

From Last Class.....

The following statements relate to the Kinetic Molecular Theory of Gases. All but one are true or all but one are false. Choose the statement that doesn't belong.

- If the postulates (assumptions) of the kinetic-molecular theory hold for a given gas, the gas is automatically an ideal gas.
- According to the kinetic theory of gases, pressure is proportional to the average of the square of the speed at a given temperature.
- The shape of the molecular speed distribution (i.e. relative number of molecules versus speed) changes as the temperature is raised from 0 to 100 °C.
- The energies of gas molecules are distributed over a wide range of values at constant temperature.
- At a given temperature, molecules of higher mass have a higher average speed than those of lower mass.

- a) False
- b) $PV = \frac{mN\bar{u}^2}{3}$ $P = \frac{mN\bar{u}^2}{3V}$ False
- c) True
- d) $\overline{e_k} = \frac{3}{2}RT$ False
- e) False

Calculating u_{rms} and u_{av}

Calculate the root-mean-squared and average speed (in m/s) for gaseous Ar atoms at 25 °C.

$$u_{rms} = \sqrt{\frac{3(8.3145)(298.15)}{39.948 \frac{g}{mol} \cdot \frac{1 \text{ kg}}{1000 \text{ g}}}}$$

$$\left. \begin{aligned} u_{mp} &= \sqrt{\frac{2RT}{M}} \\ u_{avg} &= \sqrt{\frac{8RT}{\pi M}} \\ u_{rms} &= \sqrt{\frac{8RT}{M}} \end{aligned} \right\} M \text{ units } \text{kg/mol}$$

$$R = 8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}}$$

Lesson 10:

- Gas Properties Relating to the Kinetic Molecular Theory
- Real Gases

Objectives: By the end of today's class you will be able to

- apply Graham's law to determine characteristics (amount, molar mass, and speed) of an effusing gas.
- justify and apply the van der Waals equation.

Diffusion vs. Effusion

Diffusion: migration of molecules from region of high to low concentration as a result of random molecular motion.



Effusion: escape of gas molecules from their container through a tiny pinhole or porous membrane.



Graham's Law

The rate of effusion of a gas is inversely proportional to the square root of its molar mass.

$$\text{rate of effusion of gas} \propto u_{rms} \propto \sqrt{\frac{1}{M}}$$

When comparing two gases:

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{(u_{rms})_A}{(u_{rms})_B} = \sqrt{\frac{3RT/M_A}{3RT/M_B}} = \sqrt{\frac{M_B}{M_A}}$$

$$\text{Or... } \frac{n_B \text{ effused}}{n_A \text{ effused}} = \frac{d_A \text{ traveled}}{d_B \text{ traveled}} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{\text{effusion time for A}}{\text{effusion time for B}} = \sqrt{\frac{M_B}{M_A}}$$

Example 1 (Ch6 #85)

It takes 22 hours for a neon-filled balloon to shrink to half its original volume at STP. If the same balloon had been filled with helium, then how long would it have taken for the balloon to shrink to half its original volume at STP?

$$M_{Ne} = 20.17979 \text{ g/mol}$$

$$M_{He} = 4,002609 \text{ /mol}$$

$$\frac{t_{Ne}}{t_{He}} = \sqrt{\frac{M_{Ne}}{M_{He}}}$$

$$\frac{2.2}{t_{He}} = \sqrt{\frac{20.1797}{4.00260}}$$

$$t_{He} = 9.8 \text{ hr}$$

For a real (nonideal) gas:

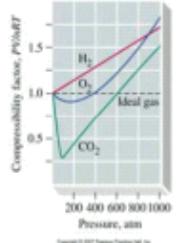
$$\frac{PV}{nRT} = Z$$

compressibility factor

For a given volume, temperature and amount of gas

$$Z = \frac{P_{\text{real}}}{P_{\text{ideal}}}$$

Generally $0.1 < Z < 1.5$



For a real (nonideal) gas:

$$\frac{PV}{nRT} = 1$$

For a real (nonideal) gas:
 $PV \neq nRT$
 $\frac{PV}{nRT} = Z = \text{compressibility factor}$

$$\frac{PV}{nRT} = Z = \text{compressibility factor}$$

For a given volume, temperature and amount of gas

$$Z = \frac{P_{real}}{P_{ideal}}$$

Generally $0.1 < z < 1.5$

Assumption #1:

Gas molecules have no molecular volume.

$$PV = nRT \quad \text{therefore} \quad V = \frac{nRT}{P}$$

When $T=0K$ or at very high P ,
 $V=0$

Correction #1:

Molecules do occupy space!

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

b: unit l/mole

or

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

FIGURE 11-21 The effect of finite molecular size.



Assumption #2:

Assumption #2: There are no intermolecular forces between molecules.

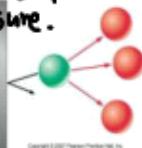
More likely true for non-polar gases
at low p and high T .

Correction #2:

Intermolecular forces between molecules lowers the pressure.

$$P = \frac{nRT}{V-bn} - \frac{an^2}{V^2}$$

a: unit $\frac{\text{L}^2 \cdot \text{atm}}{\text{mol}}$



Other forms of the van der Waals equation:

$$P = \frac{nRT}{V - bn} - \frac{an^2}{V^2}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(P + \frac{an^2}{V^2} \right) (V - bn) = nRT$$

$$PV^3 - (bnP + nRT)V^2 + an^2V - abn^3 = 0$$

Example 1:

Calculate the pressure exerted by 1.00 mol Cl₂ (g) confined to a volume of 2.0 L at:

- a) 0 °C
- b) 100 °C
- c) 200 °C
- d) 400 °C

From these results, confirm the statement that a gas tends to be more ideal at high temperatures than at low temperatures.

For Cl₂:

$$a = 6.49 \text{ L}^2\cdot\text{atm}\cdot\text{mol}^{-2}$$

$$b = 0.0562 \text{ L}\cdot\text{mol}^{-1}$$

Example 2:

Propane is stored at 69 bar and 422 K in an insulated tank. Calculate the volume required to store 1.0 kmol of propane at these conditions using:

- a) Ideal gas law
- b) van der Waals equation

Data:

$$a = 9.38 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}$$

$$b = 9.04 \times 10^{-2} \text{ dm}^3\cdot\text{mol}^{-1}$$

Suggested Readings

- 6.8 Gas Properties Relating to the Kinetic-Molecular Theory
- 6.9 Nonideal (Real) Gases
