Kinetic Theory of Gases

The kinetic theory of gases attempts to explain the microscopic properties of a gas in terms of the motion of its molecules. The gas is assumed to consist of a large number of identical, discrete particles called molecules, a molecule being the smallest unit having the same chemical properties as the substance. Elements of kinetic theory were developed by Maxwell, Boltzmann and Clausius between 1860-1880's. Kinetic theories are available for gas, solid as well as liquid. However this chapter deals with kinetic theory of gases only.

Postulates of kinetic theory of gases

- 1) Any gas consist large number of molecules. These molecules are identical, perfectly elastic and hard sphere.
- 2) Gas molecules do not have preferred direction of motion, their motion is completely random.
- 3) Gas molecules travels in straight line.
- 4) The time interval of collision between any two gas molecules is very small.
- 5) The collision between gas molecules and the walls of container is perfectly elastic. It means kinetic energy and momentum in such collision is conserved.
- 6) The motion of gas molecules is governed by Newton's laws of motion.
- 7) The effect of gravity on the motion of gas molecules is negligible.

Maxwell's law of distribution of velocities

This law is to find the number of molecules which have a velocity within small interval (ie. c to c + dc).

For deriving this equation Maxwell did following assumptions.

- a) Speed of gas molecules ranges from zero to infinity.
- b) In the steady state, the density of gas remains constant.
- c) Though the speed of the individual molecule changes, definite number of gas molecules have speed between definite range.

Consider a gas containing N number of molecules having velocity c and its X, Y and Z components are u, v and w respectively. From the probability theory, the probability of molecules having velocity component u to u + du is f(u)dusimilarly the probability of molecules having velocity component v to v + dv is f(v)dv and the probability of molecules having velocity component w to w + dw is f(w)dw. Thus the number of molecules whose velocity lies between u to +du, v to v + dv and w to w + dw is given by

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

 $dN = N f(u) f(v) f(w) du dv dw \dots \dots (1)$



If velocity components u, v and walong the three axis. The space formed is called as the velocity space. A molecule having velocity components u, v, w be represented by a point p. Let the small volume $du \, dv \, dw$ around p contains dN number of molecules. Thus molecules have a resultant velocity c is given by $c^2 = u^2 + v^2 + w^2$ Differentiating on both side, we get $0 = 2u \, du + 2v \, dv + 2w \, dw$ $\because c = constant$ $\therefore u \, du + v \, dv + w \, dw = 0$ (2)

The probability density f(u) f(v) f(w) should depend only on the magnitude but not the direction of *c*.

$$\therefore f(u) f(v) f(w) = f(c^2) \quad (where f(c^2) is function of c^2)$$

Differentiating on both side, we get

$$d[f(u) f(v) f(w)] = 0 \qquad \because c^2 = constant$$
$$f'(u)duf(v)f(w) + f'(v) dvf(u)f(w) + f'(w)dwf(v)f(v) = 0$$

Dividing above equation by f(u) f(v) f(w), we get

$$\frac{f'(u)}{f(u)}du + \frac{f'(v)}{f(v)}dv + \frac{f'(w)}{f(w)}dw = 0 \quad \dots \dots \dots (3)$$

Multiplying the equation (2) by an arbitrary constant (β) and adding to equation (3), we get

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

As *du*, *dv* & *dw* can not be zero independently, so we get

$$\frac{f'(u)}{f(u)} + \beta u = 0 \qquad \frac{f'(v)}{f(v)} + \beta v = 0 \qquad \frac{f'(w)}{f(w)} + \beta w = 0$$
$$\frac{f'(u)}{f(u)} = -\beta u$$

