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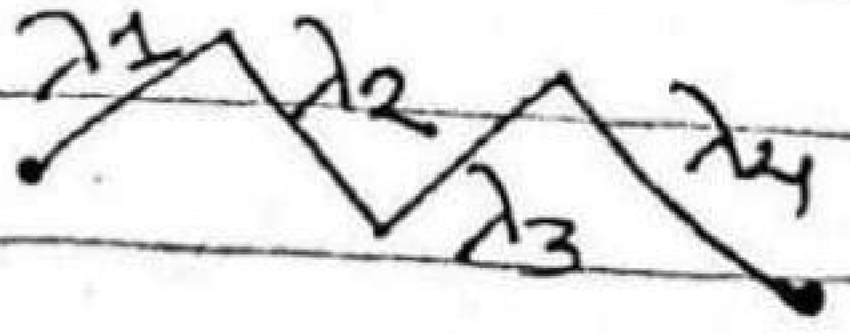
# Transport phenomena

## # Mean free path

· At a given temperature, the molecules suffer continuous collisions with one another. Between any two collision, the molecules travels freely a certain distance in a straight line. This distance is known as free path. Thus a path covered by a gas molecules between any two consecutive collision in a straight line, is called free path. The direction of the molecule is changed after every collision. After a number of collision, the total path appears to be zig-zag and free path is not constant as shown in figure. Therefore, a mean free path is used and defined as the average distance travelled by a gas molecules between two successive collisions. It is denoted by $\lambda$.

If the total distance travelled after N-collisions is S, then mean free path is given by

