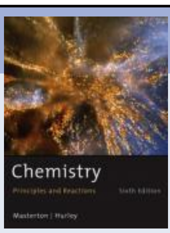

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Chapter 5
Gases

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Outline

- Measurements on Gases
- The Ideal Gas Law
- Gas Law Calculations
- Stoichiometry of Gaseous Reactions
- Gas Mixtures: Partial Pressures and Mole Fractions
- Kinetic Theory of Gases
- Real Gases

Introduction to Gases

- Gases have been known to exist since ancient times
  - The Greeks considered gases one of the four fundamental elements of nature
- 18th Century
  - Lavoisier, Cavendish and Priestley: Air is primarily nitrogen and oxygen, with trace components of argon, carbon dioxide and water vapor

Current Interest

- Gases in the news
  - Ozone depletion in the stratosphere
  - Carbon dioxide and global warming

State Variables

- State variables describe the state of a system under study
- To specify the state of a gas, four quantities must be known
  - Volume
  - Amount
  - Temperature
  - Pressure

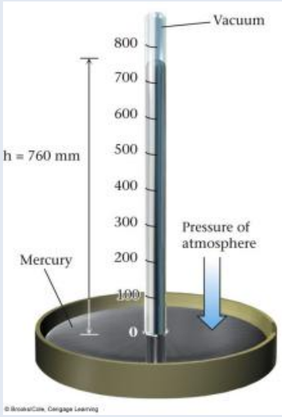
Volume, Amount and Temperature

- A gas expands uniformly to fill the container in which it is placed
  - The volume of the container is the volume of the gas
  - Volume may be in liters, mL, or cm^3
- The temperature of a gas must be indicated on the Kelvin scale
  - Recall that K = $^{\circ}$C + 273.15
- Amount of a gas is the number of moles

Pressure

- Pressure is force per unit area
  - In the English system, pounds per square inch or psi
  - Atmospheric pressure is about 14.7 psi

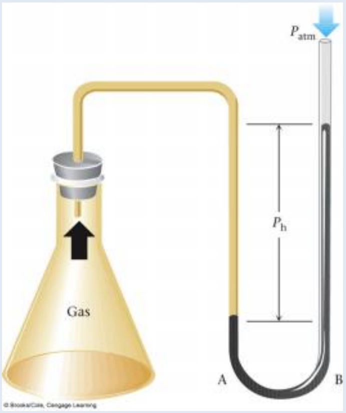
Measuring Pressure – The Barometer



The Barometer

- The barometer measures pressure in terms of the height of a column on liquid mercury
  - The atmosphere exerts a force on a pool of mercury, causing it to rise
  - One standard atmosphere of pressure is a column of mercury 760 mm high
  - Mercury is used to keep the column a manageable height

The Manometer



Gas Pressure Measurement

- The manometer measures gas pressure by differential
  - The height of the column of liquid is proportional to the pressure
  - Gas pressure can be more or less than atmospheric pressure

Other Units of Pressure

- 1 atm = 14.7 psi
- 1 atm = 760 mmHg
  - The mmHg is also called the Torr after Torricelli, inventor of the barometer
- SI unit of measurement, the pascal (Pa)
  - 1 Pa is the pressure exerted by a 0.1 mm high film of water on the surface beneath it
  - The bar = 10^5 Pa
  - 1.013 bar = 1 atm = 760 mmHg = 14.7 psi = 100 kPa

Example 5.1

Example 5.1 At room temperature, dry ice (solid CO_2) becomes a gas. At 77°F, 13.6 oz of dry ice are put into a steel tank with a volume of 10.00 ft^3. The tank's pressure gauge registers 11.2 psi. Express the volume (V) of the tank in liters, the amount of CO_2 in grams and moles (n), the temperature (T) in °C and K and the pressure (P) in bars, mm Hg, and atmospheres.

Strategy Use the following conversion factors:

$$\frac{14.7\text{ psi}}{1\text{ atm}} \qquad \frac{760\text{ mm Hg}}{1\text{ atm}} \qquad \frac{1.013\text{ bar}}{1\text{ atm}}$$

$$\frac{44.0\text{ g }CO_2}{1\text{ mol }CO_2} \qquad \frac{28.32\text{ L}}{1\text{ ft}^3} \qquad \frac{0.03527\text{ oz}}{1\text{ g}}$$

Most of these conversion factors can be found in Table 1.3. For the temperature conversion, use the relation:

$$t_{°F} = 1.8t_{°C} + 32$$

Example 5.1

SOLUTION

$$V = 10.00\text{ ft}^3 \times \frac{28.32\text{ L}}{1\text{ ft}^3} = 283.2\text{ L}$$

$$m = 13.6\text{ oz} \times \frac{1\text{ g}}{0.03527\text{ oz}} = 386\text{ g}$$

$$n_{CO_2} = 386\text{ g} \times \frac{1\text{ mol}}{44.0\text{ g}} = 8.77\text{ mol}$$

$$t_{°C} = \frac{77 - 32}{1.8} = 25°C$$

$$T_K = 25 + 273 = 298\text{ K}$$

$$P = 11.2\text{ psi} \times \frac{1\text{ atm}}{14.7\text{ psi}} = 0.762\text{ atm}$$

