90 g, which is too high.

Thus, the compound must contain one Cl atom and two O atoms and have the formula ClO_2, which has a molar mass of 67.45 g.

Gas Stoichiometry



Example 5.6

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

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

The nitrogen gas produced quickly inflates the bag between the driver and the windshield and dashboard.

Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3.

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

Example 5.6

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

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

Because the mass of NaN_3 is given, we can calculate the number of moles of NaN_3 and hence the number of moles of N_2 produced.

Finally, we can calculate the volume of N_2 using the ideal gas equation.

Example 5.6

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

$$\text{grams of NaN}_3 \longrightarrow \text{moles of NaN}_3 \longrightarrow \text{moles of N}_2$$

so that

$$\text{moles of N}_2 = 60.0 \ \cancel{\text{g NaN}_3} \times \frac{1 \ \cancel{\text{mol NaN}_3}}{65.02 \ \cancel{\text{g NaN}_3}} \times \frac{3 \text{ mol N}_2}{2 \ \cancel{\text{mol NaN}_3}}$$

$$= 1.38 \text{ mol N}_2$$

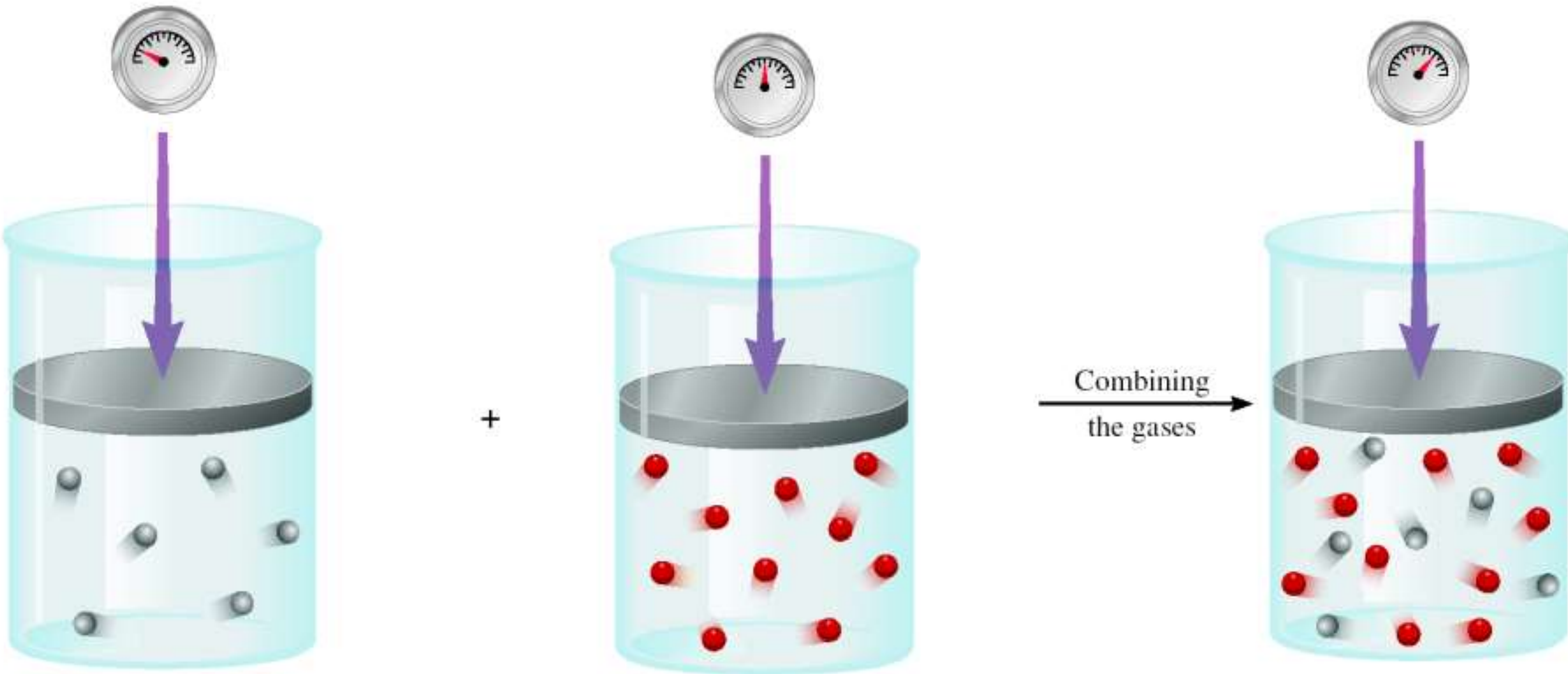
The volume of 1.38 moles of N_2 can be obtained by using the ideal gas equation:

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

$$= 36.9 \text{ L}$$

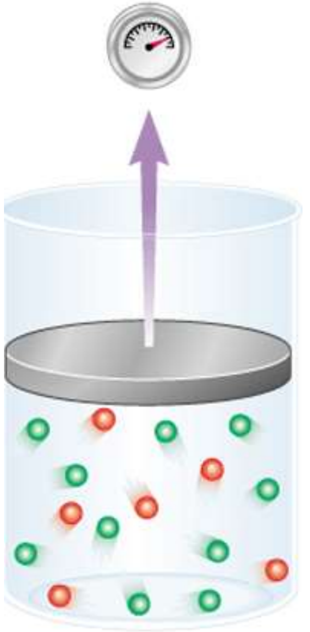
Dalton's Law of Partial Pressures

V and *T* are **constant**



P_1 P_2 $P_{\text{total}} = P_1 + P_2$

Consider a case in which two gases, A and B, are in a container of volume V.



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

n_A is the number of moles of A

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

n_B is the number of moles of B

$$P_T = P_A + P_B \qquad X_A = \frac{n_A}{n_A + n_B} \qquad X_B = \frac{n_B}{n_A + n_B}$$

$$P_A = X_A P_T \qquad P_B = X_B P_T$$

$$\boxed{P_i = X_i P_T}$$

mole fraction $(X_i) = \dfrac{n_i}{n_T}$

Example 5.7

A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe).

Calculate the partial pressures of the gases if the total pressure is 2.00 atm at a certain temperature.

Example 5.7

Strategy What is the relationship between the partial pressure of a gas and the total gas pressure?

How do we calculate the mole fraction of a gas?