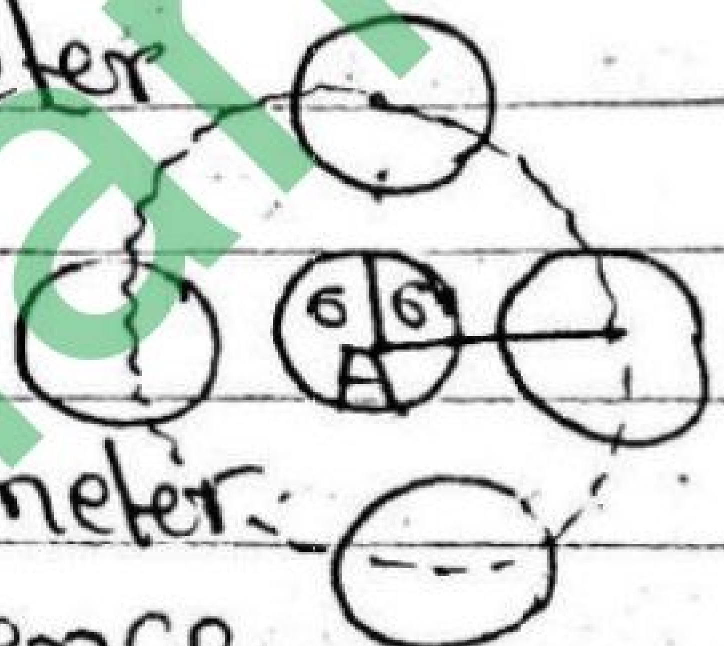


$$\lambda = \frac{S}{N}.$$

# Collision cross-section

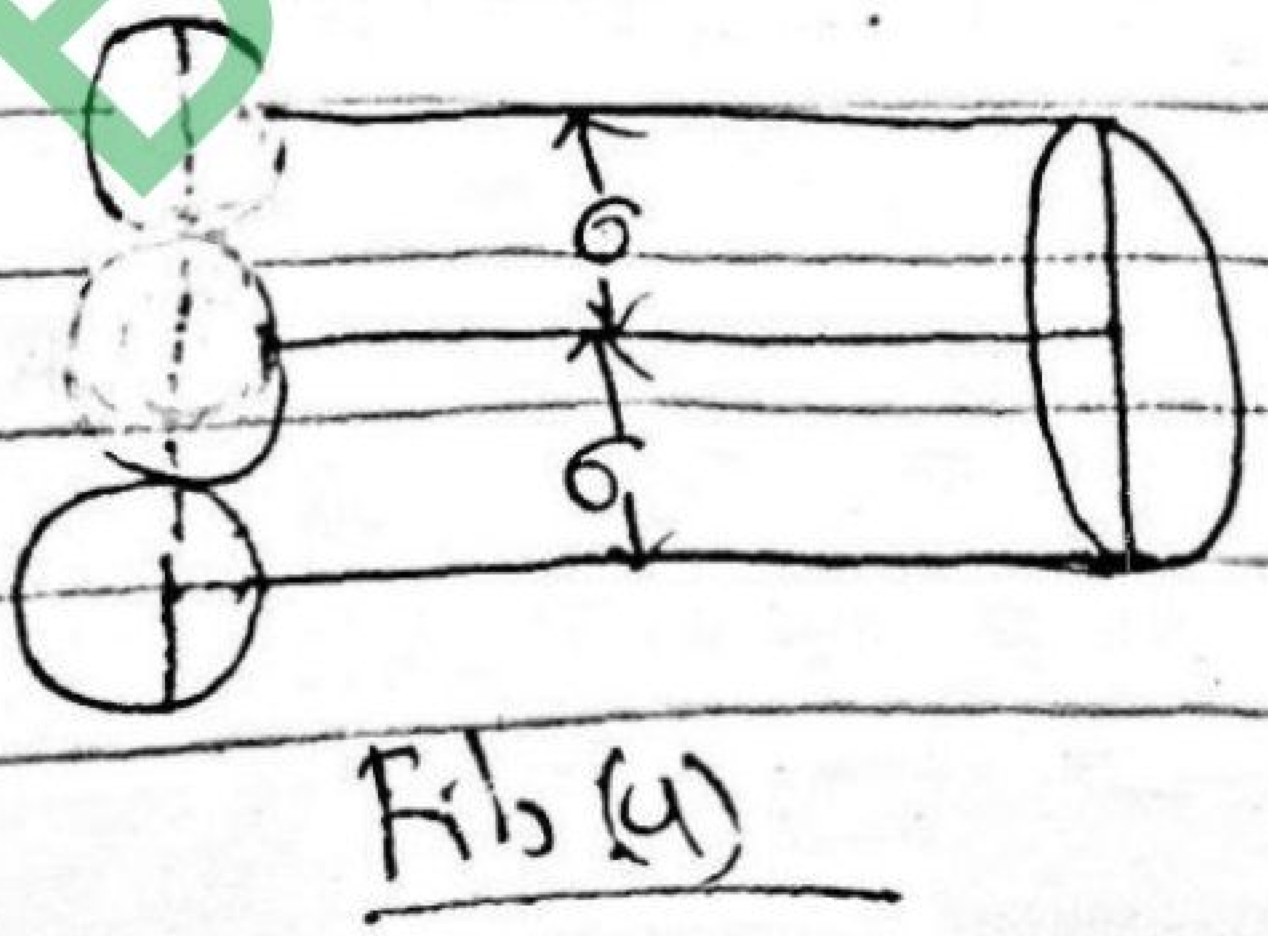
In the kinetic theory for an ideal gas, it is assumed that all the gas molecules are identical and perfectly elastic spheres moving randomly in all possible direction. For the sake of simplicity of calculations it is assumed that the molecules under consideration say A is in motion, all other molecules are of rest as shown in fig.

Let $\sigma$ be the diameter of each gas molecules. If we take a cross-section along the diameter of a sphere of influence.

