

The Kinetic theory of matter rests upon two fundamental hypotheses — (a) The molecular constitution of matter,  
(b) The identification of heat with the motion of molecules.

The Kinetic theory was mainly developed from a mathematical standpoint in the absence of any direct experimental proof of the existence of molecules or their motions. Gradually much evidence accumulated in favour of the existence of molecular motion, the most important one being the 'Brownian movement', discovered by the botanist Robert Brown.

#### ▣ Evidences in favour of molecular motion :-

- (i) Diffusion and solution.
- (ii) Expansion of Gases.
- (iii) Phenomena of evaporation and Vapour Pressure.
- (iv) Brownian Movement.

#### ▣ Assumption of Kinetic Theory of Gas :-

To develop the Kinetic theory of gases, the idealised assumptions are:—

- (i) A gas consists of a large number of identical

molecules which are rigid, elastic sphere constantly moving about all possible directions with different velocities in a random fashion.

(ii) During the motion, the molecules collide with one another and also with the walls of the container. The collisions are perfectly elastic.

(iii) Between two successive collisions the molecules move in straight lines with uniform velocity.

(iv) The collisions are instantaneous, that is the duration of a collision is insignificant compared to the time between collisions.

(v) The actual volume occupied by them is negligible compared to the total volume of the gas.

### ▣ Deduction of Perfect Gas Equation :-

Consider a perfect gas enclosed in a container such that one of its surface is perpendicular to the  $x$  axis.

Now any velocity  $c$  of a particle in space can be resolved into components  $u, v, w$  along the three axes such that

$$c^2 = u^2 + v^2 + w^2$$

the limits of  $u, v$  and  $w$  are from  $-\infty$  to  $+\infty$ , those of  $c$  from 0 to  $\infty$ .

Now,  $u$  suffers a change in direction on reflection from the wall  $BAE$ . (But  $v$  &  $w$  remain unchanged).

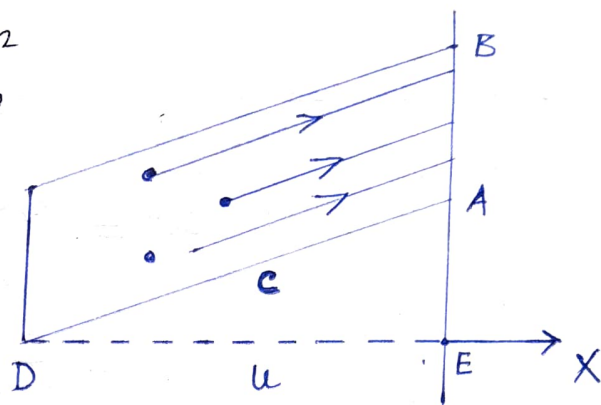


Fig-  $BAE$  surface perpendicular to  $x$  axis.

$\therefore$  The change in momentum per reflection of a molecule is  $mu - (-mu) = 2mu$

If  $n_u$  be the number of molecules per unit volume moving with velocity  $u$ , the numbers striking unit area of the wall in time  $dt$  would be contained in a cylinder of cross-sectional area unity and vertical height  $u dt$ .

$\therefore$  Volume of the cylinder =  $u dt$ .

Number of molecules in the cylinder =  $n_u u dt$

$\therefore$  change in momentum by the above molecules in time  $dt$  is

$$2mu \times n_u u dt = 2m n_u u^2 dt$$

$\therefore$  Total change in momentum per unit area

$$dp = 2m \sum_{u=0}^{\infty} n_u u^2 dt$$

$$\therefore \delta \vec{F} \cdot dt = 2m \sum_{u=0}^{\infty} n_u u^2 dt$$

$$\Rightarrow \delta \vec{F} = 2m \sum_{u=0}^{\infty} n_u u^2$$

Since the area involved is unity, then  $\delta \vec{F} = \vec{p}$

$$\therefore p = 2m \sum_{u=0}^{\infty} n_u u^2$$

Let,  $\overline{u^2}$  be the mean square velocity along x, then we can write,

$$\begin{aligned}\overline{u^2} &= \frac{n_1 u_1^2 + n_2 u_2^2 + \dots + n_m u_m^2 + \dots}{n_1 + n_2 + \dots + n_m + \dots} \\ &= \frac{\sum n_i u_i^2}{\sum n_i} \\ &= \frac{\sum n_i u_i^2}{n/2}\end{aligned}$$

[ $\sum n_i = n/2$  because only the molecules in the positive x direction are being considered]

$$\therefore \sum_0^{\infty} n_u u^2 = \frac{1}{2} n \overline{u^2}$$

[ $n$  = Total no. of molecules per unit volume]

$$\therefore P_x = 2m \times \frac{1}{2} n \overline{u^2} = m n \overline{u^2}$$

$$P_y = m n \overline{v^2}$$

$$P_z = m n \overline{w^2}$$

$\therefore$  The expression for the pressure is

$$P = P_x = P_y = P_z = m n \overline{u^2} = m n \overline{v^2} = m n \overline{w^2}$$

$$\text{But, } \overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3} \overline{c^2}$$

$$\therefore P = \frac{1}{3} m n \overline{c^2}$$

$$= \frac{1}{3} m n c_{rms}^2$$

where,

$\overline{c^2}$  = mean square velocity of the molecules.

$c_{rms} = \sqrt{\overline{c^2}}$ , is the r.m.s. or root mean square velocity of the molecules.

The expression can be written as

$$p = \frac{1}{3} \rho c_{rms}^2$$

[ $\rho = mn =$  density of the gas]

### ▣ Deductions from Pressure Expressions:-

#### 1. R.M.S. Velocity:-

The pressure  $p$  is given by -

$$p = \frac{1}{3} \rho c_{rms}^2$$

$$\Rightarrow c_{rms} = \sqrt{\frac{3p}{\rho}}$$

Now, let for one mole of gas,  $\rho = \frac{M}{V}$ , where  $M$  is molecular weight and  $V$  is volume occupied by one mole of gas,

$$\therefore p = \frac{1}{3} \frac{M}{V} c_{rms}^2$$

$$\text{on, } pV = \frac{1}{3} M c_{rms}^2 = RT \quad [\text{as for 1 mole } pV = RT]$$

$$\therefore c_{rms} = \sqrt{\frac{3pV}{M}} = \sqrt{\frac{3RT}{M}}$$

\* From the above equation,  $c_{rms}^2 \propto T$

#### 2. Pressure and Kinetic Energy:-

$$p = \frac{1}{3} \rho c_{rms}^2$$

$$= \frac{2}{3} \times \frac{1}{2} \rho c_{rms}^2$$

$$= \frac{2}{3} E_m$$

$$\therefore p = \frac{2}{3} E_m$$

[ $E_m = \frac{1}{2} \rho c_{rms}^2 =$  mean K.E. of gas molecules per unit volume]

The above equation gives the relationship between molecular quantities and the value of the pressure that characterise a gas as a whole. So it is a fundamental equation of the kinetic theory.