Integrating wrt u, we get

 $\log f(u) = -\frac{1}{2} \beta u^{2} + \log a$ (Where log a is integration constant) Taking antilog on both side, we get $f(u) = ae^{-\frac{1}{2}\beta u^{2}} = ae^{-bu^{2}} \qquad (Where, b = -\frac{1}{2} \beta = constant)$ Similarly, $f(v) = ae^{-bv^{2}} \& f(w) = ae^{-bw^{2}}$ Substituting f(u), f(v) & f(w) in eqn (1), we get $dN = N (ae^{-bu^{2}}) (ae^{-bv^{2}}) (ae^{-bw^{2}}) du dv dw$ $dN = Na^{3} e^{-b(u^{2}+v^{2}+w^{2})} du dv dw$ $\because c^{2} = u^{2} + v^{2} + w^{2}$ $dN = Na^{3} e^{-bc^{2}} du dv dw \dots (4)$

In this equation constant *a* and *b* is found to be

 $a = \sqrt{\frac{m}{2\pi kT}}$ and $b = \frac{m}{2kT}$, where *m* is the mass of the gas particle, *k* is Boltzmann constant and *T* is temperature of gas

$$dN = N \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} du \, dv \, dw \dots \dots (5)$$

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This is one form of Maxwell's law of distribution of velocities.



The number of molecules lies within box of volume $du \, dv \, dw$ whose velocity lies within c to c + dc is the same as number of molecules within the spherical shell of inner radius c and outer radius c + dc. Hence volume $du \, dv \, dw$ can be replaced volume of the shell $4\pi c^2 dc$. Therefore equation (5)

becomes

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

The above equation is called as Maxwell's equation of distribution of velocity which gives the value of number molecules dN having velocity c to c + dc.

Mean or Average velocity (C_{av})

The average speed is the sum of all the velocities ranging from 0 to ∞ divided by total number of molecules N.

$$\therefore C_{av} = \frac{\int_0^\infty dN \, X \, c}{N}$$

Substituting the value of dN in in above equation

$$C_{av} = \frac{\int_0^\infty \left(4\pi N \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 dc\right) X c}{N}$$

$$\begin{aligned}
C_{av} &= 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_{0}^{\infty} e^{-\frac{mc^{2}}{2kT}} c^{3} dc \\
C_{av} &= 4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \int_{0}^{\infty} e^{-bc^{2}} c^{3} dc \\
\mathbf{1} & \because \int_{0}^{\infty} e^{-bc^{2}} c^{3} dc = \frac{1}{2b^{2}} \\
(\text{Where } b &= \frac{m}{2kT}) \\
C_{av} &= 4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \frac{1}{2b^{2}} \\
C_{av} &= \sqrt{\frac{4}{\pi b}} \\
\therefore C_{av} &= \sqrt{\frac{4}{\pi (\frac{m}{2kT})}} \\
\therefore C_{av} &= \sqrt{\frac{8kT}{\pi m}}
\end{aligned}$$

Where *m* is the mass of gas molecule. If *M* is molecular weight which can be given by $M = mN_A$. Then $m = \frac{M}{N_A}$ Therefore the above equation becomes.

$$C_{av} = \sqrt{\frac{8kT}{\pi\left(\frac{M}{N_A}\right)}}$$

$$\therefore C_{av} = \sqrt{\frac{8kN_AT}{\pi M}}$$
$$\therefore C_{av} = \sqrt{\frac{8RT}{\pi M}} \qquad \because kN_A = R$$

Root Mean Square Velocity (C_{rms})

The rms speed is the square root of the sum of all the squared velocities ranging from 0 to ∞ divided by total number of molecules N.

$$\therefore C_{rms} = \sqrt{\frac{\int_0^\infty dN \ X \ c^2}{N}}$$

Substituting the value of dN in in above equation

$$C_{rms} = \sqrt{\frac{\int_0^\infty \left(4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 dc\right) X c^2}{N}}{N}$$

$$C_{rms} = \sqrt{4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{mc^2}{2kT}} c^4 dc}$$

$$= \sqrt{4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \int_0^\infty e^{-bc^2} c^4 dc}$$
(Where $b = \frac{m}{2kT}$)

$$= \sqrt{4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} X \frac{3}{8} \left(\frac{\pi}{b^5}\right)^{\frac{1}{2}}}$$
$$= \sqrt{\frac{3}{2b}}$$
$$= \sqrt{\frac{3}{2\left(\frac{m}{2kT}\right)}}$$
$$C_{rms} = \sqrt{\frac{3kT}{m}}$$