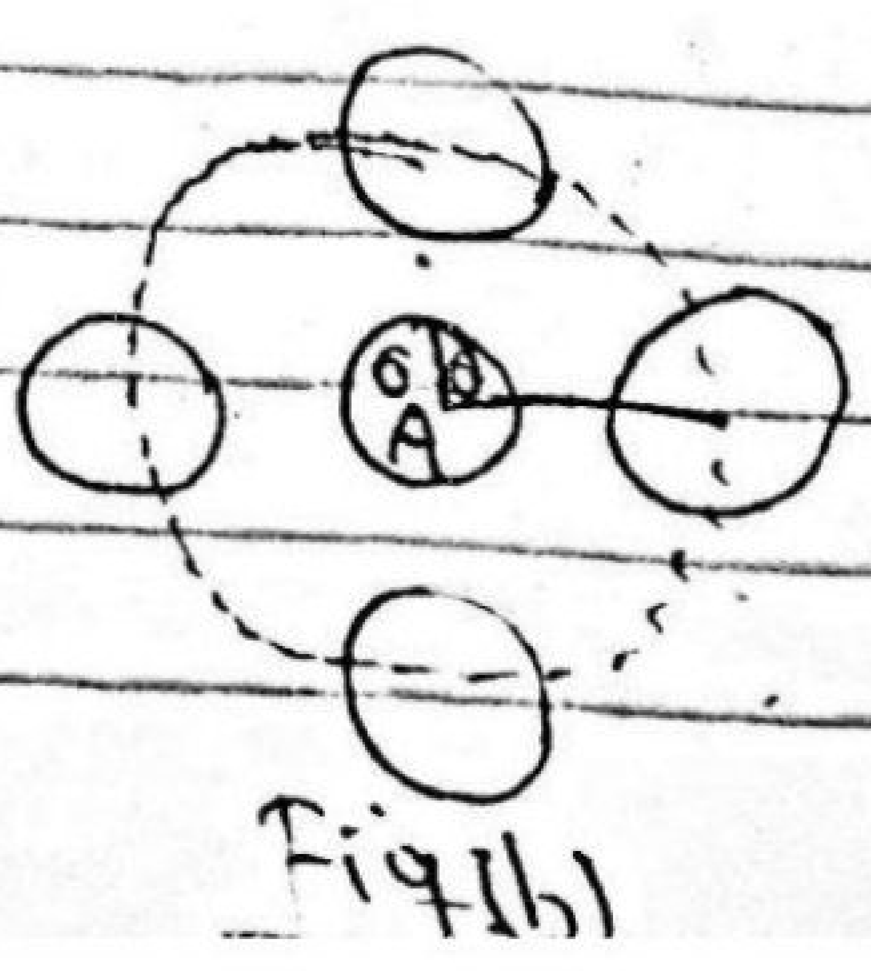


we get a collision cross-section. The area $\pi\sigma^2$ is called collision cross-section as shown by dotted lines in fig.

# Relation between collision frequency and mean free path



Fib (a)



Fig(b)

Suppose the gas molecules of are all identical perfectly elastic sphere of diameter $\sigma$. To simplify the calculations we further that (i) only the molecule under consideration is in motion while all other molecules are at rest.

(ii) The sphere of influence of the molecule has a radius $\sigma$ i.e. equal to the diameter of the molecule as shown in fig (b).

Let v be the average velocity of molecule 'A' and n be the no. of molecule per unit volume in one second, A will collide with all the molecules whose centre lie within a cylinder of radius $\sigma$ and length v.

∴ No. of molecules in the cylinder $(N) = \pi\sigma^2 v n$

and No. of molecules collision made by molecule 'A' in 1 sec or 'collision' frequency $= \pi\sigma^2 v n$

As the distance traversed by the molecule in 1 sec is v so the mean free path is given by

$$\lambda = \frac{\text{Total distance traversed in one second}}{\text{no. of collision suffered by the molecules in one second}}$$

$$= \frac{v}{\pi\sigma^2 v n}$$

$$\therefore \lambda = \frac{1}{\pi\sigma^2 n} \longrightarrow (1)$$

This is clausius expression for meanfree path.

Also, collision frequency (F) = $\pi\sigma^2 v n$.

$$\therefore f = \frac{v}{\lambda}$$

$$\therefore \lambda = \frac{v}{f} \longrightarrow (2)$$

Which is the required relation between mean free path and collision frequency

Maxwell's formula for λ

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

## ① # Expression for mean free path

Consider 1 mole of an ideal gas then,

$PV = RT$

dividing by Avogadro number N then

$$\frac{PV}{N} = \frac{RT}{N}$$

$$P = \frac{N}{V}\frac{R}{N}T$$

or, $P = nKT$

where $n$ = no. of molecules per unit volume

$= \frac{N}{V}$

$K$ = Boltzmann constant $= \frac{R}{N}$

$n = \frac{P}{KT}$

But, we know mean free path, $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$

Then,

$\lambda = \frac{KT}{\sqrt{2}\pi\sigma^2 P}$

Thus, $\frac{K}{\sqrt{2}\pi\sigma^2}$ is constant.

Therefore the mean free path varies directly proportional to ~~tem~~ absolute temperature and inversely proportional to pressure

i.e. $\lambda \propto T$ and $\lambda \propto P$

$\lambda \propto \frac{T}{P}$

# Transport phenomena

If the gas is not in equilibrium state, we may have any of the following three cases. They are;

(a) The different part of gas may have different velocities so there will be a reactive motion of the layer of gas with respect to one another. This gives rises to the phenomenon of viscosity.

(b) The different part of gas may have different temperatures so the molecules of the gas will carry kinetic energy from region of higher temperature to the region of lower temperature to bring the equilibrium state. This gives to the phenomena of conduction.

(c) The different part of the gas may have different molecular concentrations i.e. the no. of molecules per unit volume so the molecules of gas will carry the mass from regions of higher concentrations to those of lower concentrations to bring the equilibrium state. It gives the phenomena of diffusion.

This all three phenomena are called transport phenomena.

# Viscocity

Let us consider a mass of gas moving in parallel layers between two horizontal planes AB and CD. suppose the velocity of the layer of gas in contact with the plane AB is zero and increases as we pass towards the plane CD. Also consider intermediate plane MN.