### 3. Boyle's Law :-

Pressure Expression -

$$p = \frac{1}{3} \rho c_{rms}^2$$

If  $M'$  be the mass of a gas that occupies a volume  $V$ ,  $\rho = M'/V$ .

$$\therefore p = \frac{1}{3} \frac{M'}{V} c_{rms}^2$$

$$\Rightarrow pV = \frac{1}{3} M' c_{rms}^2$$

Now at constant temperature  $T$ ,  $c_{rms}^2$  is a constant  
or,  $c_{rms}^2 \propto T$ .

$$\therefore pV = \text{constant}$$

which is Boyle's Law.

### 4. Charles' Law :-

From the above treatment, we can write -

$$pV = \frac{1}{3} M' c_{rms}^2$$

$$\therefore pV \propto c_{rms}^2 \text{ and } c_{rms}^2 \propto T$$

$$\therefore pV \propto T$$

$$\text{or, } \boxed{\frac{V}{T} = \text{constant}}, \text{ at constant pressure (p)}$$

It is well known expression of Charles' Law.

▣ Show that no. of molecules per unit volume of an ideal gas is given by,  $n = \frac{PN}{RT}$ .

$$\begin{aligned} \Rightarrow \text{From Pressure expression, } p &= \frac{1}{3} m n c_{rms}^2 \\ &= \frac{1}{3} \frac{m}{N_A} \cdot m N_A c_{rms}^2 \end{aligned}$$

$$= \frac{1}{3} \frac{n}{N_A} \cdot M \cdot \frac{3RT}{M}$$

$$= \frac{nRT}{N_A}$$

$$\therefore p = \frac{nRT}{N_A}$$

$$\text{or, } \boxed{\eta = \frac{p N_A}{RT}}$$

$$\left[ \begin{array}{l} \text{as, } m N_A = M, \text{ molecular} \\ \text{weight.} \\ C_{rms} = \sqrt{\frac{3RT}{M}}, \text{ for} \\ \text{ideal gas} \end{array} \right.$$

$$N_A = \text{Avogadro Number} \\ = 6.02 \times 10^{23} \text{ per mole.}$$

## 5. Clapeyron's equation:-

From the above expression -

$$p = \frac{nRT}{N_A}$$

$$\text{or, } p = \eta \cdot \left(\frac{R}{N_A}\right) T$$

$$\text{or, } \boxed{p = \eta K T}$$

$$\text{where, } \frac{R}{N_A} = K = \text{Boltzmann Constant} = 1.38 \times 10^{-23} \text{ J/K}$$

## ▣ Introduction to Temperature:-

$$C_{rms}^2 = \frac{3RT}{M}$$

From above equation,  $C_{rms}^2$  is proportional to absolute temperature. But mean K.E. of translation is proportional to  $C_{rms}^2$ .

So we may consider, mean K.E. of translation manifest itself as the temperature of the gas. This is the Kinetic interpretation of temperature.

$$\text{again, } C_{rms}^2 = \frac{3RT}{M}$$

$$\Rightarrow \frac{1}{2} M C_{rms}^2 = \frac{3}{2} RT$$

$$\Rightarrow \frac{1}{2} \frac{M C_{rms}^2}{N_A} = \frac{3}{2} \frac{R}{N_A} T$$

[ Dividing both side by  $N_A$  ]

$$\Rightarrow \boxed{\frac{1}{2} m C_{rms}^2 = \frac{3}{2} K T}$$

### ▣ Average or Mean Speed:

Let,  $n_1$  molecules have speed  $c_1$ ,  $n_2$  have speed  $c_2$  and so on.  
So by definition, the average or mean speed  $\bar{c}$  is given by -

$$\bar{c} = \frac{n_1 c_1 + n_2 c_2 + n_3 c_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i c_i}{\sum n_i}$$
$$= \frac{\int_0^\infty c dN_c}{\int_0^\infty dN_c} = \frac{1}{N} \int_0^\infty c dN_c$$

$$\therefore \bar{c} = \frac{1}{N} \int_0^\infty c (4\pi N A^3 e^{-bc^2} c^2 dc)$$

$$= \frac{4\pi N A^3}{N} \int_0^\infty e^{-bc^2} c^3 dc \quad \left[ \because dN_c = 4\pi N A^3 e^{-bc^2} c^2 dc \right]$$

$$= 4\pi A^3 \int_0^\infty e^{-z} \cdot \frac{z}{b} \cdot \frac{dz}{2b}$$

$$= \frac{4\pi A^3}{2b^2} \int_0^\infty e^{-z} \cdot z dz$$

$$= \frac{4\pi A^3}{2b^2} \Gamma_2$$

$$= \frac{4\pi A^3}{2b^2}$$

$$\left[ \because \Gamma_2 = 1! = 1 \right]$$

$$= \frac{2\pi (m/2\pi K T)^{3/2}}{(m/2K T)^2} = \sqrt{\frac{8KT}{\pi m}}$$

$$\boxed{\bar{c} = \sqrt{\frac{8KT}{\pi m}}}$$

### ▣ R.M.S. speed:-

The r.m.s or root mean square speed  $c$  is defined



or  $c = \sqrt{\bar{c}^2}$ , where  $\bar{c}^2 =$  the mean square velocity.

$$\bar{c}^2 = \frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i c_i^2}{\sum n_i}$$

$$\therefore \bar{c}^2 = \frac{1}{N} \int_0^\infty c^2 dN_c \quad [\because \sum n_i = N]$$

$$= \frac{4\pi N A^3}{N} \int_0^\infty c^4 e^{-bc^2} dc \quad [\because dN_c = 4\pi N A^3 e^{-bc^2} c^2 dc]$$

$$= 4\pi A^3 \int_0^\infty c^4 e^{-bc^2} dc$$

$$= 4\pi A^3 \cdot \frac{1}{2b^{5/2}} \cdot \Gamma(5/2)$$

$$= 4\pi A^3 \cdot \frac{1}{2b^{5/2}} \cdot \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi} \quad \left[ \because \Gamma(5/2) = \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi} \right]$$

$$= \frac{3\pi^{3/2} \cdot (m/2\pi kT)^{3/2}}{2 \cdot (m/2kT)^{5/2}}$$

[substituting the values of A and b]

$$= \frac{3kT}{m}$$

$$\therefore \text{R.M.S. speed, } c = \sqrt{\bar{c}^2} = \sqrt{\frac{3kT}{m}}$$

### Most Probable speed:

Maxwell's speed distribution law -

$$dN_c = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} c^2 dc$$

$$\text{or, } \frac{dN_c}{N} = 4\pi A^3 e^{-bc^2} c^2 dc$$

$$\text{or, } \frac{dN_c}{N} = F dc$$

$$\therefore F = 4\pi A^3 e^{-bc^2} c^2$$

The value of  $c$  for which  $F$  is maximum is the most

probable velocity ( $c_m$ ).

$$\therefore \frac{dF}{dc} = 8\pi A^3 c e^{-bc^2} - 8\pi A^3 bc^3 e^{-bc^2}$$

Now,  $\frac{dF}{dc} = 0$ , for maximum or minimum for  $c = c_m$ .

$$\therefore 8\pi A^3 c_m e^{-bc_m^2} = 8\pi A^3 bc_m^3 e^{-bc_m^2}$$

$$\text{or, } c_m^2 = \frac{1}{b}$$

$$\text{or, } c_m = \sqrt{\frac{1}{b}} = \sqrt{\frac{2KT}{m}}$$

$$\therefore c_m = \sqrt{\frac{2KT}{m}}$$

[\*  $\frac{d^2F}{dc^2}$  appears negative at the  $c_m$  value. So  $c_m$  corresponds to maximum  $F$ .]

