

Kinetic Theory of Gases & Radiation

- **Kinetic Theory of Matter:-**

- (a) **Solids:-** It is the type of matter which has got fixed shape and volume. The force of attraction between any two molecules of a solid is very large.

- (b) **Liquids:-** It is the type of matter which has got fixed volume but no fixed shape. Force of attraction between any two molecules is not that large as in case of solids.

- (c) **Gases:-** It is the type of matter does not have any fixed shape or any fixed volume.

- **Ideal Gas:-** A ideal gas is one which has a zero size of molecule and zero force of interaction between its molecules.

- **Ideal Gas Equation:-** A relation between the pressure, volume and temperature of an ideal gas is called ideal gas equation.

$$PV/T = \text{Constant} \text{ or } PV = nRT$$

Here, n is the number of moles and R is the universal gas constant.

- **Gas Constant:-**

- (a) **Universal gas constant (R):-**

$$\begin{aligned} R &= P_0 V_0 / T_0 \\ &= 8.311 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

- (b) **Specific gas constant (r):-**

$$\begin{aligned} PV &= (R/M) T = rT, \\ \text{Here, } r &= R/M \end{aligned}$$

- **Real Gas:-** The gases which show deviation from the ideal gas behavior are called real gas.

- **Vander wall's equation of state for a real gas:-**

$$[P + (na/V)^2][V - nb] = nRT$$

Here n is the number of moles of gas.

- **Avogadro's number (N):-** Avogadro's number (N), is the number of carbon atoms contained in 12 gram of carbon-12.

$$N = 6.023 \times 10^{23}$$

- (a) **To calculate the mass of an atom/molecule:-**

Mass of one atom = atomic weight (in gram)/ N

Mass of one molecule = molecular weight (in gram)/ N

- (b) **To calculate the number of atoms/molecules in a certain amount of substance:-**

Number of atoms in m gram = $(N/\text{atomic weight}) \times m$

Number of molecules in m gram = $(N/\text{molecular weight}) \times m$

(c) Size of an atom:-

Volume of the atom, $V = (4/3)\pi r^3$

Mass of the atom, $m = A/N$

Here, A is the atomic weight and N is the Avogadro's number.

Radius, $r = [3A/4\pi N\rho]^{1/3}$

Here ρ is the density.

• **Gas laws:-**

(a) Boyle's law:- It states that the volume of a given amount of gas varies inversely as its pressure, provided its temperature is kept constant.

$PV = \text{Constant}$

(b) Charlers law or Gey Lussac's law:- It states that volume of a given mass of a gas varies directly as its absolute temperature, provided its pressure is kept constant.

$V/T = \text{Constant}$

$V - V_0/V_0t = 1/273 = \gamma_p$

Here $\gamma_p (=1/273)$ is called volume coefficient of gas at constant pressure.

Volume coefficient of a gas, at constant pressure, is defined as the change in volume per unit volume per degree centigrade rise of temperature.

(c) Gay Lussac's law of pressure:- It states that pressure of a given mass of a gas varies directly as its absolute temperature provided the volume of the gas is kept constant.

$P/T = P_0/T_0$ or $P - P_0/P_0t = 1/273 = \gamma_p$

Here $\gamma_p (=1/273)$ is called pressure coefficient of the gas at constant volume.

Pressure coefficient of a gas, at constant volume, is defined as the change in pressure per unit pressure per degree centigrade rise of temperature.

(d) Dalton's law of partial pressures:-

Partial pressure of a gas or of saturated vapors is the pressure which it would exert if contained alone in the entire confined given space.

$P = p_1 + p_2 + p_3 + \dots$

$nRT/V = p_1 + p_2 + p_3 + \dots$

(e) Graham's law of diffusion:- Graham's law of diffusion states that the rate of diffusion of gases varies inversely as the square root of the density of gases.

$R \propto 1/\sqrt{\rho}$ or $R_1/R_2 = \sqrt{\rho_2/\rho_1}$

So, a lighter gas gets diffused quickly.

(f) Avogadro's law:- It states that under similar conditions of pressure and temperature, equal volume of all gases contain equal number of molecules.

For m gram of gas, $PV/T = nR = (m/M) R$

• **Pressure of a gas (P):-** $P = 1/3 (M/V) C^2 = 1/3 (\rho) C^2$

• **Root mean square (r.m.s) velocity of the gas:-** Root mean square velocity of a gas is the square root of the mean of the squares of the velocities of individual molecules.

$C = \sqrt{[c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2]/n} = \sqrt{3P/\rho}$

- **Pressure in terms of kinetic energy per unit volume:-** The pressure of a gas is equal to two-third of kinetic energy per unit volume of the gas.

$$P = \frac{2}{3} E$$

- **Kinetic interpretation of temperature:-** Root mean square velocity of the molecules of a gas is proportional to the square root of its absolute temperature.

$$C = \sqrt{3RT/M}$$

Root mean square velocity of the molecules of a gas is proportional to the square root of its absolute temperature.

$$\text{At, } T=0, C=0$$

Thus, absolute zero is the temperature at which all molecular motion ceases.