Let n be the no. of molecules per unit volume and $\bar{v}$ is their average speed. The molecules are moving due to thermal agitation in all possible direction, it may be supposed that one third of the molecules are moving each of three directions parallel to three co-ordinate axis, so that on average one sixth of the molecules move parallel to any one axis in particular direction.

The no. of molecules crossing the plane MN upwards or downwards per unit area per second $= \frac{n\bar{v}}{6}$

Let $G$ be the momentum of each molecule in the plane MN and if the momentum changes according to distance then the momentum gradient $= \frac{dG}{dz}$

where $dG$ is the change in momentum in distance $z$.

$\therefore$ change in momentum for a distance $\lambda$ is $\lambda \frac{dG}{dz}$

Let each of the planes AB and CD at a distance $\lambda$ from MN and $\lambda$ is free mean path. so the momentum of each molecule at the plane

$$CD = G + \lambda \frac{dG}{dz} \longrightarrow (1)$$

$$\text{And } AB = G - \lambda \frac{dG}{dz} \longrightarrow (2)$$

$\therefore$ The momentum carried by molecules crossing per unit area per second from upper layer CD in downward.

$$= \frac{1}{6} n\bar{v} \left( G + \lambda \frac{dG}{dz} \right)$$

Similarly, the momentum carried by molecules crossing per unit area per second from lower layer AB in upward direction.

$$= \frac{1}{6} n\bar{v}\left(G - \lambda \frac{dG}{dz}\right)$$

The total momentum transferred downward per unit are per second through the MN.

$$= \frac{1}{6} n\bar{v}\left(G + \lambda \frac{dG}{dz}\right) - \frac{1}{6} n\bar{v}\left(G - \lambda \frac{dG}{dz}\right)$$

$$= \frac{1}{6} n\bar{v}\left(G + \lambda \frac{dG}{dz} - G + \lambda \frac{dG}{dz}\right)$$

$$= \frac{1}{6} n\bar{v} \cdot 2\lambda \frac{dG}{dz}$$

$$= \frac{1}{3} n\bar{v} \lambda \frac{dG}{dz},$$

$$= \frac{1}{3} n\bar{v} \lambda \frac{d}{dz}(mu)$$

Since $G = mu$, $u$ being the velocity of molecules at plane MN.

$$= \frac{1}{3} n m \bar{v} \lambda \frac{du}{dz}$$

∴ Coefficient of viscosity $\eta = \dfrac{\text{tangentia stress}}{\text{velocity gradient}}$

$$= \frac{\frac{1}{3} mn\bar{v}\lambda \frac{du}{dz}}{\frac{du}{dz}}$$

$$= \frac{1}{3} mn\bar{v}\lambda$$

But $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$

$\therefore \eta = \frac{m\bar{v}}{3\sqrt{2}\pi\sigma^2}$

Since $\bar{v} \propto \sqrt{T}$

$\therefore$ The coefficient of viscosity is directly proportional to the square root of the absolute temperature of the gas.

But also, $\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p}$

$\therefore \eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3}\rho\bar{v}\lambda$

or, $\lambda = \frac{3\eta}{\rho v}$

# Thermal conductivity.

Let us consider a mass of gas is at rest. The layers, AB, MN and CD are such that the temperature increases as we go from the plane AB to CD through MN.

Let E be the energy of each molecule in the plane MN and $\frac{dE}{dz}$ be the energy gradient in an upward direction.

Let AB and CD are at λ distance from MN where λ is the ~~fr~~ mean free path. Then the energy of each molecule at plane

$$CD = E + \lambda \frac{dE}{dz} \longrightarrow (1)$$

and the energy of each molecule at the

$$AB = E - \lambda \frac{dE}{dz} \longrightarrow (2)$$

The no. of molecules crossing the plane MN upwards or downwards per unit area per second $= \frac{n\bar{v}}{6}$

Therefore, the energy carried [illegible]wards by the molecules crossing unit area per sec the plane CD

$$= \frac{1}{6} n\bar{v}\left(E + \lambda \frac{dE}{dz}\right) \longrightarrow (3)$$

Therefore, the energy carried upwards by the molecules crossing unit area per second from the plane AB

$$= \frac{1}{6} n\bar{v}\left(E - \lambda \frac{dE}{dz}\right) \longrightarrow (4)$$

Therefore, the net energy transferred downwards across unit area per second.