### Ratio of the three speeds :-

The ratio of the average, r.m.s and most probable velocities at a given temperature -

$$\begin{aligned} \bar{c} : c_{rms} : c_m &= \sqrt{\frac{8KT}{\pi m}} : \sqrt{\frac{3KT}{m}} : \sqrt{\frac{2KT}{m}} \\ &= \sqrt{\frac{8}{\pi}} : \sqrt{3} : \sqrt{2} \end{aligned}$$

The ratio of the speeds in ascending orders

$$c_m : \bar{c} : c_{rms} = 1 : 1.128 : 1.224$$

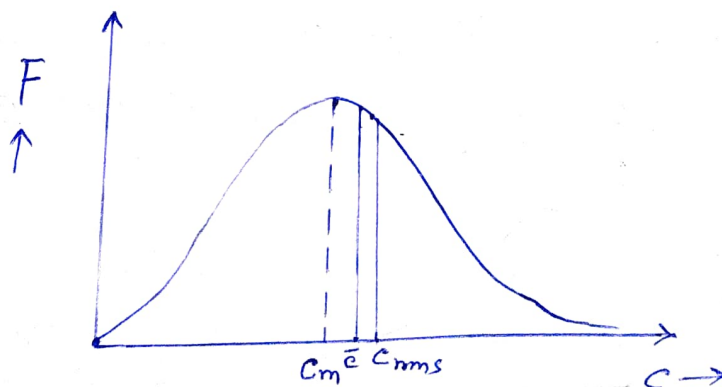


Fig - Average, r.m.s. and most probable speed.

## ▣ Energy Distribution of molecules :-

The kinetic energy  $E$  is given by

$$E = \frac{1}{2} mc^2$$

$$\text{or, } dE = mc \, dc$$

$$\text{or, } dc = \frac{dE}{mc}$$

$$\text{or, } dc = \frac{dE}{m \times \sqrt{\frac{2E}{m}}}$$

$$\text{or, } dc = \frac{dE}{\sqrt{2mE}}$$

From Maxwell's velocity distribution law, the number of molecules  $dN_c$  having velocity lying between  $c$  and  $c+dc$  is

$$dN_c = 4\pi N \left( \frac{m}{2\pi KT} \right)^{3/2} e^{-mc^2/2KT} c^2 dc$$

$\therefore$  The number of molecules  $dN_E$  having energy lying between  $E$  and  $E+dE$  i.e., energy distribution among the molecules is -

$$dN_E = 4\pi N \left( \frac{m}{2\pi KT} \right)^{3/2} e^{-E/KT} \cdot \frac{2E}{m} \cdot \frac{dE}{\sqrt{2mE}}$$

$$\text{or, } \frac{dN_E}{N} = 2 \left( \frac{E}{\pi} \right)^{1/2} (KT)^{-3/2} e^{-E/KT} dE$$

- This is fraction of molecules having specified energy lying between  $E$  and  $E+dE$ .

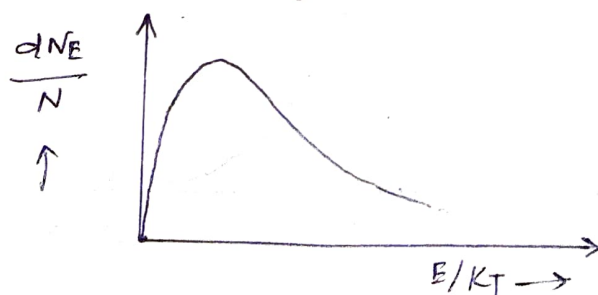


Fig - Maxwell-Boltzmann energy distribution curve.

## ■ Momentum distribution:-

The momentum  $p = mc$

$$\text{or, } dp = mdc$$

$$\text{or, } dc = \frac{dp}{m}$$

∴ The number of molecules  $dN_p$ , having momentum between  $p$  and  $p+dp$  is given by —

$$\begin{aligned} dN_p &= 4\pi N \left( \frac{m}{2\pi KT} \right)^{3/2} e^{-p^2/2mKT} \cdot \left( \frac{p^2}{m^2} \right) \frac{dp}{m} \\ &= 4\pi N (2\pi mKT)^{-3/2} e^{-p^2/2mKT} \cdot p^2 dp \end{aligned}$$

This is momentum distribution law.

## ■ Temperature Dependence of Velocity Distribution:-

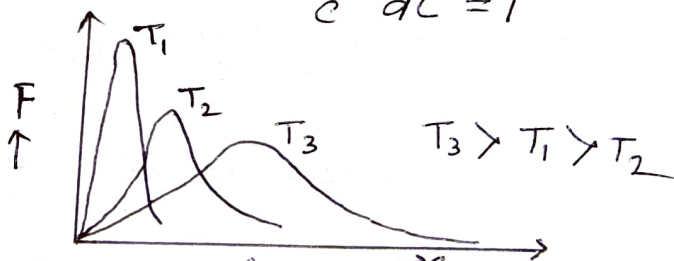
The fraction of molecules having velocity between  $c$  and  $c+dc$  is —

$$\frac{dN_c}{N} = 4\pi \left( \frac{m}{2\pi KT} \right)^{3/2} e^{-mc^2/2KT} c^2 dc$$

If we integrate the expression with respect to  $c$  for all the possible values of it —

$$\int_0^{\infty} 4\pi \left( \frac{m}{2\pi KT} \right)^{3/2} e^{-mc^2/2KT} c^2 dc = 1$$

$$\text{or, } \int_0^{\infty} F dc = 1$$



This means that the area under the distribution curve of molecular velocity i.e.,  $F$  vs  $c$  plot is unity.

But the maximum of  $F-c$  curve occurs at —

$$c_m = \sqrt{\frac{2KT}{m}}$$

So when Temperature increases, the peak of the curve should get shifted to a higher  $c$  value. But the area is fixed to unity. So the curve would be broadened with increase in temperature.

The broadening will naturally depend on the mass-value of the gas molecules.

So temperature may thus be taken as a measure of broadening of the distribution curve.

### ▣ Reduced form of Maxwell's speed distribution Law:-

Expressing the velocity  $c$  as a fraction of the most probable velocity  $c_m$ , i.e. the so called reduced velocity  $c_r$ .

$$c_r = \frac{c}{c_m} = \frac{c}{\sqrt{2KT/m}}$$

$$\text{or, } c = \sqrt{\frac{2KT}{m}} c_r \quad \text{and} \quad dc = \sqrt{\frac{2KT}{m}} dc_r$$

Substituting these values in Maxwell's equation-

$$dN_c = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} \cdot e^{-c^2 \left(\frac{2KT}{m}\right)^{3/2}} \cdot c_r^2 dc_r$$

$$= \frac{4}{\sqrt{\pi}} N e^{-c_r^2} \cdot c_r^2 dc_r$$

- Which is the reduced form of the Maxwell's equation in speed distribution. Reduced form is independent of temperature.