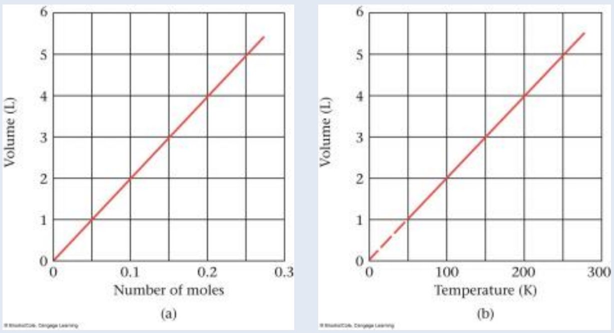
$$P = 0.762\text{ atm} \times \frac{760\text{ mm}}{1\text{ atm}} = 579\text{ mm Hg}$$

$$P = 0.762\text{ atm} \times \frac{1.013\text{ bar}}{1\text{ atm}} = 0.772\text{ bar}$$

The Ideal Gas Law

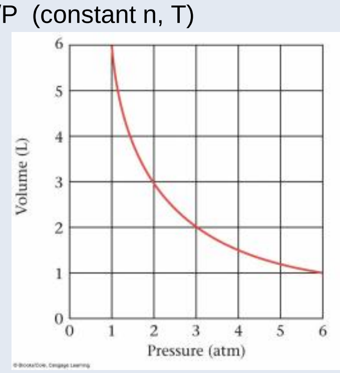
1. Volume is directly proportional to amount
   - $V = k_1n$ (constant T, P)
2. Volume is directly proportional to absolute temperature
   - $V = k_2T$ (constant n, P)

Figure 5.3

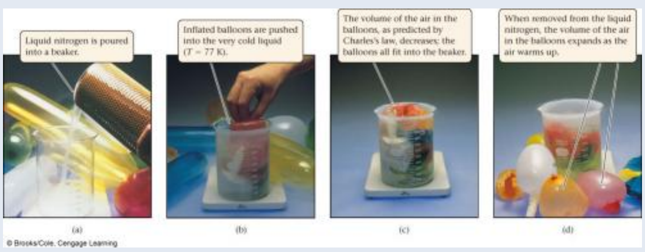


The Ideal Gas Law

3. Volume is inversely proportional to pressure
   - $V = k_3/P$ (constant n, T)



Temperature Effects – Charles's Law



The Ideal Gas Law

- Collect k_1, k_2 and k_3 into a new constant
- PV = nRT
- R is the gas constant
- Units of R:

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$$

Table 5.1 – Units of R

Table 5.1 Values of *R* in Different Units

Value	Where Used	How Obtained
$0.0821 \frac{L \cdot atm}{mol \cdot K}$	Gas law problems with *V* in liters, *P* in atm	From known values of *P*, *V*, *T*, *n*
$8.31 \frac{J}{mol \cdot K}$	Equations involving energy in joules	$1\ L \cdot atm = 101.3\ J$
$8.31 \times 10^3 \frac{g \cdot m^2}{s^2 \cdot mol \cdot K}$	Calculation of molecular speed (page 119)	$1\ J = 10^3 \frac{g \cdot m^2}{s^2}$

Standard Temperature and Pressure

- STP
  - 1 atm P
  - 273 K
- At STP, the molar volume of a gas can be calculated as follows:

$$V = \frac{nRT}{P} = \frac{1\,mol \times 0.0821 \frac{L \cdot atm}{mol \cdot K} \times 273\ K}{1\,atm} = 22.4\ L$$

Gas Law Calculations

- Final and initial state problems
- Single-state problems
- Density problem

Final and Initial State Problems

- In this type of problem, a gas undergoes a change from its initial to its final state
- The ideal gas equation is written twice, once for the initial state (1) and once for the final state (2)

Example 5.2

Example 5.2 A sealed 15.0-L steel tank is used to deliver propane (C_3H_8) gas. It is filled with 24.6 g of propane at 27°C. The pressure gauge registers 0.915 atm. (Assume that the expansion of steel from an increase in temperature is negligible.)

(a) If the tank is heated to 58°C, what is the pressure of propane in the tank?
(b) The tank is fitted with a valve to open and release propane to maintain the pressure at 1.200 atm. Will heating the tank to 58°C release propane?
(c) At 200°C, the pressure exceeds 1.200 atm. How much propane is released to maintain 1.200 atm pressure?