$$= \frac{1}{6} n\bar{v}\left(E + \lambda \frac{dE}{dz} - E + \lambda \frac{dE}{dz}\right)$$

$$= \frac{1}{3} n\bar{v}\lambda \frac{dE}{dz} \longrightarrow (5)$$

But $E = mC_v dT$

Where $C_v$ be the specific heat of the gas at constant volume and temperature (T)

$$\therefore \frac{1}{3} n\bar{v}\lambda \frac{d}{dz}(mC_v dT) = \frac{1}{3} n\bar{v}\, mC_v \frac{dT}{dz}\lambda$$

The coefficient of thermal conductivity (K)

$$= \frac{\frac{1}{3} mn\bar{v}\lambda C_v \frac{dT}{dz}}{\frac{dT}{dz}} = \frac{1}{3} mn\bar{v}\lambda C_v$$

but $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$ then,

$$\therefore K = \frac{1}{3\sqrt{2}} \frac{m\bar{v}C_v}{\pi\sigma^2} \longrightarrow (6)$$

This is required expression for thermal conductivity of gas.

Here K does not depends upon pressure but depends upon the absolute temperature.

$K \propto \bar{v}$ but $\bar{v} \propto \sqrt{T}$

$\therefore K \propto \sqrt{T}$

we have,

coeff. of viscosity, $\eta = \frac{m\bar{v}}{3\sqrt{2}\pi\sigma^2}$

or, $m\bar{v} = \eta 3\sqrt{2}\pi\sigma^2$

from eqn. (6)

$$\therefore K = \frac{1}{3\sqrt{2}\pi\sigma^2} C_v \eta 3\sqrt{2}\pi\sigma^2$$

$$\therefore \frac{K}{\eta} = C_v$$

Which is relation between thermal conductivity and coefficient of viscocity of gas

Now, from eqn. (6)

$$K = \frac{1}{3\sqrt{2}\pi\sigma^2} \bar{v}\, m C_v$$

$$= \frac{1}{3\sqrt{2}} \frac{\bar{v}}{\pi\sigma^2} \left(\frac{M}{N}\right) \frac{C_v}{M} \qquad \left[\because m = \frac{M}{N}\right]$$

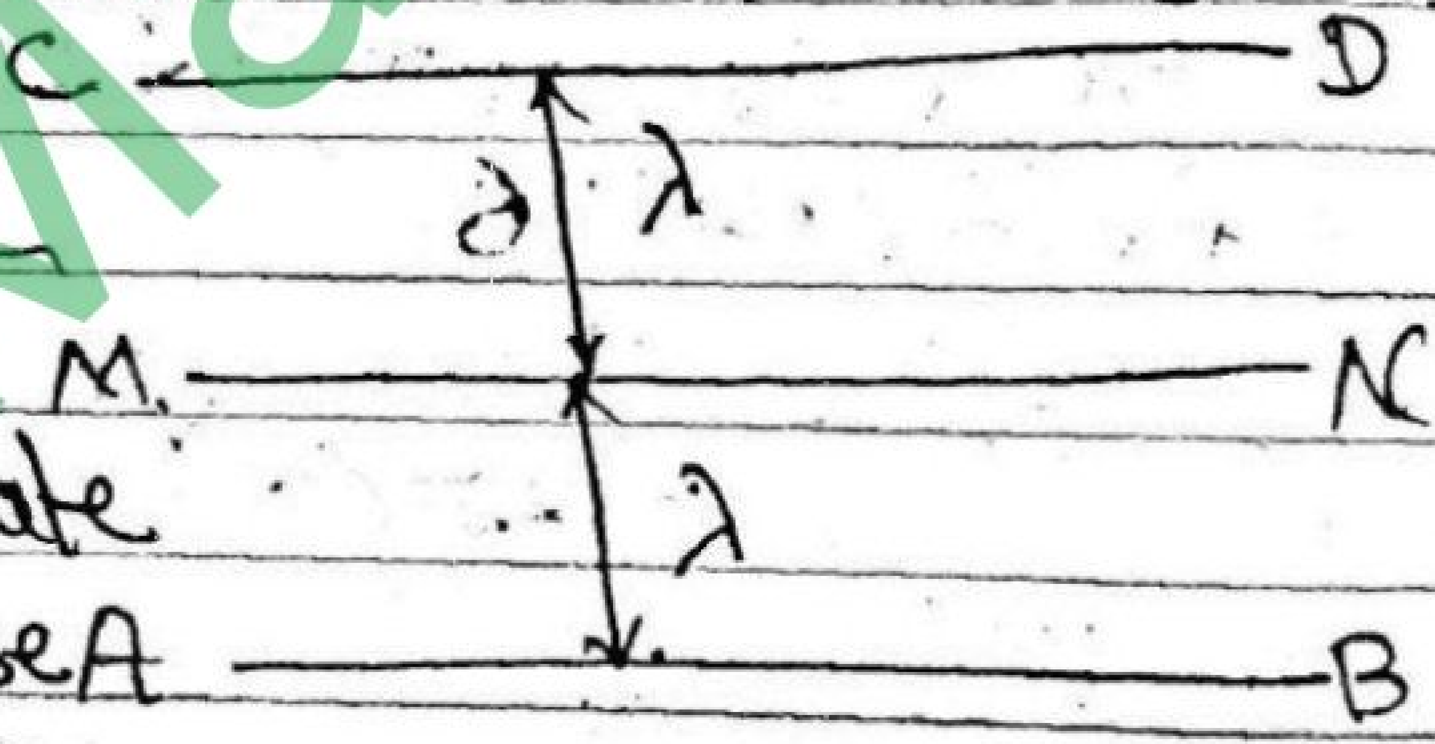
$$\left[\because C_v = \frac{C_v}{M}\right]$$