The above relation shows that mean K.E. of translation per molecule is  $\frac{3}{2}KT$ , that is proportional to the absolute temperature.

### ● Concept of Probability:-

The probability of an event is the limit to which the ratio of the numbers of trials resulting in occurrence of the event to the total number of trials when it tends to infinite.

Let,  $N'$  = the number of occurrence of the event we are interested.

$N$  = Total number of trials.

$$\therefore \text{Probability, } P = \lim_{N \rightarrow \infty} \frac{N'}{N}$$

### ▣ Summation of Probability:-

If  $P_1, P_2, P_3, \dots$  are the probability of several mutual exclusive events, then the probability that one of them will happen is the sum of the probabilities of happening for the separate events. i.e.,

$$P = P_1 + P_2 + P_3 + \dots$$

### ▣ Multiplication of Probability:-

The probability of the simultaneous happening of two or several independent events equals to the product of the probabilities of each of them happening separately. That is

$$P_{1,2,\dots} = P_1 \times P_2 \times \dots$$

## ● Distribution of Velocities or Speeds :-

The distribution of molecules by velocities may apparently mean that the determination of the number of molecules having a specified velocity. But, the probable number of molecules with mathematically exact velocity is zero. So it is clear, the number of different values of the velocity is infinite, the number of molecules is infinite.

### ▣ Distribution Function :-

Let,  $dN =$  The number of molecules in unit volume, whose velocity are in the range  $c$  and  $c+dc$ .

$N =$  The number of molecules per unit volume.

$\therefore dN$  is proportional to  $dc$

$$dN \propto dc$$

$$\text{and, } dN \propto N$$

$$\therefore dN \propto N dc$$

$$\text{or, } dN = a N dc \quad , \quad \text{where } a = \text{proportionality constant.}$$

The constant  $a$  is also function of velocity  $c$ ,

$$a = f(c)$$

$$\therefore dN = f(c) N dc$$

$$\Rightarrow f(c) = \frac{dN}{N dc}$$

The function  $f(c)$  is called the distribution function.

$$\text{If, } dc = 1, \text{ then, } f(c) = \frac{dN}{N}$$

So, the distribution function is the fraction of molecules

whose velocities are within a unit interval of velocities at  $c$ .

### ▣ Probability Density :-

The quantity  $\left(\frac{dN}{N}\right)$  has the meaning of Probability. It is the probability of any molecule in unit volume having a velocity that is within a unit interval near the velocity  $c$ .

So, the distribution function is also called probability density.



whose velocities are within a unit interval of velocities at  $c$ .

### ▣ Probability Density :-

The quantity  $\left(\frac{dN}{N}\right)$  has the meaning of Probability. It is the probability of any molecule in unit volume having a velocity that is within a unit interval near the velocity  $c$ .

So, the distribution function is also called probability density.

### ▣ Maxwell's Velocity or Speed Distribution Law :-

Let us represent all the gas molecules in a velocity diagram having  $OX, OY, OZ$  as the axes of co-ordinate with  $O$  at origin.

Let  $u, v, w$  be the components of any velocity vector  $c$ , along the axes.

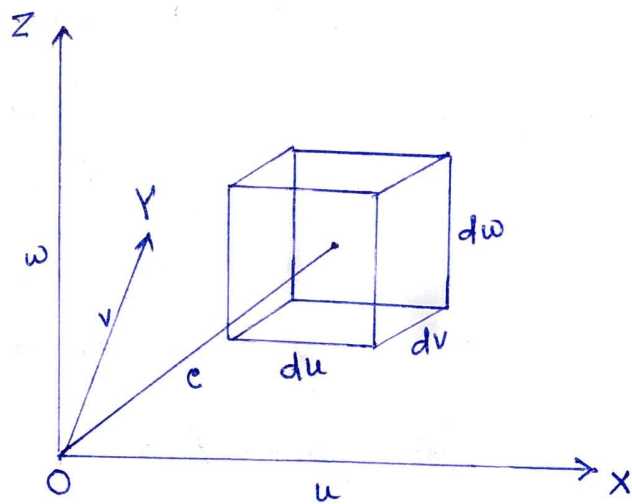


Fig: Velocity Diagram.

$$\therefore u^2 + v^2 + w^2 = c^2 \quad \text{----- (1)}$$

Now differentiating both side we get -

$$u du + v dv + w dw = 0 \quad \text{----- (2)}$$

According to Maxwell, since  $u, v, w$  are mutually orthogonal, the distribution of any one component is

independent of the values of the other components.

now let,  $f(u)du$  = The probability that a molecule selected at random has a velocity between  $u$  and  $u+du$ .

Similarly, the probabilities that a molecule has velocity components lying between  $v+dv$  and  $w+dw$  are respectively  $f(v)dv$  and  $f(w)dw$ .

$\therefore$  The molecules having component of velocities between  $u$  and  $u+du$ ,  $v$  and  $v+dv$ ,  $w$  and  $w+dw$  will be found in the volume element ( $du dv dw$ ) of velocity space.

$\therefore$  The numbers  $dN$  of such molecule is

$$dN = N f(u) f(v) f(w) du dv dw$$

[where  $N$  is the total number of molecules in the gas assembly.]

$$\Rightarrow \frac{dN}{du dv dw} = N f(u) f(v) f(w)$$

$$\Rightarrow \rho = N f(u) f(v) f(w) \text{ ----- (3)}$$

[  $\rho$  = number density of molecules in velocity space ]

Since the gas is in a steady state, then  $\rho = \text{constant}$ .

$$\therefore d\rho = 0$$

$$\Rightarrow d[N f(u) f(v) f(w)] = 0$$

$$\Rightarrow N [f'(u) f(v) f(w) du + f(u) f'(v) f(w) dv + f(u) f(v) f'(w) dw] = 0$$

Dividing throughout by  $f(u) f(v) f(w)$ , we obtain —

$$\Rightarrow \frac{f'(u)}{f(u)} du + \frac{f'(v)}{f(v)} dv + \frac{f'(w)}{f(w)} dw = 0 \quad \text{--- (4)}$$

Now multiplying equation (2) by  $\alpha$  and adding the product with equation (4) we get -

$$\left\{ \frac{f'(u)}{f(u)} + \alpha u \right\} du + \left\{ \frac{f'(v)}{f(v)} + \alpha v \right\} dv + \left\{ \frac{f'(w)}{f(w)} + \alpha w \right\} dw = 0$$

[where  $\alpha$  is an undetermined multiplier of Lagrange]