Strategy

(a) Read the problem carefully, and note that the volume of the tank and the number of moles of gas remain constant. (It is a *sealed, steel* tank.)
(b) Check both the calculated pressure at 58°C and the pressure at which propane is released.
(c) The problem now has three variables. Only volume remains constant.

Example 5.2 (cont'd)

SOLUTION

(a) initial state: $\frac{P_1}{T_1} = \frac{nR}{V}$

final state: $\frac{P_2}{T_2} = \frac{nR}{V}$

It follows that

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

Because $P_1 = 0.915$ atm; $T_1 = 27 + 273 = 300$ K; and $T_2 = 58 + 273 = 331$ K,

$$P_2 = 0.915 \text{ atm} \times \frac{331 \text{ K}}{300 \text{ K}} = 1.01 \text{ atm}$$

(b) Since 1.01 atm < 1.200 atm, the valve will not open.

(c) initial state: $\frac{P_1}{n_1T_1} = \frac{R}{V}$

final state: $\frac{P_2}{n_2T_2} = \frac{R}{V}$

Example 5.2 (cont'd)

Because $P_1 = 0.915$ atm; $T_1 = 300$ K; $n_1 = \frac{24.6 \text{ g}}{44.1 \text{ g/mol}} = 0.558$ mol; $P_2 = 1.200$ atm; and $T_2 = 473$ K,

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

$$= 0.558 \text{ mol} \times \frac{1.200 \text{ atm}}{0.915 \text{ atm}} \times \frac{300 \text{ K}}{473 \text{ K}}$$

$$= 0.464 \text{ mol}$$

The tank had 0.558 moles at the start and 0.464 moles after the release of propane. Hence, 0.094 mol of propane (MM = 44.1 g/mol) was released:

$$0.094 \text{ mol} \times \frac{44.1 \text{ g}}{1 \text{ mol}} = 4.15 \text{ g}$$

Reality Check The volume of the tank is never used in any of the calculations for the different parts of the problem. The mass of the propane is relevant only in part (c).

Single state problems – Calculating P, V, n or T

- In this type of problem, one of the state variables is not known
- The ideal gas equation can be solved for the unknown
- Take care to follow the units through the calculation!

Example 5.3

Example 5.3 Sulfur hexafluoride is a gas used as a long-term tamponade (plug) for a retinal hole to repair detached retinas in the eye. If 2.50 g of this compound is introduced into an evacuated 500.0-mL container at 83°C, what pressure in atmospheres is developed?

Strategy Substitute directly into the ideal gas law and solve for P. Note that V, n, and T have to be in units consistent with $R = 0.0821$ L · atm/mol · K.

SOLUTION Converting to the appropriate units,

$$V = 500.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.5000 \text{ L}$$

$$T = 83 + 273 = 356 \text{ K}$$

The molar mass of sulfur hexafluoride, SF_6, is 146.07 g/mol.

$$n = 2.50 \text{ g} \times \frac{1 \text{ mol}}{146.07 \text{ g}} = 0.0171 \text{ mol}$$

Substituting into the ideal gas law,

$$P = \frac{nRT}{V} = \frac{0.0171 \text{ mol} \times 0.0821 \text{ L} \cdot \text{atm/(mol} \cdot \text{K)} \times 356 \text{ K}}{0.5000 \text{ L}} = 1.00 \text{ atm}$$

Molar Mass and Density

- Density = mass/volume
- Recall that the molar mass has units of grams (mass) per mole
- Now, look at the ideal gas law:
  - The number of moles appears
  - Moles, n, can be expressed as mass/MM
  - There is also a volume term in the ideal gas law

Rewriting the Ideal Gas Law in Density Terms

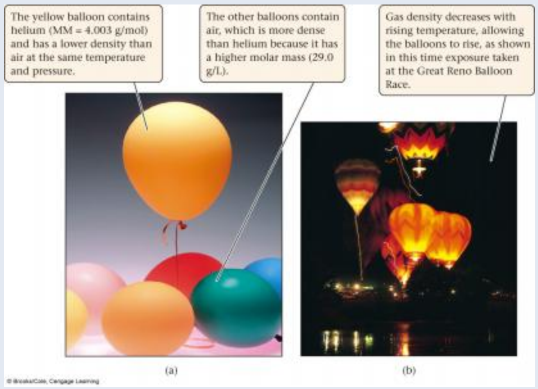
$$PV = \frac{m}{MM} RT$$

$$d = \frac{m}{V} = \frac{P \times MM}{R \times T}$$

Density of Gases

- Density is an extensive property
  - Does not depend on the amount of substance
- Density of a gas does depend on
  - Pressure
  - Temperature
  - Molar mass

Balloons



(a) (b)

Example 5.4

Example 5.4 Graded

Acetone is widely used as a nail polish remover. A sample of liquid acetone is placed in a 3.00-L flask and vaporized by heating to 95°C at 1.02 atm. The vapor filling the flask at this temperature and pressure weighs 5.87 g.

