Kinetic Theory of Gases

1) Assumptions

a) Every gas consists of extremely small particles called molecules.

b) The molecules of a gas are identical, spherical, rigid a perfectly elastic point masses.

c) Their size is negligible in comparison to intermolecular distance (10^{-9} m)

d) The volume of molecules is negligible in comparison to the volume of gas.

e) Molecules of a gas are in random motion in all directions with all possible velocities.

f) The speed of gas molecules lies between zero and infinity

g) The gas molecules collide among themselves as well as with the walls of vessel. These collisions are perfectly elastic.

h) The time spent in a collision between two molecules is negligible in comparison to time between two successive collisions.

i) The number of collisions per unit volume in a gas remains constant.

j) No attractive or repulsive force acts between gas molecules.

k) Gravitational attraction among the molecules is negligible due to their small masse and very high speed.

l) The change in momentum is transferred to the walls of the container causes pressure.

m) The density of gas is constant at all points of the container.

2) Avogadro's law: Equal volume of all the gases under similar conditions of temperature and pressure contain equal number of molecules *i.e.* $N_1 = N_2$.

3) Graham's law of diffusion: When two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas *i.e.* $r \propto \frac{1}{\sqrt{\rho}} \propto \frac{1}{\sqrt{M}}$ (M is the molecular weight of the gas) $\Rightarrow \frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}}$

If V is the volume of gas diffused in t *sec* then

$$r = \frac{V}{t} \Rightarrow \frac{r_1}{r_2} = \frac{V_1}{V_2} \times \frac{t_2}{t_1}$$

4) Dalton's law of partial pressure: The total pressure exerted by a mixture of non-reacting gases occupying a vessel is equal to the sum of the individual pressures which each gases exert if it alone occupied the same volume at a given temperature.

For n gases $P = P_1 + P_2 + P_3 + \ldots\ldots P_n$

Where P = Pressure exerted by mixture and $P_1, P_2, P_3, \ldots\ldots P_n =$ Partial pressure of component gases.

5) Vander Waal's gas equations

For 1 *mole* of gas $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

For μ *moles* of gas $\left(P + \frac{a\mu^2}{V^2}\right)(V - \mu b) = \mu RT$

Here a and b are constant called Vander Waal's constant

Dimension: $[a] = [ML^5T^{-2}]$ and $[b] = [L^3]$

Units: $a = N \times m^4$ and $b = m^3$.

6) Pressure of an Ideal Gas

Pressure exerted by an ideal gas $P = \frac{1}{3} mn\overline{v}^2$ where m is the mass of each molecule, n is the number molecules per unit volume and $\overline{v}^2$ is the mean square velocity of gas molecules. Here $\overline{v}^2 = \overline{v}_x^2 + \overline{v}_y^2 + \overline{v}_z^2$ where $\overline{v}_x^2, \overline{v}_y^2$ *and* $\overline{v}_z^2$ are mean square velocity components along x, y and z directions.

$P = \frac{1}{3} m \frac{N}{V} \overline{v}^2$ Where N is the total number of molecules in the average of volume V

$$\overline{v}^2 = \frac{v_1^2 + v_2^2 + v_3^3 + --- \overline{v}^2_n}{N}$$

$mn = m\frac{N}{V} = \rho$ is the density of the gas

$$\therefore P = \frac{1}{3} \rho \overline{v}^2$$

7) Various Speeds of Gas Molecules

The motion of molecules in a gas is characterized by any of the following three speeds.

(1) **Root mean square speed:** It is defined as the square root of mean of squares of the speed of different molecules

i.e. $v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + ...}{N}} = \sqrt{\overline{v^2}}$

(i) From the expression of pressure $P = \frac{1}{3} \rho v_{rms}^2$

$$\Rightarrow v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3PV}{\text{Mass of gas}}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

where $\rho = \frac{\text{Mass of gas}}{V}$ = Density of the gas, $M = \mu \times$(mass of gas), $pV = \mu RT$, $R = kN_A$, k = Boltzmann's constant,

$m = \frac{M}{N_A}$ = mass of each molecule.

(ii) With rise in temperature *rms* speed of gas molecules increases as $v_{rms} \propto \sqrt{T}$.

(iii) With increase in molecular weight *rms* speed of gas molecule decreases as $v_{rms} \propto \frac{1}{\sqrt{M}}$. *e.g.*, *rms* speed of hydrogen molecules is four times that of oxygen molecules at the same temperature.