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

need to find

$$P_{Ne} = X_{Ne} P_T$$

want to calculate

given

Example 5.7

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

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

$$= 0.607$$

Therefore,

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

Example 5.7

Similarly,

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

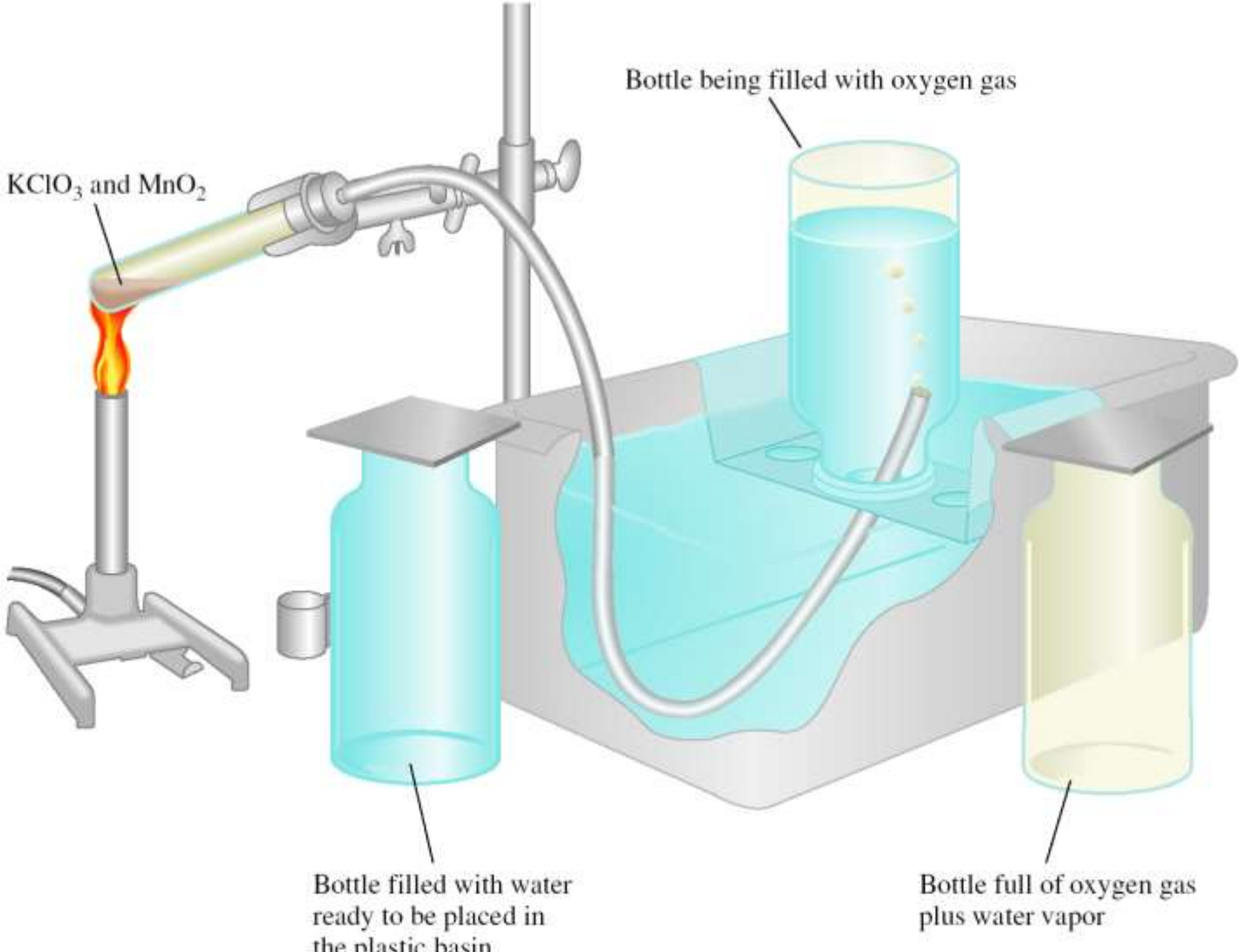
and

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

Check Make sure that the sum of the partial pressures is equal to the given total pressure; that is,