* (a) What is the density of acetone vapor under these conditions?

** (b) Calculate the molar mass of acetone.

*** (c) Acetone contains the three elements, C, H, and O. When 1.000 g of acetone is burned, 2.27 g of CO_2 and 0.932 g of H_2O are formed. What is the molecular formula of acetone?

Example 5.4 (cont'd)

SOLUTION

(a) $$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.87\ \text{g}}{3.00\ \text{L}} = 1.96\ \text{g/L}$$

(b) Perhaps the simplest approach here is to use the ideal gas law to solve for n. When the number of moles and the mass in grams, m, are known, the molar mass, MM, is readily calculated from the relation

$$m = \text{MM} \times n$$

$$n = \frac{PV}{RT} = \frac{(1.02\ \text{atm})(3.00\ \text{L})}{(0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(368\ \text{K})} = 0.101\ \text{mol}$$

Substituting in the equation

$$m = \text{MM} \times n \qquad 5.87\ \text{g} = \text{MM} \times 0.101\ \text{mol}$$

Solving for MM

$$\text{MM} = 5.87\ \text{g}/0.101\ \text{mol} = 58.1\ \text{g/mol}$$

(c) Recall from Chapter 3 that the simplest formula of a compound can be determined from combustion data (Example 3.6, page 58).

$$\text{mass C in 1.000-g sample} = 2.27\ \text{g}\ CO_2 \times \frac{12.01\ \text{g C}}{44.01\ \text{g}\ CO_2} = 0.619\ \text{g C}$$

$$\text{mass H in 1.000-g sample} = 0.932\ \text{g}\ H_2O \times \frac{2.016\ \text{g H}}{18.016\ \text{g}\ H_2O} = 0.104\ \text{g H}$$

$$\text{mass O} = 1.000\ \text{g} - 0.619\ \text{g} - 0.104\ \text{g} = 0.277\ \text{g O}$$

Converting these masses to moles, you should find that in this sample of acetone there are 0.0515 mol C, 0.103 mol H, and 0.0173 mol O.

It follows that the simplest formula is C_3H_6O, which has a molar mass of 58.1 g/mol. Clearly the molecular formula is also the simplest formula, C_3H_6O.

Stoichiometry in Gaseous Reactions

- Gases can participate as reactants or products in any chemical reaction
- Gases are balanced in the same way as liquids, solids, or aqueous solutions in chemical equations

Example 5.5

Example 5.5 Hydrogen peroxide, H_2O_2, is a common bleaching agent. It decomposes quickly to water and oxygen gas at high temperatures.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

How many liters of oxygen are produced at 78°C and 0.934 atm when 1.27 L of H_2O_2 (d = 1.00 g/mL) decompose?

Example 5.5 (cont'd)

Strategy Determine the mass of H_2O_2 using the density and convert °C to K. Use the following scheme:

$$m_{H_2O_2} \xrightarrow{MM} n_{H_2O_2} \xrightarrow[\text{ratio}]{\text{molar}} n_{O_2} \xrightarrow{PV = nRT} V_{O_2}$$

SOLUTION

$$m_{H_2O_2} = 1.27\ \text{L} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times 1.00\ \frac{\text{g}}{\text{mL}} = 1270\ \text{g}$$

$$n_{H_2O_2} = 1270\ \text{g} \times \frac{1\ \text{mol}}{34.02\ \text{g}} = 37.3\ \text{mol}$$

$$n_{O_2} = 37.3\ \text{mol } H_2O_2 \times \frac{1\ \text{mol } O_2}{2\ \text{mol } H_2O_2} = 18.7\ \text{mol } O_2$$

$$V_{O_2} = \frac{18.7\ \text{mol} \times 0.0821\ \text{L·atm/mol·K} \times (78 + 273)\ \text{K}}{0.934\ \text{atm}}$$

$$= 577\ \text{L}$$

Example 5.6

Example 5.6 Graded

Sodium bicarbonate (baking soda) is widely used to absorb odors inside refrigerators. When acid is added to baking soda, the following reaction occurs:

$$NaHCO_3(s) + H^+(aq) \longrightarrow Na^+(aq) + CO_2(g) + H_2O$$

All experiments here are performed with 2.45 *M* HCl and 12.75 g of $NaHCO_3$ at 732 mm Hg and 38°C.

*(a) If an excess of HCl is used, what volume of CO_2 is obtained?

**(b) If $NaHCO_3$ is in excess, what volume of HCl is required to produce 2.65 L of CO_2?

***(c) What volume of CO_2 is produced when all the $NaHCO_3$ is made to react with 50.0 mL of HCl?

Strategy Do not forget to convert temperature and pressure to the appropriate units.