Where,
M = molecular weight of gas
N = Avogadro's number
Cv = molar specific heat capacity of gas at constant volume.

$$\therefore K = \frac{1}{3\sqrt{2}} \frac{\bar{v}}{\pi\sigma^2} \frac{C_v}{N} \longrightarrow (1)$$

# Transport of mass diffusion

Let us consider a mass of the gas is moving in parallel layers between the plane AB and CD. MN is an intermediate plane. Let us suppose that the concentration i.e. no. of molecules per unit volume increases in vertical direction as we go from plane AB to CD. So that the molecules will move from CD to AB to establish equilibrium. This phenomenon is called transport of mass.



Let n be the concentration at the plane MN and $\frac{dn}{dz}$ is the rate of change of concentration ~~at the plane~~ with distance in an upward direction. Let AB and CD be at a distance $\lambda$ from the plane MN where $\lambda$ is the mean free path. The concentration at the plane CD $= n + \lambda \frac{dn}{dz}$ → (1)

The concentration at the plane AB

$$= n - \lambda \frac{dn}{dz} \longrightarrow (2)$$

The no. of molecules coming from the plane CD crossing MN downwards per unit area per second $= \frac{1}{6}\bar{v}\left(n + \lambda\frac{dn}{dz}\right)$.

And the no. of molecules coming from the plane AB and crossing unit area of molecules upwards per second,

$$= \frac{1}{6}\bar{v}\left(n - \lambda\frac{dn}{dz}\right) \longrightarrow (3)$$

The net no. of molecules crossing unit area of the plane MN downwards per second

$$= \frac{1}{3}\bar{v}\frac{dn}{dz}\lambda$$

The coeff. of diffusion, $D = \dfrac{\frac{1}{3}\bar{v}\lambda\frac{dn}{dz}}{\frac{dn}{dz}}$

$$\therefore D = \frac{1}{3}\bar{v}\lambda \longrightarrow (4)$$

$$\text{or, } D = \frac{1}{3}\frac{\rho\bar{v}\lambda}{\rho} = \frac{\eta}{\rho} \quad \left[\because \eta = \frac{1}{3}\rho\bar{v}\lambda\right]$$

or, $D = \eta/\rho$

Where, $\eta = \frac{1}{3}\rho\bar{v}\lambda$ = coeff. of viscosity

Since, $\lambda \propto \frac{1}{n} \propto \frac{T}{P}$ and $\bar{v} \propto \sqrt{T}$

From eq$^n$ (4)

$\therefore D \propto P^{-1}T^{+3/2}$

Also, $\frac{K}{\eta} = C_v$ i.e. $\eta = K/C_v$ and $\eta = D\rho$

$\therefore K/C_v = D\rho$

# Brownian Motion

It is observed microscopically that pollen suspended in water move to and fro continuously. These particles are dancing about in a state of random motion. This irregular motion is "Brownian motion". The suspended particles are called the Brownian particles. The gas molecules are of same nature as the Brownian particles only the differences is that the Browian particles are larger than the gas molecules. All the laws of kinetic theory of gases are obeyed by these particles.