Again,  $du$ ,  $dv$  and  $dw$  are independent, so we can write -

$$\left. \begin{aligned} \frac{f'(u)}{f(u)} + \alpha u &= 0 \\ \frac{f'(v)}{f(v)} + \alpha v &= 0 \\ \frac{f'(w)}{f(w)} + \alpha w &= 0 \end{aligned} \right\} \text{--- (5)}$$

Now,  $\frac{f'(u)}{f(u)} + \alpha u = 0$

$$\Rightarrow \frac{f'(u)}{f(u)} = -\alpha u$$

$$\Rightarrow \frac{f'(u)}{f(u)} du = -\alpha u du$$

Integrating we get -

$$\ln f(u) = -\frac{\alpha u^2}{2} + \ln A$$

$$\text{or, } \ln \frac{f(u)}{A} = -\frac{\alpha u^2}{2}$$

$$\text{or, } f(u) = A e^{-\frac{\alpha u^2}{2}}$$

Similarly,  $f(v) = Ae^{-\alpha v^2/2}$  and  $f(w) = Ae^{-\alpha w^2/2}$

Now, from equation (3) we get -

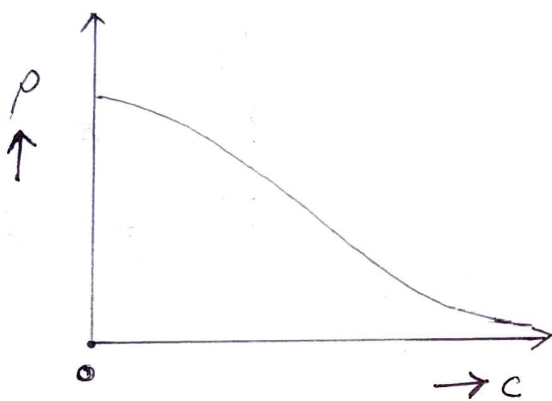
$$\rho = N f(u) f(v) f(w)$$

$$\text{or, } \rho = NA^3 e^{-\alpha/2 (u^2 + v^2 + w^2)}$$

$$\text{or, } \frac{dN}{du dv dw} = NA^3 e^{-\frac{\alpha}{2} (u^2 + v^2 + w^2)}$$

$$\text{or, } dN = NA^3 e^{-\frac{\alpha}{2} (u^2 + v^2 + w^2)} du dv dw$$

$$\text{or, } \boxed{dN = NA^3 e^{-bc^2} du dv dw} \text{ ----- (6)}$$



[where,  $b = \alpha/2$ ,  $u^2 + v^2 + w^2 = c^2$ ]

$$* \frac{dN}{du dv dw} = NA^3 e^{-bc^2}$$

$$\Rightarrow \boxed{\rho = NA^3 e^{-bc^2}} \text{ ----- (7)}$$

Fig: Molecular density in velocity space vs velocity.

### ● Evaluation of 'A':

The total number of molecules in a gas assembly is  $N$ .

$$\int_{-\alpha}^{+\alpha} \int_{-\alpha}^{+\alpha} \int_{-\alpha}^{+\alpha} NA^3 e^{-b(u^2 + v^2 + w^2)} du dv dw = N$$

$$\text{or, } \int_{-\alpha}^{+\alpha} e^{-bu^2} du \int_{-\alpha}^{+\alpha} e^{-bv^2} dv \int_{-\alpha}^{+\alpha} e^{-bw^2} dw = \frac{1}{A^3}$$

$$\text{let, } I = \int_{-\alpha}^{+\alpha} e^{-bu^2} du = \int_{-\alpha}^{+\alpha} e^{-bv^2} dv = \int_{-\alpha}^{+\alpha} e^{-bw^2} dw$$

$$\therefore I^3 = \frac{1}{A^3}$$

$$\text{or, } I = \frac{1}{A}$$

$$\text{or, } A = \frac{1}{I}$$

We have, 
$$I = \int_{-\infty}^{+\infty} e^{-bu^2} du = 2 \int_0^{\infty} e^{-bu^2} du$$

[Let,  $bu^2 = x$

or,  $2bu du = dx$

or,  $du = \frac{dx}{2bu} = \frac{dx}{2b\sqrt{x/b}}$  ]

$\therefore I = \frac{2}{2\sqrt{b}} \int_0^{\infty} e^{-x} x^{-1/2} dx$

$= \frac{1}{\sqrt{b}} \Gamma_{1/2}$

$= \frac{\sqrt{\pi}}{\sqrt{b}}$

$= \sqrt{\frac{\pi}{b}}$

$\therefore A = \frac{1}{I} = \sqrt{\frac{b}{\pi}}$

\* Gamma Function:-

$\int_0^{\infty} e^{-x} x^n = \Gamma(n+1)$

$\int_0^{\infty} e^{-x} x^{n-1} = \Gamma n$

$\Gamma_1 = 1$

$\Gamma_{1/2} = \sqrt{\pi}$

$\Gamma(n+1) = n \Gamma n$

### ● Evaluation of 'b' :-

The pressure  $p$  of the gas is given by the eqn -

$$p = 2m \sum_{n=0}^{\infty} n u u^2$$

where,  $n_u =$  no. of molecules per unit volume with velocities between  $u$  and  $u+du$ .

$n_u = n f(u) du$ ,  $n =$  no. of molecules per unit volume.

$\therefore p = 2m n \int_0^{\infty} f(u) u^2 du$

$$\begin{aligned}
 \therefore p &= 2mn \int_0^{\infty} f(u) u^2 du \\
 &= 2mn A \int_0^{\infty} e^{-bu^2} u^2 du \quad [ \because f(u) = Ae^{-bu^2} ] \\
 &= 2mn A \times \frac{1}{4} \sqrt{\frac{\pi}{b^3}} \\
 &= \frac{mn}{2} \sqrt{\frac{b}{\pi}} \sqrt{\frac{\pi}{b^3}} \quad [ \because A = \sqrt{\frac{b}{\pi}} ] \\
 &= \frac{mn}{2b}
 \end{aligned}$$

$$\therefore b = \frac{mn}{2p} = \frac{mn}{2nKT} = \frac{m}{2KT}$$

So, 
$$\boxed{b = \frac{m}{2KT}} \quad \text{and} \quad \boxed{A = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi KT}}}$$

So, finally from equation (7) we can write -

$$\boxed{\rho = N \left( \frac{m}{2\pi KT} \right)^{3/2} e^{-mc^2/2KT}} \quad \text{----- (8)}$$

$\rho$  is the number of specified molecules per unit volume. So the number of molecules  $dN_c$  having velocity lying between  $c$  and  $c+dc$  is  $\rho$  times the volume between the two spheres (spherical shell) of radius  $c$  and  $c+dc$ . The volume of the spherical shell is  $4\pi c^2 dc$ .

$$\therefore dN_c = \rho \cdot 4\pi c^2 dc$$

$$\text{or } \boxed{dN_c = 4\pi N \left( \frac{m}{2\pi KT} \right)^{3/2} \times e^{-mc^2/2KT} \cdot c^2 dc}$$

This is Maxwell's velocity or speed distribution law. ----- (9)

## ① Distribution Curve of Molecular Speed:-

From Maxwell's velocity or speed distribution law -

$$dN_c = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 dc$$

$$\text{or, } \frac{dN_c}{N} = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 dc$$

$$= F dc$$

$$\text{where, } F = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2$$

A plot of function  $F$  against  $c$  gives the distribution curve of molecular velocity.