(a) $m_{NaHCO_3} \xrightarrow{MM} n_{NaHCO_3} \xrightarrow[\text{ratio}]{\text{molar}} n_{CO_2} \xrightarrow{PV = nRT} V_{CO_2}$

(b) $V_{CO_2} \xrightarrow{PV = nRT} n_{CO_2} \xrightarrow[\text{ratio}]{\text{molar}} n_{H^+} \xrightarrow{n = V \times M} V_{H^+}$

(c) This is a limiting reactant problem.

$n_{H^+} \longrightarrow n_{CO_2}$ compare to $n_{NaHCO_3} \longrightarrow n_{CO_2}$

Use the ideal gas law to convert the smaller number of moles of CO_2 to volume.

Example 5.6 (cont'd)

SOLUTION

(a) $n_{NaHCO_3} = 12.75\ \text{g} \times \frac{1\ \text{mol}}{84.01\ \text{g}} = 0.1518\ \text{mol}$

$$n_{CO_2} = 0.1518\ \text{mol NaHCO}_3 \times \frac{1\ \text{mol } CO_2}{1\ \text{mol NaHCO}_3} = 0.1518\ \text{mol}$$

$$V_{CO_2} = \frac{0.1518\ \text{mol} \times 0.0821\ \text{L-atm/mol-K} \times (38 + 273)\ \text{K}}{732/760\ \text{atm}} = 4.02\ \text{L}$$

Example 5.6 (cont'd)

(b) $n_{CO_2} = \frac{2.65\ \text{L} \times 732/760\ \text{atm}}{0.0821\ \text{L-atm/mol-K} + (38 + 273)\ \text{K}} = 0.100\ \text{mol}$

$$n_{H^+} = 0.100\ \text{mol } CO_2 \times \frac{1\ \text{mol } H^+}{1\ \text{mol } CO_2} = 0.100\ \text{mol}$$

$$V_{H^+} = \frac{n}{M} = \frac{0.100\ \text{mol}}{2.45\ \text{mol/L}} = 0.0408\ \text{L} = 40.8\ \text{mL}$$

(c) $n_{CO_2} = n_{H^+} = V \times M = 0.0500\ \text{L} \times 2.45\ \text{mol/L} = 0.1225\ \text{mol}$

$n_{CO_2} = n_{NaHCO_3} = 0.152\ \text{mol (see (a))}$

The limiting reactant is H^+.

$$V_{CO_2} = \frac{0.1225\ \text{mol} \times 0.0821\ \text{L-atm/mol-K} \times (38 + 273)\ \text{K}}{732/760\ \text{atm}} = 3.25\ \text{L}$$

Gas Mixtures: Partial Pressures and Mole Fractions

- The ideal gas law applies to all gases, so it applies to mixtures of gases as well
- A new term is needed for a mixture of gases
  - Partial pressure, the part of the total pressure due to each gas in the mixture
  - Sum of the partial pressures is the total pressure

Dalton's Law of Partial Pressures

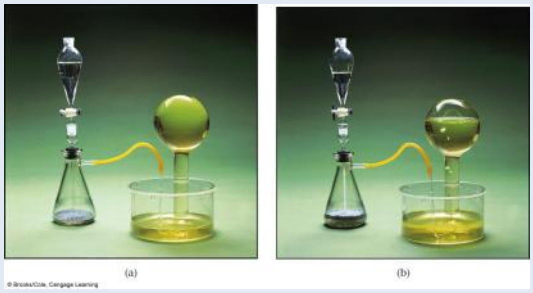
- The total pressure of a gas mixture is the sum of the partial pressures of the gases in the mixture
- Consider a mixture of hydrogen and helium:
  - P H_2 = 2.46 atm
  - P He = 3.69 atm
  - P total = 6.15 atm

Vapor Pressure

- The vapor pressure of a substance is the pressure of the gaseous form of that substance
  - Vapor pressure is an intensive property
  - Vapor pressure depends on temperature

Collecting a Gas Over Water

- When a gas is collected over water, the total pressure is the pressure of the gas plus the vapor pressure of water



Wet Gases

- P H_2O is the vapor pressure of water
- P H_2O is dependent on temperature
- Consider H_2 gas collected over water:

$$P_{tot} = P_{H_2O} + P_{H_2}$$

Example 5.8

Example 5.8 A student prepares a sample of hydrogen gas by electrolyzing water at 25°C. She collects 152 mL of H_2 at a total pressure of 758 mm Hg. Using Appendix 1 to find the vapor pressure of water, calculate

(a) the partial pressure of hydrogen.
(b) the number of moles of hydrogen collected.

Strategy

(a) Use Dalton's law to find the partial pressure of hydrogen, P_{H_2}.
(b) Use the ideal gas law to calculate n_{H_2}, with P_{H_2} as the pressure.