$$(1.21 + 0.20 + 0.586) \text{ atm} = 2.00 \text{ atm}.$$

Collecting a Gas over Water



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

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

Vapor of Water and Temperature

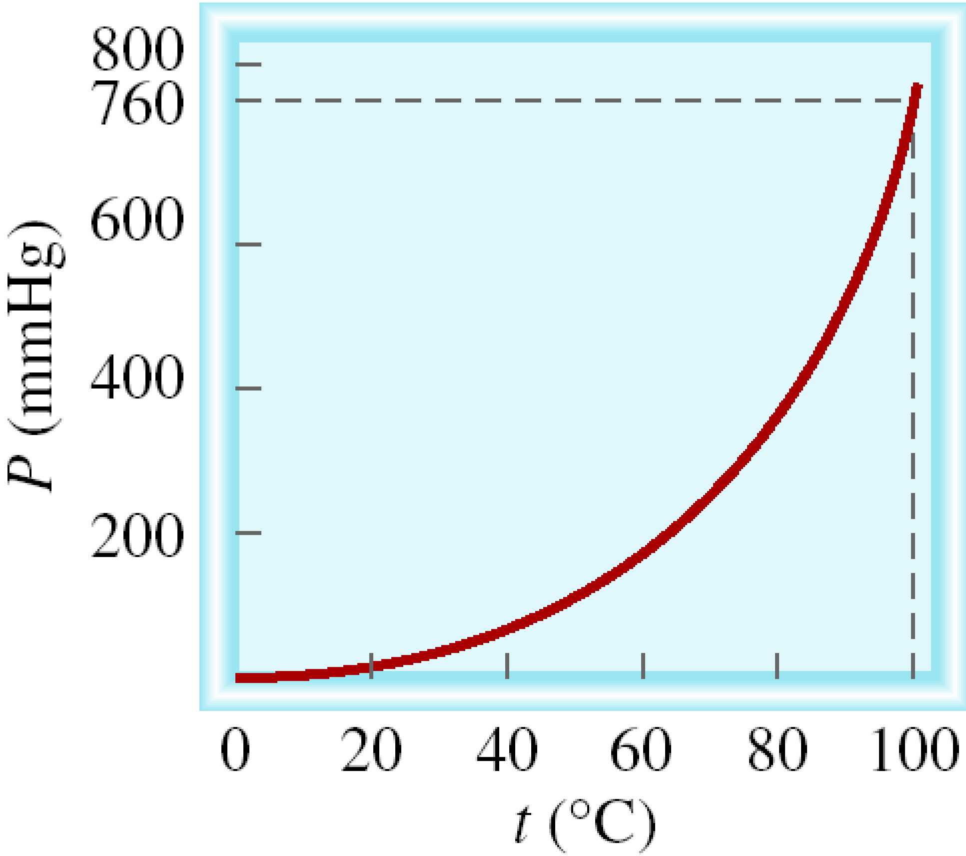


Table 5.3

van der Waals Constants of Some Common Gases

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

Example 5.8

Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in Figure 5.15.

The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL.

Calculate the mass (in grams) of oxygen gas obtained.

The pressure of the water vapor at 24°C is 22.4 mmHg.

Example 5.8

Strategy To solve for the mass of O_2 generated, we must first calculate the partial pressure of O_2 in the mixture.

What gas law do we need?

How do we convert pressure of O_2 gas to mass of O_2 in grams?

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

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

Example 5.8

Therefore,

$$P_{O_2} = P_T - P_{H_2O}$$
$$= 762 \text{ mmHg} - 22.4 \text{ mmHg}$$
$$= 740 \text{ mmHg}$$

From the ideal gas equation we write

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

where m and $\mathscr{M}$ are the mass of O_2 collected and the molar mass of O_2, respectively.

Example 5.8

Rearranging the equation we obtain

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

$$= 0.164\text{ g}$$

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

Kinetic Molecular Theory of Gases

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be *points*; that is, they possess mass but have negligible volume.

2. Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic.

