

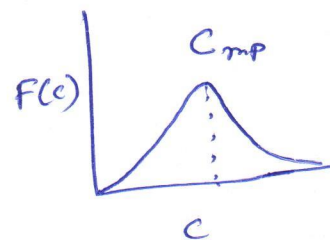
Derivation of most probable speed:-

$$F(c) = \frac{1}{n} \frac{dn}{dc} = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \cdot c^2 \cdot e^{-\frac{mc^2}{2kT}}$$

Differentiating  $F(c)$  w.r.t  $c$

$$\frac{d}{dc} [F(c)] = A \left[ 2c e^{-\frac{mc^2}{2kT}} - e^{-\frac{mc^2}{2kT}} \cdot \frac{2mc}{2kT} \cdot c^2 \right]$$

$$\text{where } A = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2}$$



At maxima,  $\frac{d}{dc} [F(c)] = 0$

$$\text{Thus, } AC e^{-\frac{mc^2}{2kT}} \left[ 2 - \frac{mc^2}{kT} \right] = 0$$

Now, since  $A \neq 0$

$$\begin{aligned} \text{Either } & \text{i) } c = 0 \\ & \text{or ii) } e^{-\frac{mc^2}{2kT}} = 0 \quad \text{or } c \Rightarrow \infty \\ & \text{or iii) } 2 - \frac{mc^2}{kT} = 0 \end{aligned}$$

But case (i) and (ii) correspond to the minima situation as evident from distribution curve.

$$\text{Thus, for the maxima, } 2 - \frac{mc_{mp}^2}{kT} = 0$$

$$\Rightarrow c_{mp} = \sqrt{\frac{2kT}{m}}$$

## Application of Maxwell's Speed distribution:—

Average of any molecular property which is function of speed can be derived using Maxwell's speed distribution as follows;

$$q = f(c)$$

$$\bar{q} = \frac{1}{n} \int_0^{\infty} q \, dn_c$$

$q$ : molecular property which is function of speed.

### ① Derivation of average speed ( $\bar{c}$ ):—

$$\bar{c} = \frac{1}{n} \int_0^{\infty} c \, dn_c$$

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

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

### ② Derivation of root mean square speed:—

$$\bar{c^2} = \frac{1}{n} \int_0^{\infty} c^2 \, dn_c$$

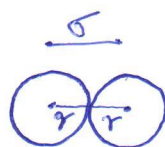
$$\sqrt{\bar{c^2}} = \sqrt{\frac{3KT}{m}}$$

## Collision number & collision frequency:-

Collision number: - Number of collision made by gas molecules in unit time.

Collision frequency: - Number of collision occurring between gas molecules in unit time and in unit volume.

As the molecules are in random motion, so they collide with themselves also. The molecules are assumed as rigid spheres,

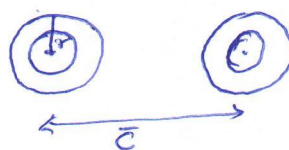


so when the molecules collide, the centre of two molecules can not approach beyond a certain distance. This distance is called distance of closest approach or collision diameter ( $\sigma$ ) of the molecules, where  $2r = \sigma$



Therefore, each molecule can be considered to be surrounded by an imaginary sphere of radius  $2r$  such that if any other molecules come within this spherical region, it will make a collision with the molecule under consideration. This sphere is called sphere of influence.

The molecule travel  $\bar{c}$  distance in 1 sec ( $\bar{c}$  = Avg. velocity)



$\therefore$  Volume swept by the imaginary sphere in 1 sec =  $\pi \sigma^2 \bar{c}$

If  $n$  be the number of molecules per unit volume, then number of molecules within the swept volume or in other words number of collision the molecules will make with other molecules in 1 sec =  $\pi \sigma^2 \bar{c} n$

Since all the molecules are mobile, therefore in the above calculation relative velocity must be considered.

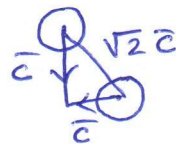


Two molecules may collide at different possible angles but the two extreme cases are collision at  $180^\circ$  (head on collision) & collision at  $0^\circ$  (grazing collision)

→ ○ ○ ← Head on collision;  
Angle =  $180^\circ$

○ →  
○ → Grazing collision;  
Angle =  $0^\circ$

Average collision angle =  $90^\circ$



Since the relative velocity is  $\sqrt{2} \bar{c}$ , therefore, no. of collisions one molecule makes in 1 sec =  $\pi \sigma^2 \sqrt{2} \bar{c} \cdot n$

$$Z_1 = \sqrt{2} \pi \sigma^2 \bar{c} n$$

$\pi \sigma^2 \bar{c} \rightarrow \text{vol/time}$   
 $n \rightarrow \text{mol/vol}$   
per unit time

$\therefore$  Collision frequency should be equals to  $\sqrt{2} \pi \sigma^2 \bar{c} n \cdot n$

To avoid double counting the above number should be divided by 2. Hence, collision frequency betw. similar molecules,

$$Z_{AA} = \frac{1}{2} \cdot \sqrt{2} \pi \sigma^2 \bar{c} n^2$$

(per unit time per unit volume)

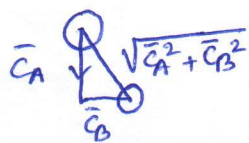
$$= \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{c} n^2$$