• From Maxwell's Law:-

i)  $dN_c = 0$ , when  $c = 0$   
and  $c = \infty$ .

(ii) There is a value of  $c$  for which  $F$  is max.  
(dotted ordinate).

Maximum no. of molecules will possess this velocity, called most probable velocity.

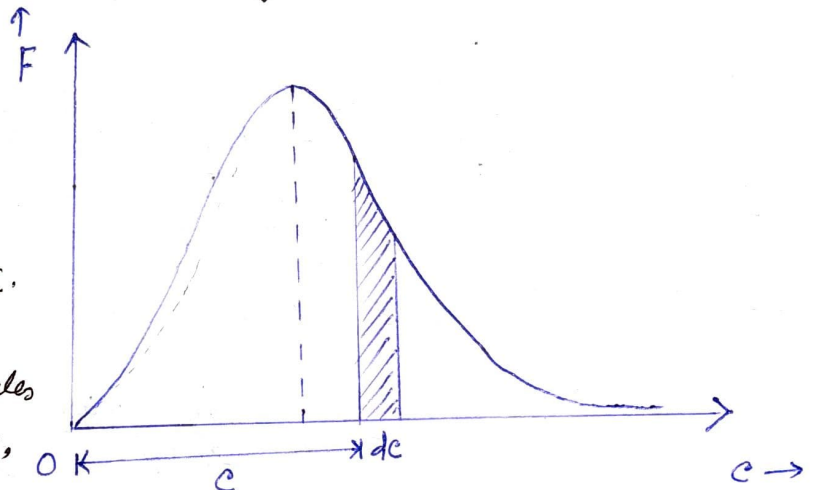


Fig.: Plot of function  $F$  against  $c$ .

⇒ If at a distance  $c$  from the origin, a thin strip of thickness  $dc$  is taken, then the area of the strip  $Fdc$  represents the fraction of the total numbers of molecules with velocity lying between  $c$  and  $c+dc$ , that is  $dN_c/N$ .

### ▣ Average or Mean Speed:

Let,  $n_1$  molecules have speed  $c_1$ ,  $n_2$  have speed  $c_2$  and so on.  
So by definition, the average or mean speed  $\bar{c}$  is given by -

$$\bar{c} = \frac{n_1 c_1 + n_2 c_2 + n_3 c_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i c_i}{\sum n_i}$$
$$= \frac{\int_0^\infty c dN_c}{\int_0^\infty dN_c} = \frac{1}{N} \int_0^\infty c dN_c$$

$$\therefore \bar{c} = \frac{1}{N} \int_0^\infty c (4\pi N A^3 e^{-bc^2} c^2 dc)$$
$$= \frac{4\pi N A^3}{N} \int_0^\infty e^{-bc^2} c^3 dc \quad [ \because dN_c = 4\pi N A^3 e^{-bc^2} c^2 dc ]$$
$$= 4\pi A^3 \int_0^\infty e^{-z} \cdot \frac{z}{b} \cdot \frac{dz}{2b}$$
$$= \frac{4\pi A^3}{2b^2} \int_0^\infty e^{-z} \cdot z dz$$
$$= \frac{4\pi A^3}{2b^2} \Gamma_2$$
$$= \frac{4\pi A^3}{2b^2} \quad [ \because \Gamma_2 = 1\Gamma_1 = 1 ]$$
$$= \frac{2\pi (m/2\pi kT)^{3/2}}{(m/2kT)^2} = \sqrt{\frac{8kT}{\pi m}}$$

$$\boxed{\bar{c} = \sqrt{\frac{8kT}{\pi m}}}$$



## ■ Degrees of Freedom:-

Degrees of freedom is the numbers of variable required to describe the motion of a particle completely. For an atom moving in 3-dimensional space, three coordinate are adequate. The particle has now three degrees of freedom. Its motion is purely translational. If we have a molecule made of  $N$  atoms (or ions), the degrees of freedom becomes  $3N$ , because each atom has 3 degrees of freedom.

However, molecules are not geometric points but are of finite size. They possess not only mass but also moment of inertia and therefore have K.E. of rotation, apart from that of translation. So molecules are expected to have rotational degrees of freedom. If the molecules are of perfectly rigid structures, they could also vibrate, giving rise to the degrees of freedom.

- The total numbers of independent coordinates necessary for specifying the position and configuration in space of a dynamical system is known as degrees of freedom.

If there is a material system consisting of  $N$  particles  $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_N, y_N, z_N)$ , subjected to smooth constraints represented by  $m$  equations.

∴ The numbers of degrees of freedom  $f$  of the system is given by —

$$f = 3N - m$$

## Principle of Equipartition of Energy:-

The mean kinetic energy of a system of molecules in thermal equilibrium at the temperature  $T$ , is uniformly distributed among all the degrees of freedom and for each degree of freedom of a molecule it is equal to  $\frac{1}{2}KT$ .

where  $K$  is the Boltzmann constant.

This theorem of uniform distribution of kinetic energy among the degrees of freedom is known as the principle of equipartition of energy. In classical statistical physics, such a theorem has been proved.

## Degrees of Freedom and Ratio of Heat Capacities:-

Let a system of particles consist of only free particles having  $f$  degrees of freedom. From the laws of equipartition of energy, energy corresponding to each degree of freedom is  $\frac{1}{2}KT$ .

$\therefore$  Energy per mole of the system,

$$E = \frac{1}{2}KT \cdot f \cdot N_A$$

$$= \frac{1}{2}fRT \quad [ \because KN_A = R ]$$

$$\therefore \text{Molar heat capacity, } C_v = \left( \frac{dE}{dT} \right)_v = \frac{d}{dT} \left( \frac{1}{2}fRT \right)$$

$$= \frac{1}{2}fR$$

$$\text{Again, } C_p - C_v = R$$

$$\text{or, } C_p = R + C_v$$

$$= R + \frac{1}{2}fR$$

$$= R \left( 1 + \frac{f}{2} \right)$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{R(1 + f/2)}{\frac{1}{2}fR} = 1 + \frac{2}{f}$$

$$\gamma = 1 + \frac{2}{f}$$

▣ Some Examples of Degrees of Freedom and value of  $\gamma$ :-

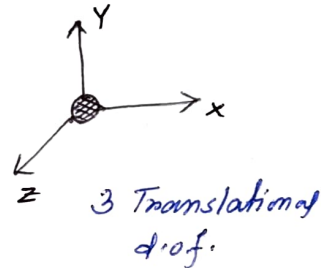
(a) Monoatomic Gas:-

A monoatomic gas consist of a single atom and the energy is fully kinetic energy of translation.