3. Gas molecules exert neither attractive nor repulsive forces on one another.

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

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

Kinetic theory of gases and …

- Compressibility of Gases
- Boyle's Law

  P α collision rate with wall

  Collision rate α number density

  Number density α $1/V$

  P α $1/V$

- Charles's Law

  P α collision rate with wall

  Collision rate α average kinetic energy of gas molecules

  Average kinetic energy α T

  P α T

Kinetic theory of gases and …

- Avogadro's Law

  $P \propto$ collision rate with wall

  Collision rate $\propto$ number density

  Number density $\propto n$

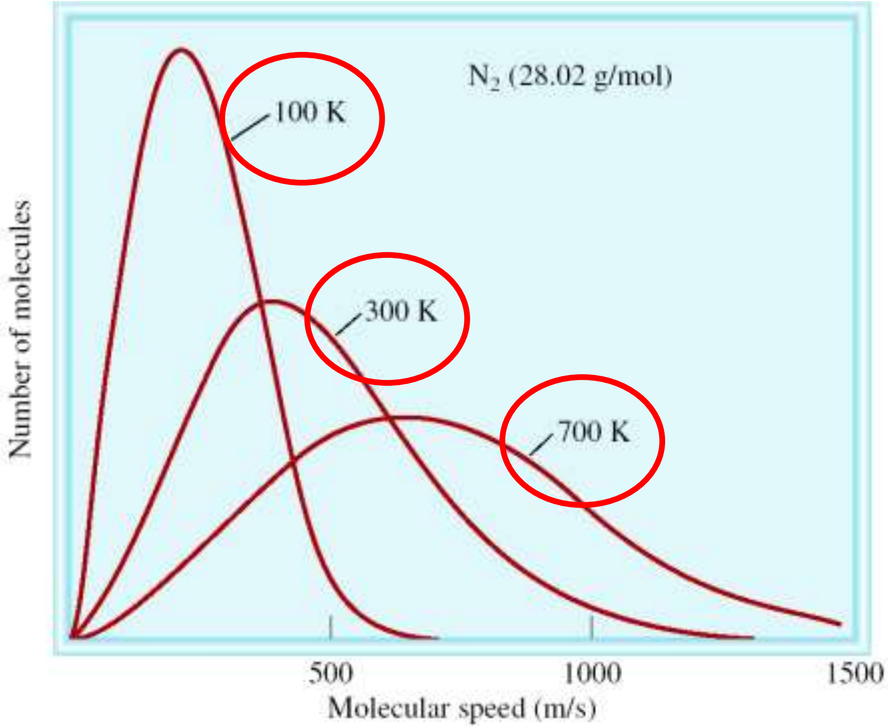
  $P \propto n$

- Dalton's Law of Partial Pressures

  Molecules do not attract or repel one another

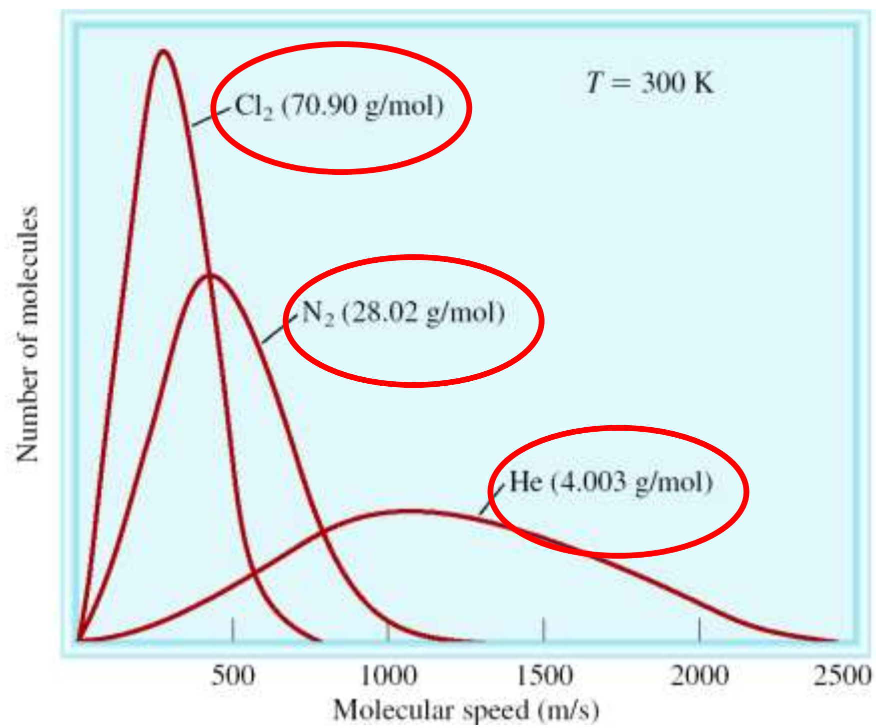
  P exerted by one type of molecule is unaffected by the presence of another gas

  $P_{\text{total}} = \Sigma P_i$



The distribution of speeds
of three different gases
at the same temperature

The distribution of speeds
for nitrogen gas molecules
at three different temperatures



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

Example 5.9

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

Example 5.9

Strategy To calculate the root-mean-square speed we need Equation (5.16).

What units should we use for R and $\mathscr{M}$ so that u_{rms} will be expressed in m/s?