Example 5.8 (cont'd)

SOLUTION

(a) From Appendix 1, P_{H_2O} = 23.76 mm Hg at 25°C. The total pressure, P_{tot}, is 758 mm Hg.

$$P_{H_2} = P_{tot} - P_{H_2O} = 758 \text{ mm Hg} - 23.76 \text{ mm Hg} = 734 \text{ mm Hg}$$

(b) $$n_{H_2} = \frac{(P_{H_2})V}{RT} = \frac{(734/760 \text{ atm})(0.152 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(298 \text{ K})} = 0.00600 \text{ mol } H_2$$

Partial Pressure and Mole Fraction

- One can rearrange the Ideal Gas Law for a mixture containing two gases, A and B

$$\frac{P_A}{P_{tot}} = \frac{n_A}{n_{tot}}$$

Mole Fraction

- The mole fraction of gas A is the number of moles of A divided by the total number of moles of gas in the mixture

$$X_A = \frac{n_A}{n_{tot}}$$

Dalton's Law and Mole Fraction

- The partial pressure of gas A is its mole fraction times the total pressure

$$P_A = X_A P_{tot}$$

Example 5.9

Example 5.9 When one mole of methane, CH_4, is heated with four moles of oxygen, the following reaction occurs:

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

Assuming all of the methane is converted to CO_2 and H_2O, what are the mole fractions of O_2, CO_2, and H_2O in the resulting mixture? If the total pressure of the mixture is 1.26 atm, what are the partial pressures?

Strategy First, calculate the number of moles of each gas (remember that oxygen is in excess). Then determine the mole fractions and finally the partial pressures.

SOLUTION Since all the methane is consumed,

$$n_{CH_4} = 0; \quad n_{CO_2} = 1.00; \quad n_{H_2O} = 2.00; \quad n_{O_2} = 4.00 - 2.00 = 2.00$$

The total number of moles is 1.00 + 2.00 + 2.00 = 5.00.

$$X_{CO_2} = \frac{1.00}{5.00} = 0.200; \; X_{H_2O} = \frac{2.00}{5.00} = 0.400; \; X_{O_2} = \frac{2.00}{5.00} = 0.400$$

Example 5.9 (cont'd)

$$P_{CO_2} = 0.200 \times 1.26\text{ atm} = 0.252\text{ atm}$$
$$P_{H_2O} = 0.400 \times 1.26\text{ atm} = 0.504\text{ atm}$$
$$P_{O_2} = 0.400 \times 1.26\text{ atm} = 0.504\text{ atm}$$

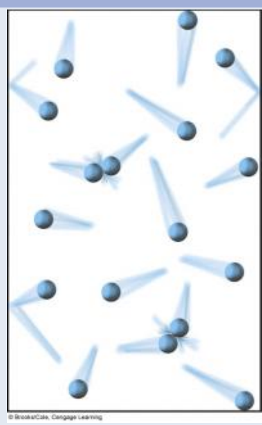
Reality Check The partial pressures (0.252 atm, 0.504 atm, 0.504 atm) add up to the total pressure, 1.26 atm, as they should according to Dalton's law. They are also in the same ratio as the mole fractions (0.200, 0.400, 0.400).

Kinetic Theory of Gases

The kinetic-molecular model

1. Gases are mostly empty space. The total volume of the molecules is small
2. Gas molecules are in constant, random motion
3. Collisions of gas particles are elastic
4. Gas pressure is caused by collisions of molecules with the walls of the container

Figure 5.7 – The Kinetic Molecular Model



New Variables

- N, the number of gas particles
- m, the mass of the gas particle
- u, the average speed of a gas particle

Pressure and the Molecular Model

$$P = \frac{Nmu^2}{3V}$$

- Notes:
  - N/V is the concentration of gas particles
  - mu^2 is a measure of the energy of the collisions

Average Kinetic Energy of Translational Motion

$$E = \frac{3RT}{2N_A}$$

- Notes:
  - R is the gas constant
  - T is the Kelvin temperature
  - N_A is Avogadro's number

Results from Kinetic Energy of Translational Motion

- At a given temperature, all molecules of all gases have the same average kinetic energy of translational motion
- The average kinetic energy of a gas particle is directly proportional to the Kelvin temperature

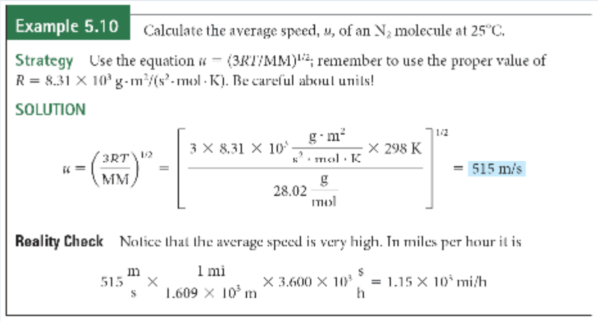
Average Speed, u

$$u = \left(\frac{3RT}{MM}\right)^{\frac{1}{2}}$$

- The average speed is proportional to the square root of the Kelvin temperature
- The average speed is proportional to the inverse of the square root of the molar mass of the gas

Figure 5.8 – Ammonia and Hydrogen Chloride

Example 5.10



Example 5.10 Calculate the average speed, u, of an N_2 molecule at 25°C.

