

## Kinetic Molecular Theory

In order for gases to behave ideally they must follow the four postulates of kinetic molecular theory:

- Gases are mostly empty space.
- Gas molecules are in constant, chaotic motion
- Collisions are elastic (no intermolecular forces)
- Gas pressure is caused by collisions of molecules with the walls of the container

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

N = number of molecules

m = mass of molecules

u = average speed (actually u = root mean squared speed of the molecules  $u_{\text{rms}} = \sqrt{u^2}$ )

The 3 is related to the fact that the particle is moving in 3 dimensional space.

N/V is the concentration of the gas;  $mu^2$  is related to the collisional energy.

The translational kinetic energy ( $E_t$ ) of a gas molecule:

$$E_t = mu^2/2 \quad \text{since } mu^2 = 3PV/N$$

$$E_t = 3PV/2N$$

$$E_t = 3nRT/2N$$

$$E_t = \mathbf{3RT/2N_A}$$

*-At a given temperature, molecules of different gases must all have the same average translational kinetic energy. (This means less massive particles are moving faster on average at a given temperature)*

*-The average translational kinetic energy of a gas molecule is directly proportional to the Kelvin temperature, T.*

Also, further substitution ( $E_t = \frac{1}{2} mu^2$ ) yields:

$$u = \sqrt{\frac{3RT}{MM}} \quad \text{where MM is the molar mass of the substance.}$$

Average speed is:

*-Proportional to the square root of the absolute temperature*

*-Inversely proportional to the square root of the molar mass*

### Graham's Law of Effusion:

Effusion: The process by which gas escapes from a container through a tiny hole.

Diffusion: The process by which one substance mixes with one or more other substances as a result of the random motion of molecules (e.g. as in the time it takes to smell someone's perfume from across the room).

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

$$\text{Rate}_1/\text{Rate}_2 = (\text{Molar mass}_2 / \text{Molar mass}_1)^{1/2}$$

or written in terms of time

$$\text{Time}_1/\text{Time}_2 = (\text{Molar mass}_1 / \text{Molar mass}_2)^{1/2}$$

This law works for diffusion as well as effusion.

**\*Remember: Rate is inversely proportional to time!**

**Example:**

In an experiment it takes an unknown gas 1.5 times longer to effuse than the same amount of oxygen gas. Find the molar mass of the unknown gas.

**Answer:**

$$1.5T_1/T_1 = (\text{MM}_2 / 32.0\text{g/mol})^{1/2} \quad \text{where } T_2 = 1.5T_1$$

solving for MM<sub>2</sub>

$$\text{MM}_2 = (1.5)^2(32.0) = \mathbf{72.0\text{g/mol}}$$

**Example: Explain why a balloon deflates so much faster when it contains helium than when it contains air, which is mostly nitrogen.**

**Answer:**

$$\text{He} = 4.00\text{g/mol} \quad \text{N}_2 = 28.02\text{g/mol}$$

Relative rates of effusion through the porous holes in a balloon

$$\text{Rate}_2 / \text{Rate}_1 = (28.02 / 4.00)^{-5} = 2.65$$

Helium effuses 2.65x faster than nitrogen.

**van der Waal Equation: For non-ideal gas behavior**

If a gas does not behave ideally (i.e. according to the postulates of kinetic molecular theory), corrections for conditions must be made for the fact that

-molecules may take up a significant amount of the free space of the container

-molecular exhibit inelastic behavior to a greater or lesser degree depending upon the substance.

*-Gases behave most ideally at high temperatures and low pressures.*

**van der Waals correction:**

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

**a and b are constants that must be determined experimentally for a particular gaseous substance.**

The  $\frac{an^2}{V^2}$  factor accounts for the attractive interactions between the particles and the walls of the container and the  $-nb$  factor corrects for the actual free space in the container.

**Example:** Calculate the difference in pressure between ideal and actual for .50mol of carbon dioxide at 30.0°C in a 2.00L container if  $a = 3.59\text{L}^2\text{atm/mol}^2$  and  $b = 0.0427\text{L/mol}$

**Answer:**

Actual:

$$(P + (3.59)(.50^2)/(2.0^2)) (2.0 - (.0427)(.50)) = (.5)(.0821)(303.15)$$

$$P = 6.06\text{atm}$$

Ideal:

$$P = (.5)(.0821)(303.15)/(2.0)$$

$$P = 6.22\text{atm}$$

$$\Delta P = .16\text{atm}$$

**Question:**

A compound composed of carbon, hydrogen and chlorine effuses through a pinhole 0.411 times as fast as neon. Select the correct molecular formula for the compound from the following choices;  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_3\text{Cl}$

**Answer:**

$$\text{Rate}_2/\text{Rate}_1 = 0.411 = (20.18\text{g/mol} / M)^{.5}$$

$$.168921 = 20.18 / M$$

**M = 119.5g/mol This molar mass is consistent with  $\text{CHCl}_3$**