Substituting $m = \frac{M}{N_A}$ in above equation. We get

$$C_{av} = \sqrt{\frac{3kT}{\left(\frac{M}{N_A}\right)}}$$

$$\therefore C_{av} = \sqrt{\frac{3kN_AT}{M}}$$

$$\therefore C_{av} = \sqrt{\frac{3RT}{M}} \qquad \because kN_A = R$$

Most Probable Velocity (C_{pr})

The most probable velocity is the velocity possessed by maximum number of molecules. For this condition is,

$$\frac{d[dN]}{dc} = 0$$

$$\therefore \frac{d}{dc} \left(4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 dc \right) = 0$$

$$4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \frac{d}{dc} \left(e^{-\frac{mc^2}{2kT}} c^2 dc \right) = 0$$

$$4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \left(e^{-\frac{mc^2}{2kT}} [2c] + \left[-\frac{2mc}{2kT} \right] e^{-\frac{mc^2}{2kT}} c^2 \right) = 0$$

$$4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} \left(2c - \left[\frac{mc}{kT} \right] c^2 \right) = 0$$

$$2c - \left[\frac{mc}{kT} \right] c^2 = 0$$

$$\therefore \frac{mc^3}{kT} = 2c$$

$$\therefore c^2 = \frac{2kT}{m}$$

$$\therefore c = \sqrt{\frac{2kT}{m}}$$

Thus most probable velocity,

$$C_{pr} = \sqrt{\frac{2kT}{m}}$$

Substituting $m = \frac{M}{N_A}$ in above equation. We get

$$C_{av} = \sqrt{\frac{2kT}{\left(\frac{M}{N_A}\right)}}$$

$$\therefore C_{av} = \sqrt{\frac{2kN_AT}{M}}$$

$$\therefore C_{av} = \sqrt{\frac{2RT}{M}} \qquad \because kN_A = R$$

Relation between C_{pr} , C_{av} & C_{rms}

$$C_{pr}: C_{av}: C_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$
$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$
$$= 1 : \frac{2}{\sqrt{\pi}} : \sqrt{\frac{3}{2}}$$
$$= 1 : 1.128 : 1.228$$

Mean free path

Mean free path of gas molecules is defined as the average distance travelled by a molecule between two successive collisions.

Expression for mean free path



Consider a gas in container having n molecules per unit volume. Let d be the diameter of molecule (A) which is assumed to be in motion, while all other molecules are at rest. The molecule A collides with other molecules like B and C whose centres are at distance d from the centre of molecule

A as shown in the figure. If molecule moves a distance L with velocity v in time t, then this molecule collides with all molecules lying inside a cylinder of volume $\pi d^2 L$.

No. of collisions suffered = No. molecules in the cylinder

by molecule A

of volume $\pi d^2 L$

= No. of molecules per unit volume

X Volume of cylinder

$$= n X \pi d^2 L$$

$$= \pi n d^2 L$$

Now mean free path of molecule is given by $\boldsymbol{\lambda},$

 $\lambda = \frac{\text{Total distance travelled in time t}}{\text{No. of collisions sufferd}}$ $= \frac{L}{-m d^{2}L}$

 $\pi n d^2 L$

also,
$$\lambda = \frac{v t}{\pi n d^2 \overline{v} t} = \frac{v}{\pi n d^2 \overline{v}} \dots (1)$$

where \bar{v} is average velocity of all particles.

Clausius Method

Clausius derived the mean free path by considering the relative velocities of gas molecules to find average velocity.