- **Kinetic energy per mole of gas:-**

$$\text{K.E. per gram mol of gas} = \frac{1}{2} MC^2 = \frac{3}{2} RT$$

- **Kinetic energy per gram of gas:-**

$$\frac{1}{2} C^2 = \frac{3}{2} r t$$

Here, $\frac{1}{2} C^2$ = kinetic energy per gram of the gas and r = gas constant for one gram of gas.

- **Kinetic energy per molecule of the gas:-**

$$\text{Kinetic energy per molecule} = \frac{1}{2} mC^2 = \frac{3}{2} kT$$

Here, k (Boltzmann constant) = R/N

Thus, K.E per molecule is independent of the mass of molecule. It only depends upon the absolute temperature of the gas.

- **Regnault's law:-** $P \propto T$

- **Graham's law of diffusion:-**

$$R_1/R_2 = C_1/C_2 = \sqrt{\rho_2/\rho_1}$$

- **Distribution of molecular speeds:-**

(a) **Number of molecules of gas possessing velocities between v and $v+dv$:-**

$$n_v dv = \frac{\sqrt{2\pi n m^3} v^2}{(\pi kT)^{3/2}} e^{-mv^2/2kT} dv$$

(b) **Number of molecules of gas possessing energy between u and $u+du$:-**

$$n_u du = \frac{2\pi n}{(\pi kT)^{3/2}} \sqrt{u} e^{-u/kT} du$$

(c) **Number of molecules of gas possessing momentum between p and $p+dp$:-**

$$n_p dp = \frac{\sqrt{2\pi n}}{(\pi m kT)^{3/2}} p^2 e^{-p^2/2mkT} dp$$

(d) Most probable speed:- It is the speed, possessed by the maximum number of molecules of a gas contained in an enclosure.

$$V_m = \sqrt{2kT/m}$$

(e) Average speed (V_{av}):- Average speed of the molecules of a gas is the arithmetic mean so the speeds of all the molecules.

$$V_{av} = \sqrt{8kT/\pi m}$$

(f) Root mean square speed (V_{rms}):- It is the square root of the mean of the squares of the individual speeds of the molecules of a gas.

$$V_{rms} = \sqrt{3kT/m}$$

- $V_{rms} > V_{av} > V_m$

- **Degree of Freedom (n):-** Degree of freedom, of a mechanical system, is defined as the number of possible independent ways, in which the position and configuration of the system may change. In general, if N is the number of particles, not connected to each other, the degrees of freedom n of such a system will be, $n = 3N$

If K is the number of constraints (restrictions), degree of freedom n of the system will be, $n = 3N - K$

- **Degree of freedom of a gas molecule:-**

(a) Mono-atomic gas:- Degree of freedom of monoatomic molecule, $n = 3$

(b) Di-atomic gas:-

At very low temperature (0-250 K):- Degree of freedom, $n = 3$

At medium temperature (250 K – 750 K):- Degree of freedom, $n = 5$ (Translational = 3, Rotational = 2)

At high temperature (Beyond 750 K):- Degree of freedom, $n = 6$ (Translational = 3, Rotational = 2, Vibratory = 1), For calculation purposes, $n = 7$

- **Law of equipartition of energy:-** In any dynamical system, in thermal equilibrium, the total energy is divided equally among all the degrees of freedom and energy per molecule per degree of freedom is $\frac{1}{2} kT$.

$$E = \frac{1}{2} kT$$

- **Mean Energy:-** K.E of one mole of gas is known as mean energy or internal energy of the gas and is denoted by U .

$$U = \frac{n}{2} RT \quad (\text{Here } n \text{ is the degree of freedom of the gas.})$$

(a) Mono-atomic gas ($n = 3$):- $U = \frac{3}{2} RT$

(b) Diatomic gas:-

At low temperature ($n=3$):- $U = \frac{3}{2} RT$

At medium temperature ($n=5$):- $U = \frac{5}{2} RT$

At high temperature ($n=7$):- $U = \frac{7}{2} RT$

- **Relation between ratio of specific heat capacities (γ) and degree of freedom (n):-**

$$\gamma = C_p/C_v = [1 + (2/n)]$$

(a) For mono-atomic gas ($n=3$):- $\gamma = [1 + (2/n)] = 1 + (2/3) = 5/3 = 1.67$

(b) For diatomic gas (at medium temperatures ($n=5$)):- $\gamma = [1 + (2/5)] = 1 + (2/5) = 7/5 = 1.4$

(c) For diatomic gas (at high temperatures ($n=7$)):- $\gamma = [1 + (2/7)] = 9/7 = 1.29$