$$N=1 \text{ and } m=0$$

$$\therefore f = 3N - m = 3$$

$$\text{and, } \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} = 1.67$$



(b) Diatomic Gas:-

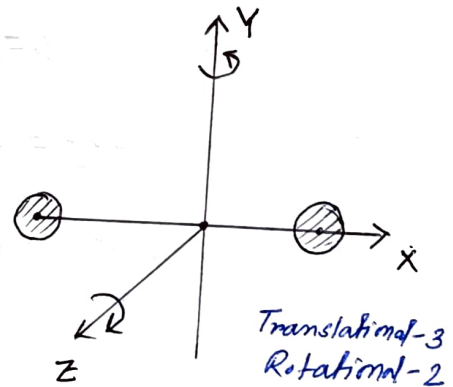
In a diatomic gas consist of two atoms at a certain distance from each other and joined rigidly like a dumbbell. So there is a constraint that the interatomic distance is fixed.

$$N=2 \text{ and } m=1$$

$$\therefore f = 3N - 1 = 5$$

[ Translational d.o.f = 03 and rotational = 02 ]

$$\gamma = 1 + \frac{2}{5} = 1.40$$



[ \*\* If the atomic bond is not rigid, the atoms may vibrate along the line joining. So extra two vibrational d.o.f. is introduced as the vibrational energy is partly K.E and P.E.

$$\text{So, } f = 7 \text{ and } \gamma = 1 + \frac{2}{7} = 1.28$$

The vibrational energy at room temperature is negligible. ]

(c) Triatomic Gas:-

(i) Linear Triatomic Gas:-

If the atoms are linearly arranged, the number of constraints is two i.e., the distances between the first, second and third atoms.

$$N = 3, \quad m = 2$$

$$\therefore f = 3 \times 3 - 2 = 7$$

$$\text{and } \gamma = 1 + \frac{2}{7} = 1.28$$

$$\text{Translational d.o.f.} = 3$$

$$\text{Rotational d.o.f.} = 2$$

$$\text{Vibrational d.o.f.} = 2$$

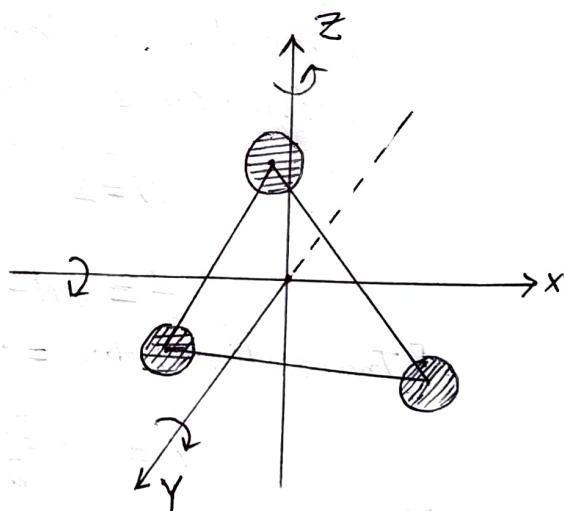
(ii) Non-Linear Triatomic Gas:-

If the three atoms are arranged at the vertices of a triangle, the number of constraints is three i.e., corresponding to the three sides of the triangle.

$$N = 3, \quad m = 3$$

$$\therefore f = 3 \times 3 - 3 = 6$$

$$\text{and, } \gamma = 1 + \frac{2}{6} = 1.33$$



$$\text{Translational d.o.f.} = 3$$

$$\text{Rotational d.o.f.} = 3$$

▣ 'γ' For a Mixture of two Ideal Gases:-

Let,  $N_1$  moles of an ideal gas with  $f_1$  degrees of freedom per molecule are mixed with  $N_2$  moles

of another ideal gas with  $f_2$  degrees of freedom per molecule at a particular temperature.

∴ Total internal energy of the system -

$$U = \frac{1}{2} K T N_1 N_A f_1 + \frac{1}{2} K T N_2 N_A f_2$$

$$= \frac{1}{2} R T (N_1 f_1 + N_2 f_2)$$

[∵  $K N_A = R$   
 $N_A = \text{Avogadro Number}$ ]

Now,  $C_V = \left( \frac{dU}{dT} \right)_V = \frac{1}{2} R (N_1 f_1 + N_2 f_2)$

$$C_P - C_V = (N_1 + N_2) R$$

$$\therefore C_P = (N_1 + N_2) R + \frac{1}{2} R (N_1 f_1 + N_2 f_2)$$

$$= R \frac{N_1 (2 + f_1) + N_2 (2 + f_2)}{2}$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{N_1 (2 + f_1) + N_2 (2 + f_2)}{(N_1 f_1 + N_2 f_2)}$$

### ▣ Dulong and Petit's Law:-

An expression for the specific heat of solids may as well be obtained from the kinetic theory.

Let, one gm-mole of solid consisting of  $N_A$  atoms.

Where,  $N_A$  is Avogadro number. In solids, atoms occupy fixed positions in the crystal lattice. The atoms can only vibrate about their mean positions. So each atom have 3 vibrational degrees of freedom.

$$\therefore \text{Total no of d.o.f.} = 3 N_A$$

An atom has both kinetic and potential energy. So that average kinetic energy is equal to average potential energy.

$$\therefore \text{Total energy, } U = 2 \times 3 N_A \times \frac{1}{2} K T$$

$$= 3 N_A K T$$

$$= 3 R T$$

$$\therefore c_v = \left( \frac{dU}{dT} \right)_V = 3R$$

So, the molar specific heat capacity at constant volume of all pure substances in the solid state are nearly equal to  $3R$ .

\*\*⊙ This law agrees with the experiment when temp<sup>r</sup> is high. But, at very low temperature specific heat of all solid approaches to zero.

The classical theory fails to explain the discrepancy between theory and experiment at low temperature.

According to quantum theory, the molar specific heat is

$$c_v = 3R \frac{x^2 e^x}{(e^x - 1)^2}$$

$$\left[ \text{where, } x = \frac{h\nu}{KT} \right]$$

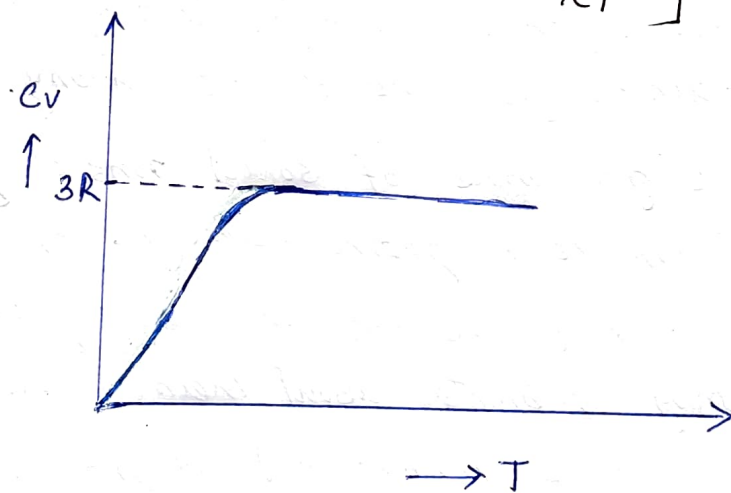


Fig:- Variation of molar specific heat at constant volume ( $c_v$ ) vs  $T$ .

