Maxwell Boltzman law of distribution of Molecular Velocities:

Maxwell and Boltzman using probability Consideration . They have shown that the distribution of molecular velocities depends on the temperature and molecular weight of a gas and is given by the expression,

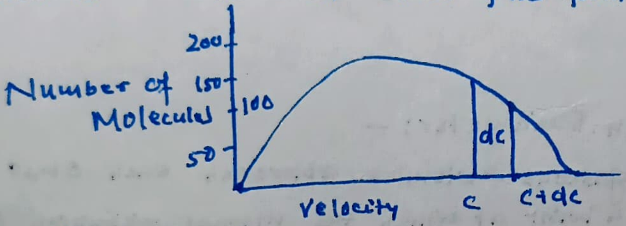
$$\frac{dn_c}{n} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mc^2}{2RT}} c^2 . dc$$

where dn_c is the number of molecules out of the total number of n molecules which have velocities between c and c+dc, T is is Temperature and M is the molecular wt of the gas. The ratio $\frac{dn_c}{n}$ gives therefore the fraction of the total number of molecules having velocities between c and c+dc

Dividing both side the above eq^n by dc, we get.

$$\frac{1}{n} \cdot \frac{dn_c}{dc} = 4\pi \left(\frac{M}{2\pi Rr}\right)^{3/2} e^{-\frac{Mc^2}{2RT}} c^2$$

The L.H.S. expression gives the probability of finding the molecules with the velocity c . If Now the fraction of the total number of molecules for any gas of known molecular wt. at any particular temperature is plotted against the velocities, a distribution Curve of the form shown in figure is obtained



The Curve shows that the fraction of molecules having Velocities between c to c+dc is given by the area under the Strip of the Curve within the velocity range. The area between two Cordinates seperated by dc is Clearly equal to $\frac{dn_c}{n}$, hence the area under the whole curve is equal to the total number of molecules and the hight of ordinate corresponds to any Velocity is Virtually a measure of the fraction of the molecules which have the Velocity.

The shape of the curve says that the fraction of molecules having too low or too high Velocities is very small and the majority of the gas molecules have some intermediate Velocity with a small range of Variation more or less around the Peak, known as the most probable Velocity.

(A) Mean Free Path: —

Gas molecules are always in state of rapid motion Colliding with each other. The distance travelled by a gas molecule before Colliding with another molecule is called Free Path, and the average length of a large number of such Path is Called Mean free Path and it is denoted by Symbol 'l'.

The expression of Mean free Path is given as follows

$$l = \frac{1}{\sqrt{2\pi\sigma^2 N}}$$

where N = Number of Molecules per Cubic Metre of the gas

σ = Molecular Diameter in Metres

(B) Collision Diameter: —

When two gaseous molecules approach each other by Continue moving till a point at which the mutual repulsion is so great that they have to retrace their paths.

The distance between Centres of two such molecules at the Point of the Closest approach is called Collision diameter. The Collision diameter is denoted by Sigma 'σ'!

(C) **Collision Frequency**:- It is denoted by N_c. The number of Collisio suffered by gas molecules per sec. per Cubic metre of a gas is Called Collision frequency of the gas. It is given by following expression:-

$$N_c = \frac{1}{\sqrt{2}}\pi v \sigma^2 N^2 = 2\sigma^2 N^2 \sqrt{\frac{\pi RT}{M}}$$

where v is the average molecular velocity in metre sec^{-1}. N is the number of molecules per Cubic metre of the gas.
σ is the molecular diameter in Metres.

At a particular temperature, distance travelled by a molecule between two Successive Collision depends upon the Pressur of the gas.

When the temperature is very high, the molecules are Comparatively near to each other and mutual Collisions are larger as Compared to those at low pressure, then the mean free path (i expressed as

$$l = \frac{c}{N_c} \quad \text{Where } C = \text{Velocity of molecule.}$$

On the basis of Kinetic gas equation find the Expression of velocities in terms of
(a) Pressure and Temp.
(b) Temperature
(c) Pressure and density

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Expression of velocities C (On the basis of Kinetic gas Equation) when
(i) Pressure and Temperature is given
(ii) When temp. is given
(iii) When Pressure and density is given.