(iv) *rms* speed of gas molecules is of the order of *km/s* *e.g.*, at NTP for hydrogen gas

$$(v_{rms}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times 8.31\times 273}{2\times 10^{3}}} = 1840\ m/s.$$

(v) *rms* speed of gas molecules is $\sqrt{\frac{3}{\gamma}}$ times that of speed of sound in gas, as

$$v_{rms} = \sqrt{\frac{3RT}{M}} \quad \text{and} \quad v_s = \sqrt{\frac{\gamma RT}{M}} \Rightarrow \quad v_{rms} = \sqrt{\frac{3}{\gamma}}v_s$$

(vi) *rms* speed of gas molecules does not depends on the pressure of gas (if temperature remains constant) because $P \propto \rho$ (Boyle's law) if pressure is increased n times then density will also increases by n times but v_{rms} remains constant.

(vii) Moon has no atmosphere because v_{rms} of gas molecules is more than escape velocity (v_e).

A planet or satellite will have atmosphere only if $v_{rms} < v_e$

(viii) At $T = 0$; $v_{rms} = 0$ *i.e.* the *rms* speed of molecules of a gas is zero at 0 *K*. This temperature is called absolute zero.

(2) **Most probable speed:** The particles of a gas have a range of speeds. This is defined as the speed which is possessed by maximum fraction of total number of molecules of the gas.

Most probable speed $v_{mp} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$

(3) **Average speed:** It is the arithmetic mean of the speeds of molecules in a gas at given temperature.

$$v_{av} = \frac{v_1 + v_2 + v_3 + v_4 + ...}{N}$$

Average speed $v_{av} = \sqrt{\frac{8P}{\pi\rho}} = \sqrt{\frac{8}{\pi}\frac{RT}{M}} = \sqrt{\frac{8}{\pi}\frac{kT}{m}}$

8) Mean Free Path.

(1) The distance travelled by a gas molecule between two successive collisions is known as free path.

$$\lambda = \frac{\text{Total distance travelled by a gas molecule between successive collisions}}{\text{Total number of collisions}}$$

During two successive collisions, a molecule of a gas moves in a straight line with constant velocity and Let $\lambda_1, \lambda_2, \lambda_3 .....$ be the distance travelled by a gas molecule during n collisions respectively, and then the mean free path of a gas molecule is given by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + ... + \lambda_n}{n}$$

(2) $\lambda = \frac{1}{\sqrt{2}\pi n d^2}$

Where d = Diameter of the molecule,

n = Number of molecules per unit volume

(3) As $PV = \mu RT = \mu NkT \Rightarrow \frac{N}{V} = \frac{P}{kT} = n =$ Number of molecule per unit volume so $\lambda = \frac{1}{\sqrt{2}} \frac{kT}{\pi d^2 P}$.

(4) From $\lambda = \frac{1}{\sqrt{2}\pi n d^2} = \frac{m}{\sqrt{2}\pi(mn)d^2} = \frac{m}{\sqrt{2}\pi d^2 \rho}$

[As m = Mass each molecule, mn = Mass per unit volume = Density = ρ]

(5) If average speed of molecule is v then $\lambda = v \times \frac{t}{N} = v \times T$

[As N = Number of collision in time t, T = time interval between two collisions].

(i) As $\lambda \propto \frac{1}{\rho}$ and $\lambda \propto m$ *i.e.* the mean free path is inversely proportional to the density of a gas and directly proportional to the mass of each molecule.

(ii) As $\lambda = \frac{1}{\sqrt{2}} \frac{kT}{\pi d^2 P}$. For constant volume and hence constant number density n of gas molecules, $\frac{P}{T}$ is constant so that λ will not depend on P and T. But if volume of given mass of a gas is allowed to change with P or T then $\lambda \propto T$ at constant pressure and $\lambda \propto \frac{1}{P}$ at constant temperature.

9. Degrees of freedom

The total number of independent ways in which a system can possess energy is called the degree of freedom (*f*).

a) Mono-atomic gas: Molecule of mono-atomic gas can have three independent motions and hence 3 degrees of freedom (all translational).

b) Diatomic gas: Molecule of diatomic gas has 5 degree of freedom.3 translational and 2 rotational.

c) Tri-atomic gas: A non-linear molecule can rotate about any of three co-ordinate axes. Hence it has 6 degrees of freedom: 3 translational and 3 rotational.