Solution

To calculate u_{rms}, the units of R should be 8.314 J/K · mol and, because 1 J = 1 kg m^2/s^2, the molar mass must be in kg/mol.

The molar mass of He is 4.003 g/mol, or 4.003×10^{-3} kg/mol.

Example 5.9

From Equation (5.16),

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

$$= \sqrt{\frac{3(8.314\ \text{J/K}\cdot\text{mol})\,(298\ \text{K})}{4.003 \times 10^{-3}\ \text{kg/mol}}}$$

$$= \sqrt{1.86 \times 10^{6}\ \text{J/kg}}$$

Using the conversion factor 1 J = 1 kg m^2/s^2 we get

$$u_{\text{rms}} = \sqrt{1.86 \times 10^{6}\ \text{kg m}^{2}/\text{kg}\cdot\text{s}^{2}}$$

$$= \sqrt{1.86 \times 10^{6}\ \text{m}^{2}/\text{s}^{2}}$$

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

Example 5.9

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

$$u_{rms} = \sqrt{\frac{3(8.314\ \text{J/K}\cdot\text{mol})(298\ \text{K})}{2.802\times10^{-2}\ \text{kg/mol}}}$$

$$= \sqrt{2.65\times10^{5}\ \text{m}^2/\text{s}^2}$$

$$= 515\ \text{m/s}$$

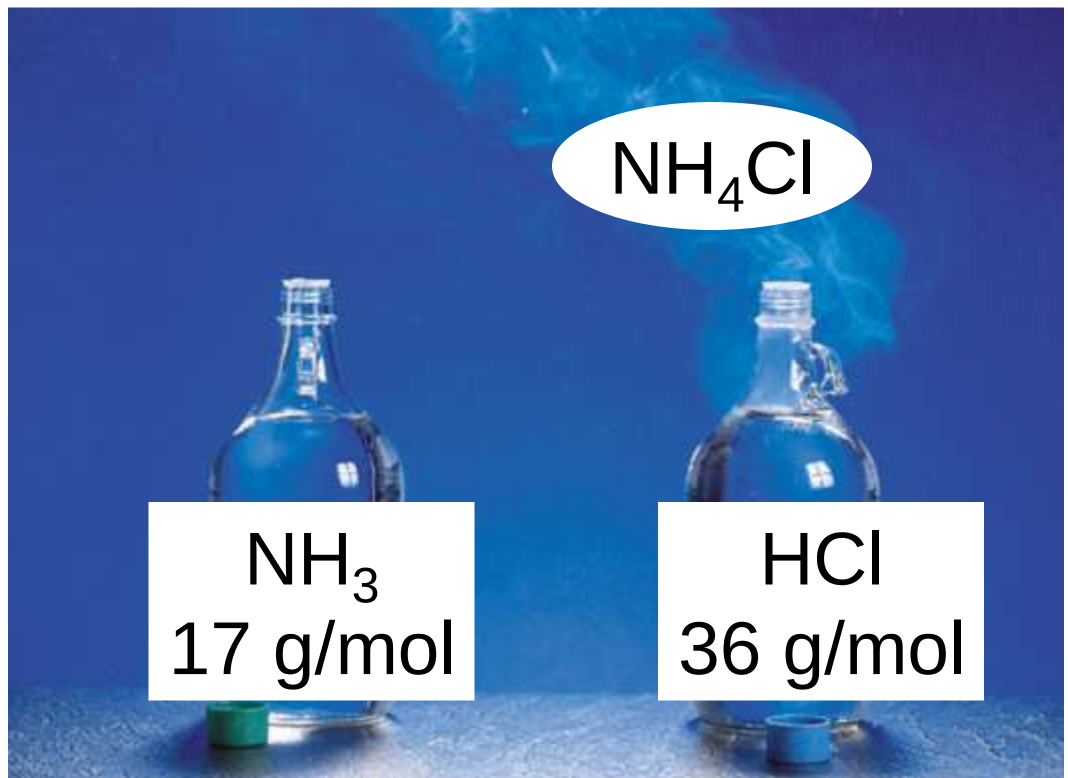
Check

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

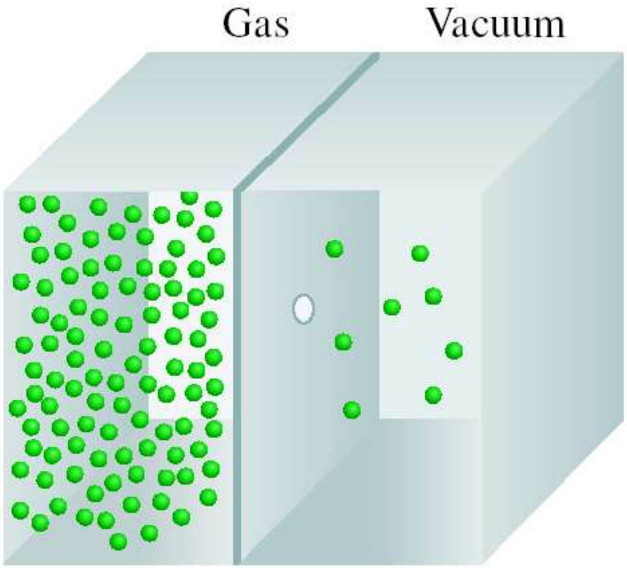
Gas diffusion is the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties.

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

molecular path