Strategy Use the equation $u = (3RT/MM)^{1/2}$; remember to use the proper value of $R = 8.31 \times 10^3\ g \cdot m^2/(s^2 \cdot mol \cdot K)$. Be careful about units!

SOLUTION

$$u = \left(\frac{3RT}{MM}\right)^{1/2} = \left[\frac{3 \times 8.31 \times 10^3 \dfrac{g \cdot m^2}{s^2 \cdot mol \cdot K} \times 298\ K}{28.02 \dfrac{g}{mol}}\right]^{1/2} = 515\ m/s$$

Reality Check Notice that the average speed is very high. In miles per hour it is

$$515 \frac{m}{s} \times \frac{1\ mi}{1.609 \times 10^3\ m} \times 3.600 \times 10^3 \frac{s}{h} = 1.15 \times 10^3\ mi/h$$

Effusion of Gases

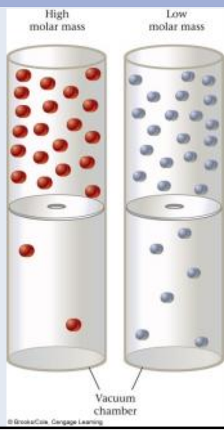
- Diffusion
  - Gases move through space from a region of high concentration to a region of low concentration
    - You can smell an apple pie baking as the particles responsible for the odor diffuse through the room
- Effusion
  - Gas particles will escape through a small hole (orifice) in a container
    - Air will slowly leak out of a tire or balloon through pores in the rubber

Graham's Law of Effusion

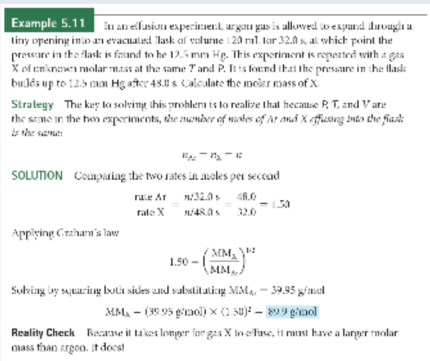
$$\frac{\text{rate of effusion of B}}{\text{rate of effusion of A}} = \left(\frac{MM_A}{MM_B}\right)^{\frac{1}{2}}$$

- The rate at which gas B escapes divided by the rate at which gas A escapes is equal to the square root of the ratio of the molar mass of gas A to gas B

Effusion of Gases



Example 5.11



Example 5.11 In an effusion experiment, argon gas is allowed to expand through a tiny opening into an evacuated flask of volume 120 mL for 32.0 s, at which point the pressure in the flask is found to be 12.5 mm Hg. This experiment is repeated with a gas X of unknown molar mass at the same T and P. It is found that the pressure in the flask builds up to 12.5 mm Hg after 48.0 s. Calculate the molar mass of X.

Strategy The key to solving this problem is to realize that because P, T, and V are the same in the two experiments, *the number of moles of Ar and X effusing into the flask is the same:*

$$n_{Ar} = n_X = n$$

SOLUTION Comparing the two rates in moles per second

$$\frac{\text{rate Ar}}{\text{rate X}} = \frac{n/32.0\ s}{n/48.0\ s} = \frac{48.0}{32.0} = 1.50$$

Applying Graham's law

$$1.50 = \left(\frac{MM_X}{MM_{Ar}}\right)^{1/2}$$

Solving by squaring both sides and substituting $MM_{Ar} = 39.95$ g/mol

$$MM_X = (39.95\ g/mol) \times (1.50)^2 = 89.9\ g/mol$$

Reality Check Because it takes longer for gas X to effuse, it must have a larger molar mass than argon. It does!

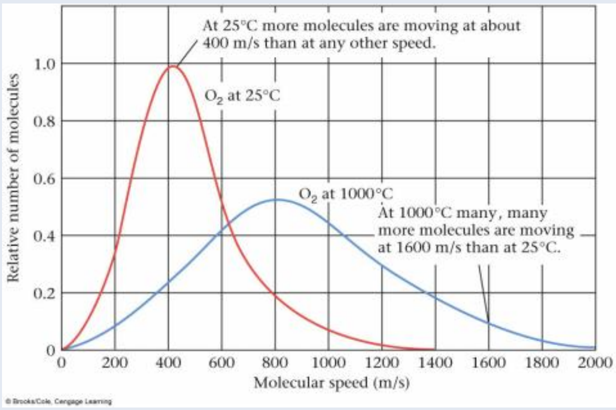
Gaseous Effusion and the Manhattan Project