# Einstein's theory of the translation Brownian motion

Einstein's theory of translation Brownian motion explains the physical nature of the phenomenon. Brownian particle due to their random motion tend to diffusion coefficient to Brownian motion. He calculated the diffusion coefficient in two ways:

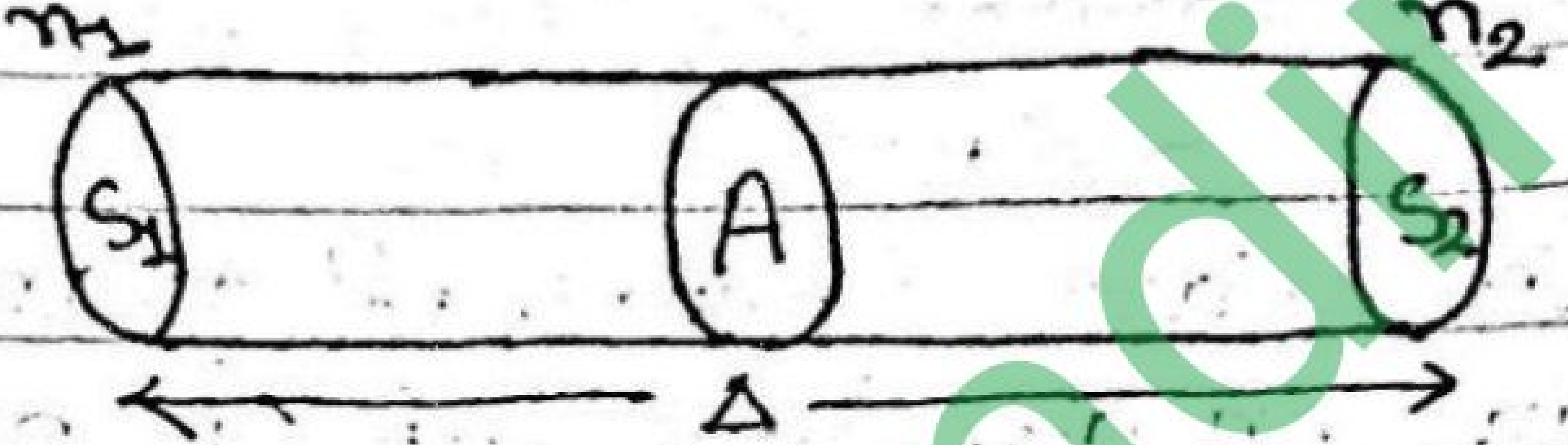
(1) From the irregular motion of the suspended particles.

(2) from the difference in osmotic pressure between different parts due to difference in the concentration of the suspended particles.

# Expression for diffusion coefficient when the molecules are in random motion:

Let us consider a cylinder of area of cross-section A having two ~~facts~~ faces $s_1$ and $s_2$ separated by a distance $\Delta$. Let $n_1$ and $n_2$ represents the molecular concentratio-

$n$ at ends $S_1$ and $S_2$ respectively. Since half of the molecules contained in imaginary cylinder move toward sides ($S_2$) and other half move towards left ($S_1$).



The no. of molecules crossing end face $S_2$ to the right in time

$$t = \frac{1}{2} n_1 \Delta A$$

The no. of molecules crossing end face $S_1$ to the left in time

$$t = \frac{1}{2} n_2 \Delta A$$

Hence the excess of particles crossing a middle layer to the right

$$= \frac{1}{2}(n_1 - n_2) \Delta A.$$

If $-dn/dx$ is the gradient of molecular concentration, then according to diffusion coefficient