Collision frequency between dissimilar/different molecules:-

In this case avg. collision diameter =  $\frac{\sigma_A + \sigma_B}{2}$

Relative resultant velocity =  $\sqrt{\bar{c}_A^2 + \bar{c}_B^2}$

$\bar{c}_A$ : Avg velocity of A molecule  
 $\bar{c}_B$ : " " " B "



$$\bar{c}_A = \sqrt{\frac{8KT}{\pi m_A}}$$

$$\bar{c}_B = \sqrt{\frac{8KT}{\pi m_B}}$$

$$\sqrt{\bar{c}_A^2 + \bar{c}_B^2} = \sqrt{\frac{8KT}{\pi} \left( \frac{1}{m_A} + \frac{1}{m_B} \right)}$$

$$= \sqrt{\frac{8KT}{\pi \mu}} \left[ \mu = \frac{m_A m_B}{m_A + m_B} \right]$$

= reduced mass

So, collision frequency =  $\pi \left( \frac{\sigma_A + \sigma_B}{2} \right)^2 \sqrt{\frac{8KT}{\pi \mu}} n_A n_B$

$$\text{Thus, } Z_{AB} = (\sigma_A + \sigma_B)^2 \sqrt{\frac{\pi KT}{2\mu}} n_A n_B$$

$n_A$ : no. of A molecules  
 $n_B$ : no. of B "

Since collision betw. dissimilar molecules are considered, no double counting takes place.

Mean free path ( $l$ ) :- It is the average distance between two successive collisions of a molecule. The free path of a molecule can range from 0 to  $\infty$  as a molecule can collide with the other molecule just immediately after the start of its motion or it can move long distance without suffering any collision.

$$l = \frac{\bar{c}}{Z_1} ; \text{ where } Z_1 \text{ is the number of collisions made by a molecule in unit time when it travels } \bar{c} \text{ distance.}$$



$$= \frac{\bar{c}}{\sqrt{2} \pi \sigma^2 \bar{c} n} = \frac{1}{\sqrt{2} \pi \sigma^2 n} ; n = \text{no. of molecules per unit volume.}$$

Effect of Pressure & Temperature on mean free path :-

Mean free path decreases with increasing pressure and increases with increasing  $T$ .  
 $l \downarrow P \uparrow ; l \uparrow T \uparrow$

Mathematical proof :-  $l = \frac{1}{\sqrt{2} \pi \sigma^2 n} \quad \text{--- (1)}$

we know for  $n'$  mole of ideal gas;  $PV = n' RT$   
 $= \frac{N}{N_A} RT$

$N = \text{Total no. of molecules}$   
 $N_A = \text{Avogadro's no.}$

$$\Rightarrow P = \frac{N}{V N_A} RT$$

$n = \text{no. of molecules per unit volume}$

$$= \frac{n}{N_A} RT$$

Thus,  $n = \frac{P N_A}{RT}$

Replacing  $n$  in eqn. (1);  $l = \frac{1}{\sqrt{2} \pi \sigma^2} \frac{RT}{P N_A}$

Thus,  $l \propto T$  and  $l \propto \frac{1}{P}$

Again,  $PV = n' RT$  [  $W = \text{mass of the gas}$   
 $M = \text{Molar mass}$  ]  
 $= \frac{W}{M} RT$

$$\Rightarrow P = \frac{W}{V M} RT = \frac{P}{M} RT ; \text{ Thus, } l = \frac{1}{\sqrt{2} \pi \sigma^2} \times \frac{M}{P N_A}$$

$$\Rightarrow \frac{RT}{P} = \frac{M}{P}$$

$$\Rightarrow l \propto \frac{1}{P}$$

As  $P \uparrow$ , the molecules come closer to each other, thus increasing the number of collision, decreasing mean free path.



## Law of equipartition of energy:-

The application

$$E = \frac{3}{2} kT \quad (E = \text{Trans. K.E of molecule})$$

Now,  $E = E_x + E_y + E_z$  ;  $E_x, E_y, E_z$  are components of Trans. KE in x-, y- and z- directions, respectively.

$$E_x = \frac{1}{2} m \bar{C}_x^2$$

$$E_y = \frac{1}{2} m \bar{C}_y^2$$

$$E_z = \frac{1}{2} m \bar{C}_z^2$$

$$\text{But, } E_x = E_y = E_z$$

$$\text{Since, } E = \frac{3}{2} kT$$

$$\text{Thus, } E_x = E_y = E_z = \frac{1}{2} kT$$

This implies that total trans. KE is equally shared among its various components and each component contributes  $\frac{1}{2} kT$  amount of energy.

Considering this argument, Law of equipartition of energy states that —

Total energy of a molecule is equally partitioned among its various degrees of freedom and each degree of freedom contributes  $\frac{1}{2} kT$  amount of energy.

[A degree of freedom is recognized by a quadratic term of velocity / position]

In case of rotation; Rotational KE is expressed as  $\frac{1}{2} I \omega^2$   
 $I \rightarrow$  Moment of inertia  
 $\omega =$  Angular velocity

In case of vibration;  $KE = \frac{1}{2} \mu (\dot{r} - \dot{r}_{eq})^2$   
 $\mu$ : Reduced mass ;  $r_{eq}$  = Equilibrium bond distance.  
 $r$ : Interatomic distance at any instance.

$$PE = \frac{1}{2} k \omega^2 ; \quad k = \text{Force const.}$$

$$\omega = \text{Vib. frequency.}$$