## Molecular Collisions

Ref. Book.

Thermal Physics

A. B. Gupta.

H. P. Roy.

### ▣ Mean Free Path :-

The path traversed by a molecule between two successive collisions is called a free path. The path will be a straight line and for a single particle the path will consist of a series of short zig-zag paths.

Some of these paths will be long and others short.

So the mean free path ( $\lambda$ ) of a molecule is the average distance traversed by it between two successive collisions.

Mean free path has a great importance to study transport phenomena of gas.

### ▣ The Distribution of free Paths :-

Let, a system having a group of molecules  $N_0$  at a given instant. Each collision knocks out the molecule from the group. Let,  $N$  is the number of molecules remaining in the group after a distance  $x$  as measured along the mean free path of each. So  $N$  molecules have not yet made any collision.

In the next additional short distance  $dx$  some of  $N$  molecules,  $dN$  will be removed from the group due to collision.

$\therefore dN$  will be proportional to  $N$  and also to  $dx$ .

$$\therefore dN = -P_c \cdot N \cdot dx \quad \text{--- ①}$$

where,  $P_c$  = proportionality constant = collision probability.

[ $P_c$  depends only on the physical conditions of gas]

[Negative sign indicates that a collision removes a molecule from that group and  $N$  decreases.]

$$\text{From equation ①, } \frac{dN}{N} = -P_c dx \quad \text{--- ②}$$

$$\text{Integrating, } \ln N = -P_c x + \text{constant}$$

At,  $x=0$ ,  $N=N_0$ . So integrating constant is  $\ln N_0$ .

$$\therefore \ln N = -P_c x + \ln N_0$$

$$\text{or, } \ln \frac{N}{N_0} = -P_c x$$

$$\text{or, } N = N_0 e^{-P_c x} \quad \text{--- ③}$$

Now, substituting the value of  $N$  from ③ in eqn. ① we get -

$$dN = -P_c \cdot N_0 \cdot e^{-P_c x} \cdot dx \quad \text{--- ④}$$

Thus,  $|dN|$  gives the numbers of molecules with free path lengths between  $x$  and  $x+dx$ .

$\therefore$  Mean free path ( $\lambda$ ) can be expressed as -

$$\lambda = \frac{x_1 dN_1 + x_2 dN_2 + \dots}{dN_1 + dN_2 + \dots} = \frac{\int x dN}{\int dN} = \frac{1}{N_0} \int x dN$$

$$= \frac{1}{N_0} \int_0^{\infty} P_c N_0 x e^{-P_c x} dx \quad \text{[using equation ④]}$$

$$= P_c \int_0^{\infty} x e^{-P_c x} dx$$

$$= P_c \frac{1}{P_c^2} \Gamma(2)$$

$$= \frac{1}{P_c} \quad \text{--- ⑤} \quad \text{[as, } \Gamma(2) = 1]$$

$$\therefore \boxed{P_c = \lambda^{-1}}$$

$\therefore$  The collision probability is equal to the reciprocal of mean free path ( $\lambda$ ).



So, from equation (3) —

$$N = N_0 e^{-x/\lambda}$$

(5)

This is also known as the survival equation. It gives the numbers of molecules  $N$  (out of  $N_0$ ) having free paths greater than  $x$  i.e., the molecules survived over a path length  $x$ .

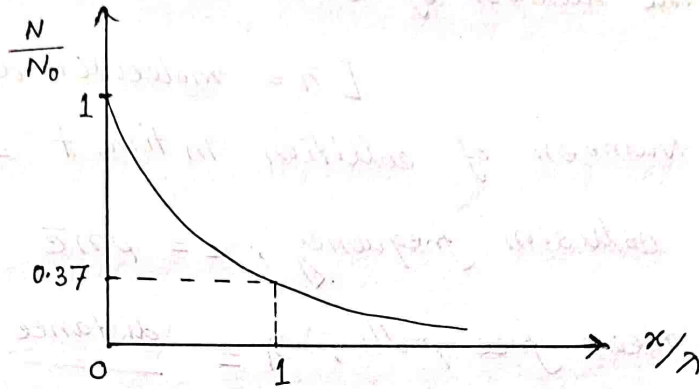


Fig:- Plot of  $N/N_0$  against  $x/\lambda$ .

### Expression for mean free Path:-

Imagine that at a certain instant all the molecules of a gas except one, are at rest. The moving molecule, among the frozen ones moves with velocity  $\bar{c}$ . We also assume the molecules are perfectly sphere of diameter  $\sigma$  and elastic. The centre to centre distance would be the same if radius of the moving molecules were increased to  $\sigma$  and other molecules at rest were, all shrunk to geometrical points.

$\therefore$  The effective cross sectional area of the mobile molecule, i.e. collision cross section  $\rho$  is given by-

$$\rho = \pi \sigma^2$$

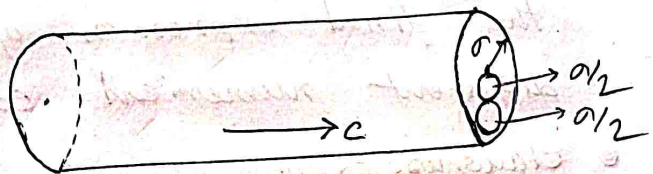
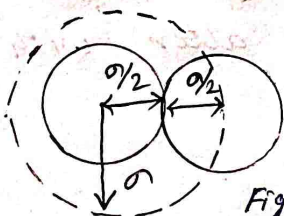


Fig: collision of two molecule with elementary treatment.

Now, in an interval  $t$ , the mobile molecule traverses a distance  $\bar{c}t$  along a zig-zag path and sweeps out a cylindrical volume of cross section  $\rho$  and length  $\bar{c}t$ . Plainly it would collide in time  $t$  with all molecules having their centres within the volume.

$$\therefore \text{The number of such molecules} = \rho n \bar{c} t$$

[  $n$  = molecular density ]

$$\therefore \text{Number of collision in time } t = \rho n \bar{c} t.$$

$$\therefore \text{collision frequency, } Z = \rho n \bar{c}$$

$$\therefore \text{Mean free path, } \lambda = \frac{\text{distance covered in time } t}{\text{no. of collision in } t}$$

$$= \frac{\bar{c} t}{\rho n \bar{c} t}$$

$$= \frac{1}{\rho n}$$

$$= \frac{1}{\pi d^2 n} \quad [ \because \rho = \pi d^2 ]$$

$$\therefore \boxed{\lambda = \frac{1}{\pi d^2 n}}$$

The above expression for  $\lambda$  is only an approximate method. Only one molecule is moving and others are frozen is too idealised. Actually all the molecules of gas are moving with different speed. By taking into account Clausius and Maxwell found new expression for mean free path ( $\lambda$ ). But the only change that the final expression of  $\lambda$  is to alter with different numerical co-efficient.

① Clausius's Expression:-  $\lambda = \frac{3}{4 \pi d^2 n}$