Gas effusion is the process by which gas under pressure escapes from one compartment of a container to another by passing through a small opening.



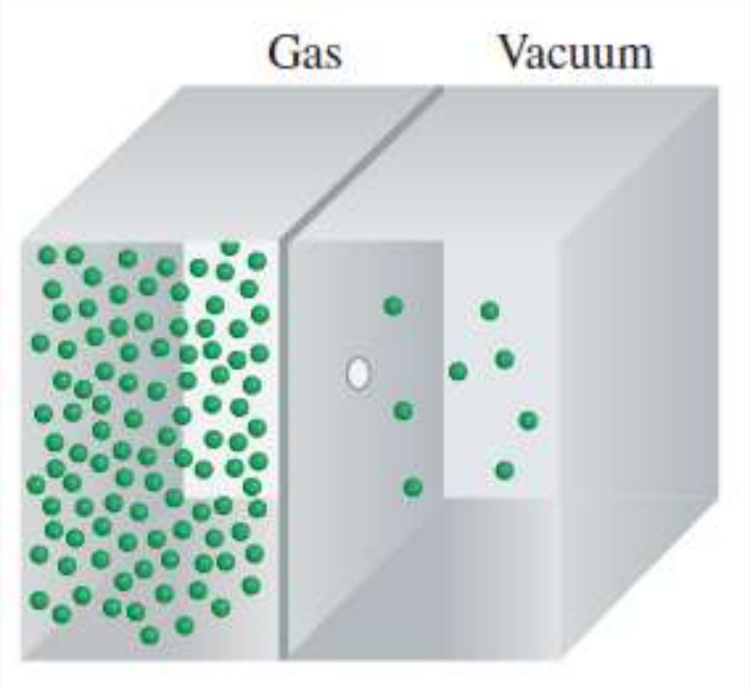
$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Example 5.10

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min.

Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier.

Calculate the molar mass of the unknown gas, and suggest what this gas might be.



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

Example 5.10

Strategy The rate of diffusion is the number of molecules passing through a porous barrier in a given time.

The longer the time it takes, the slower is the rate.

Therefore, the rate is *inversely* proportional to the time required for diffusion.

Equation (5.17) can now be written as $r_1/r_2 = t_2/t_1 = \sqrt{\mathscr{M}_2 / \mathscr{M}_1}$, where t_1 and t_2 are the times for effusion for gases 1 and 2, respectively.

Example 5.10

Solution From the molar mass of Br_2, we write

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

Where $\mathscr{M}$ is the molar mass of the unknown gas. Solving for $\mathscr{M}$ we obtain

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

$$= 16.1 \text{ g/mol}$$

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