$$D = \frac{\text{no. of molecules crossing per second per unit area}}{-dn/dx}$$

But no. of molecules crossing in time t through area A = $-D\, dn/dx\, tA$

$$\frac{1}{2}(n_1-n_2)\Delta A = -D\frac{dn}{dx}tA$$

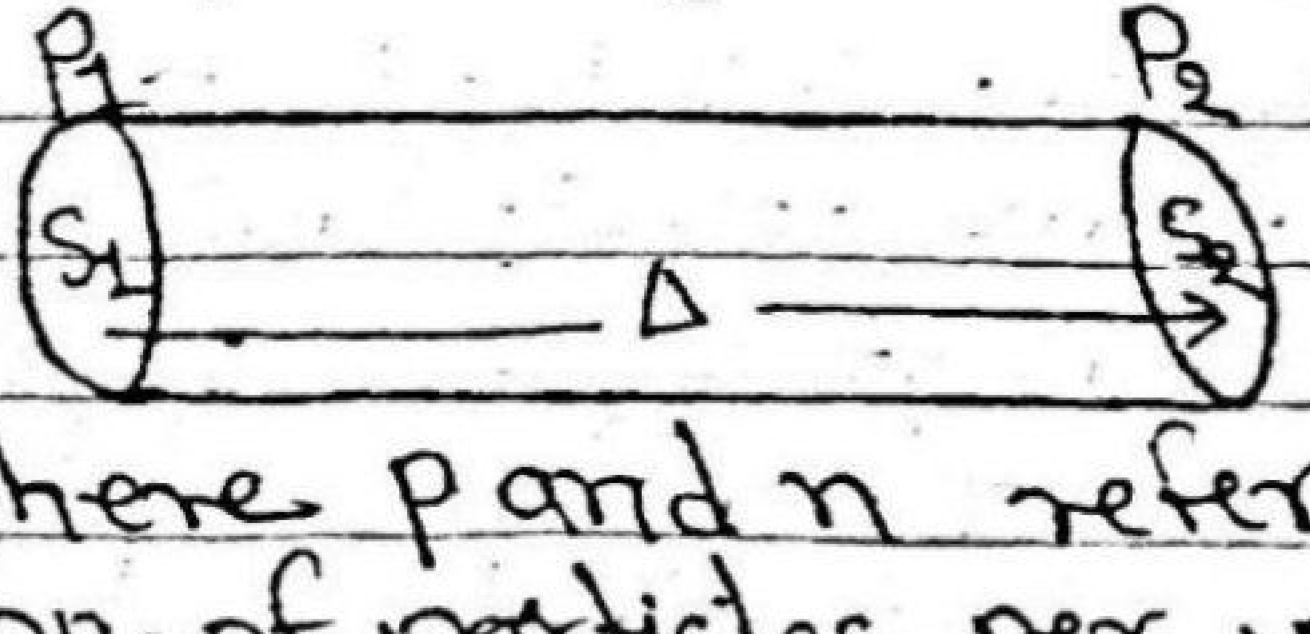
But $(n_1-n_2) = -\Delta\left(\frac{dn}{dx}\right)$

$$\therefore -\frac{1}{2}\Delta\left(\frac{dn}{dx}\right) = -D\left(\frac{dn}{dx}\right)t$$

or, $D = \frac{\Delta^2}{2t}$

# Calculation of diffusion coefficient from the difference in osmotic pressure

Let us consider a cylinder of length Δ. Let $P_1$ and $P_2$ be the osmotic pressure at end faces $S_1$ and $S_2$. In this process, temperature is same. So, from the gas laws



$P_1 = n_1KT$, where p and n refer to the pressure and no. of particles per unit volume

at temperature T.
Where K is boltzmann's constant. Due to the difference of pressure, the cylinder will experience a force equal to

$$A(P_2 - P_2) = (n_1KT - n_2KT)A$$

$$= (n_1 - n_2)KTA$$

If $n$ is the mean concentration then no. of particles contained in the cylinder

$$= n\Delta A$$

∴ Force acting on each particle

$$= \frac{(n_1 - n_2)KTA}{n\Delta A}$$

$$= \frac{KT}{n}\left(\frac{n_1 - n_2}{\Delta}\right)$$

[Since $n_1 - n_2 = -\Delta\frac{dn}{dx} \Rightarrow \frac{n_1 - n_2}{\Delta} = -\frac{dn}{dx}$]

$$= -\frac{KT}{n}\left(\frac{dn}{dx}\right)$$

But this force is equal to viscous force. Since the particles are in vicous medium. So, from stoke's law.

Viscous force $= 6\pi\eta rv$

where, $r$ = radius of particles

$v$ = steady velocity

$$\therefore 6\pi\eta r v = -\frac{KT}{n}\frac{dn}{dx}$$

$$\text{or, } nv = -\frac{KT}{6\pi\eta r}\frac{dn}{dx} \longrightarrow (1)$$

This expression represents the no. of particles moving to the right per unit area. We know,

$$D = \frac{\text{No. of particles per unit area per sec}}{dn/dx}$$

$$\therefore \text{No. of particles per unit area per sec} = D\frac{dn}{dx} \quad (2)$$

$$\therefore -D\left(\frac{dn}{dx}\right) = -\frac{KT}{6\pi\eta r}\left(\frac{dn}{dx}\right)$$

(But $K = R/N$)

$$D = \frac{RT}{6\pi\eta N r}$$

Also, we have

$$D = \frac{\Delta^2}{2t}$$

$$\text{or, } \Delta^2 = \frac{RT}{N}\frac{1}{3\pi\eta r}$$

Q→ If gas is not equilibrium state, what three possibilities may occour? [2063]

⇒ Solution,

If gas is not equilibrium state the following three cases may be possible.

(I) Different layer of gases move with different velocity. so, the momentum of each layers are different.

(II) Different layer of gases may have different temperature and hence different kinetic energy.

(III) Different layers of gas have different concentration.