- Effusion was used to separate U-238 from U-235
  - Recall that isotopes have the same chemical properties, and so cannot be separated by chemical means
- The mass of $^{238}UF_6$ is heavier than the mass of $^{235}UF_6$
  - Very small difference in mass
  - $^{235}UF_6$ effuses more quickly because of its smaller mass

Distribution of Molecular Speeds

- At a given temperature, gas particles will have a set of speeds, not a single fixed value for speeds
- Maxwell-Boltzmann Distribution

Figure 5.9



Distribution of Molecular Speeds

- Plot the fraction of molecules having a given speed vs. the molecular speed
- Curve that results has a maximum in the number of molecules with the given speed
  - Most probable speed
- As the temperature increases
  - The maximum shifts toward higher speed
  - The relative number of molecules at that speed decreases

Example 5.12

Example 5.12 Conceptual

Consider the two boxes A and B shown below. Box B has a volume exactly twice that of box A. The circles ○ and ● represent one mole of HCl and He, respectively. The two boxes are at the same temperature.

(a) Compare the pressures of the gases in the two containers.
(b) Compare the densities of the two gases.
(c) Compare the number of atoms in the two boxes.
(d) If the HCl in box A were transferred to box B, what would be the mole fraction of HCl in the mixture?
(e) Which of the two gases effuses faster?

SOLUTION

(a) Since n/V and T are the same in both cases, $P = nRT/V$ is the same for the two gases.
(b) The mass of HCl is 2(36.5 g) = 73.0 g; that of He is 4(4.00 g) = 16.0 g. Since 73.0 g/V > 16.0 g/2V, HCl has the higher density.
(c) Two moles of diatomic HCl contain the same number of atoms as four moles of He.
(d) $X_{HCl} = 2/6 = 1/3$
(e) Because HCl and He are at the same pressure, the lighter gas, He, effuses faster.

Real Gases

- Recall that the molar volume of a gas at STP is 22.4 L from the ideal gas law
- There are deviations from this volume that depend on the gas being studied
  - The molar volume of a real gas is less than that calculated by the ideal gas law

Table 5.2

Table 5.2 Real Versus Ideal Gases, Percent Deviation* in Molar Volume

	O_2			CO_2		
P(atm)	50°C	0°C	−50°C	50°C	0°C	−50°C
1	−0.0%	−0.1%	−0.2%	−0.4%	−0.7%	−1.4%
10	−0.4%	−1.0%	−2.1%	−4.0%	−7.1%	
40	−1.4%	−3.7%	−8.5%	−17.9%		
70	−2.2%	−6.0%	−14.4%	−34.2%	Condenses to liquid	
100	−2.8%	−7.7%	−19.1%	−59.0%		

$$\text{*Percent deviation} = \frac{(V_m - V_m^\circ)}{V_m^\circ} \times 100\%$$

Liquefaction of Gases

- All gases can be liquefied
  - Lowering the temperature
  - Increasing the pressure
- When a gas is liquefied, the attractive forces between gas particles becomes significant
- The closer a gas is to the liquid state, the more it will deviate from the ideal gas law

Two Factors for Real Gases

- Two factors are important to real gases
  1. The attractive forces between the gas particles
  2. The volume of the gas particles
- Both of these are ignored by the ideal gas law

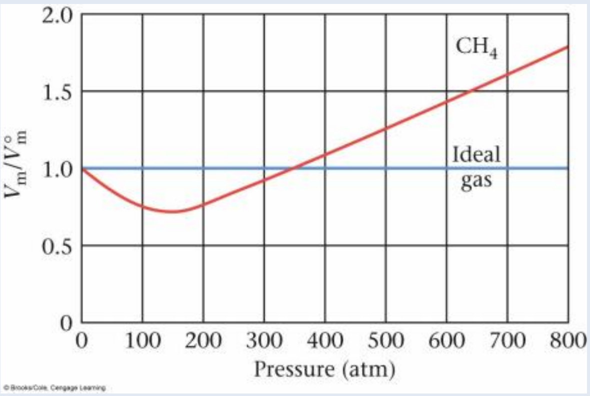
Attractive Forces

- Note that the observed molar volume for gases is lower than that calculated by the ideal gas law
  - The forces between particles pull the particles together
  - The volume occupied by the gas is then decreased
  - This is a negative deviation from the ideal gas law

Particle Volume

- Consider a plot of the observed molar volume/ideal molar volume for methane vs. pressure
  - Up to 150 atm, the deviation from ideality steadily increases
  - The volume of the gas particles becomes a more significant factor in determining the volume of the gas as the pressure increases

Figure 5.10 – Deviation from Ideal Volume



Key Concepts

1. Conversion between P, V, T and n
2. Use of the ideal gas law to:
   - Solve initial and final state problems
   - Solve single-state problems
   - Calculate the density of a gas
   - Relate amounts of gases in reactions
3. Use Dalton's Law
4. Calculate the speed of gas molecules
5. Use Graham's Law to relate the rate of effusion to the molar mass of a gas