(a) Pressure and Temperature is given

K. gas eqn; $PV = \frac{1}{3} mnc^2$

$PV = \frac{1}{3} M c^2$ $[M = mn]$

or $Mc^2 = 3PV$

$M c^2 = 3PV/M$

$C = \sqrt{\frac{3PV}{M}}$ or $C = \left(\frac{3PV}{M}\right)^{1/2}$

$$C = \sqrt{\frac{3PV}{M}}$$

(b) When Temperature is only given

We know, ideal gas equation

$PV = RT$ (For 1 mole of gas, i.e $n=1$) —①

According to Kinetic gas equation

$PV = \frac{1}{3} mnc^2$

from eqn (i), $RT = \frac{1}{3} Mc^2$ $[\because M = mn]$

$Mc^2 = 3RT$

$c^2 = \frac{3RT}{M}$ or, $C = \left(\frac{3RT}{M}\right)^{1/2}$

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

(c) When Pressure and density is given :-

We know, $\frac{1}{3} Mc^2 = PV$ $(\because M = mn)$

or $Mc^2 = 3PV$

$c^2 = \frac{3PV}{M} = \frac{3P}{M/V} = \frac{3P}{D}$ $(\because D=$

$c^2 = \frac{3P}{D}$

$$C = \sqrt{\frac{3P}{D}}$$

Define (i) Root mean Square (r.m.s) velocity (ii) Average Veloc.. (iii) Most Probable Velocity.

(1) Root mean square velocity :- R.m.s or root mean square velocity is the square root or root of the mean of squares of velocities of all gas molecules present in the gas.

$$C_{r.m.s} = \sqrt{\frac{n_1u_1^2 + n_2u_2^2 + + \cdots}{n_1 + n_2 + \cdots}}$$

or

$$C_{r.m.s} = \sqrt{\frac{C_1^2 + C_2^2 + \cdots C_n^2}{n}}$$

From Kinetic gas equation, we know $PV = \frac{1}{3}mnc^2$ $[\because mn = M]$

or $PV = \frac{1}{3}Mc^2$

$$Mc^2 = 3PV$$

$$c^2 = \frac{3PV}{M} = \frac{3P}{D} = \frac{3RT}{M}$$

$$\text{Or, } C_{r.m.s.} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{D}} = \sqrt{\frac{3RT}{M}}$$

(2) Average Velocity :- Let us suppose there are $n_1, n_2, \cdots$ molecules possessing velocities $u_1, u_2, u_3 \cdots$ respectively.

The average velocity is given by

$$\text{Average Velocity} = \frac{n_1u_1 + n_2u_2 + \cdots}{n_1 + n_2 + \cdots}$$

Or, Average velocity 'C_a' is the arithmetic mean of Velocit of all gas molecules present in a gas.

If the individual velocities of n gas mole present in gas is $C_1, C_2, \cdots C_n$, then the average velocit of the gas is given by

$$C_a = \frac{C_1 + C_2 + C_3 + \cdots + C_n}{n}$$

From Maxwell distribution of molecular velocities,
We know

$$C_a = \sqrt{\frac{8RT}{\pi M}} \quad \text{or, } C_{Ave} = \sqrt{\frac{8}{3\pi}} \times \sqrt{\frac{3RT}{M}} = \sqrt{\frac{8}{3\pi}} \cdot C_{r.ms}$$

$= 0.9213$ r.m veloc

(3) Most Probable Velocities :- Most probable velocity C_{mp} is defined as the velocity possessed by the maximum number of gas molecules present in the gas at a particular temperature

According to Maxwell the expression for most probable velocity is given as $C_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 3RT}{3\,M}} = \sqrt{\frac{2}{3}}$ r.m.s velocity

$= 0.816$ r.m.s. velocity

Establish relation between
Average, r.m.s and most Probable Velocities.

We know By the Maxwell's distribution law of molecular velocities

Average velocity, $C_{av} = \sqrt{\frac{8RT}{\pi M}} = \left(\frac{8RT}{\pi M}\right)^{1/2}$

R.M.S. velocity, $C_{r.m.s} = \sqrt{\frac{3RT}{M}} = \left(\frac{3RT}{M}\right)^{1/2}$

Most Probable velocity $C_{mp} = \sqrt{\frac{2RT}{M}} = \left(\frac{2RT}{M}\right)^{1/2}$

The relation among the above molecular velocities are as follows.

$$C_p : C_{av.} : C_{r.m.s} = \left(\frac{2RT}{M}\right)^{1/2} : \left(\frac{8RT}{\pi M}\right)^{1/2} : \left(\frac{3RT}{M}\right)^{1/2}$$

On dividing R.H.S by $\left(\frac{2RT}{M}\right)^{1/2}$

we get

$$C_p : C_{av} : C_{r.mp} = 1 : \frac{2}{\sqrt{\pi}} : \sqrt{\frac{3}{2}}$$

$$C_{mp} : C_{av} : C_{r.m.p} = 1 : 1.218 : 1.224$$