Consider two molecules are moving with velocities v_1 and v_2 and θ be the angle between them .Then relative v_r is given by,

$$v_r = \sqrt{v_1^2 + v_2^2 - 2v_1v_2\cos\theta} \dots (1)$$

If dn_{θ} is the number of molecules per unit volume in between θ to $\theta + d\theta$ with a given direction the average relative velocity $\overline{v_r}$ is given by

$$\overline{v_r} = \frac{\int v_r dn_\theta}{n} \qquad \dots \dots \dots (2)$$
From eqⁿ (1), we get
$$\overline{v_r} = \frac{\int \left(\sqrt{v_1^2 + v_2^2 - 2v_1v_2\cos\theta}\right) dn_\theta}{n}$$



To find the expression for dn_{θ} , imagine a sphere of radius r and n be the number of molecules lying in sphere again drawing two cones with semi vertical angle $\theta \& \theta + d\theta$ then number of molecules lying in this region is dn_{θ} .

 $n \alpha$ area of sphere

 $dn_{\theta} \quad \alpha \quad area \ of \ zone \ between \ \theta \ to \ \theta + d\theta$

 $\therefore \frac{dn_{\theta}}{n} = \frac{area \ of \ zone \ between \ \theta \ to \ \theta + d\theta}{area \ of \ sphere}$ $= \frac{2\pi r \ \sin \theta \ rd\theta}{4\pi r^2}$ $= \frac{1}{2} \sin \theta \ d\theta$ $dn_{\theta} = \frac{1}{2} n \sin \theta \ d\theta \qquad \dots \dots \dots (3)$ Substituting dn_{θ} in equation (3), we get $\overline{v_r} = \frac{\int \sqrt{v_1^2 + v_2^2 - 2v_1v_2 \cos \theta} \left(\frac{1}{2}n \sin \theta \ d\theta\right)}{n}$

$$\overline{v_r} = \frac{1}{2}n \frac{\int \sqrt{v_1^2 + v_2^2 - 2v_1v_2\cos\theta}\sin\theta \ d\theta}{n}$$

$$\begin{split} \overline{v}_{r} &= \frac{1}{2} \int_{0}^{\pi} \sqrt{v_{1}^{2} + v_{2}^{2} - 2v_{1}v_{2}\cos\theta} \sin\theta \ d\theta \\ \overline{v}_{r} &= \frac{1}{2} \left(\frac{1}{3v_{1}v_{2}} \left[(v_{1}^{2} + v_{2}^{2} - 2v_{1}v_{2}\cos\theta)^{\frac{3}{2}} \right]_{0}^{\pi} \right) \\ \overline{v}_{r} &= \frac{1}{6v_{1}v_{2}} \left[(v_{1}^{2} + v_{2}^{2} + 2v_{1}v_{2})^{\frac{3}{2}} - (v_{1}^{2} + v_{2}^{2} - 2v_{1}v_{2})^{\frac{3}{2}} \right] \\ \overline{v}_{r} &= \frac{1}{6v_{1}v_{2}} \left[(v_{1}^{2} + v_{2})^{3} - (v_{1} - v_{2})^{3} \right] \\ \overline{v}_{r} &= \frac{1}{6v_{1}v_{2}} \left[(v_{1}^{3} + v_{2}^{3} + 3v_{1}^{2}v_{2} + 3v_{1}v_{2}^{2}) - (v_{1}^{3} - v_{2}^{3} - 3v_{1}^{2}v_{2} + 3v_{1}v_{2}^{2}) \right] \\ \overline{v}_{r} &= \frac{1}{6v_{1}v_{2}} \left[2v_{2}^{3} + 6v_{1}^{2}v_{2} \right] \\ \overline{v}_{r} &= \frac{1}{3v_{1}} \left(v_{2}^{2} + 3v_{1}^{2} \right) \dots \dots (4) \end{split}$$

Since close gas molecules have almost same velocity. Hence we can assume that $v_2 \approx v_1 \approx v$

$$\therefore \overline{v_r} = \frac{v^2 + 3v^2}{3v}$$
$$\therefore \overline{v_r} = \frac{4}{3}v$$

Substituting $\overline{v_r}$ in mean free path, λ . We get

$$\lambda = \frac{v}{\pi n \, d^2 \left(\frac{4}{3} v\right)}$$

$$\lambda = \frac{3}{4\pi \, n \, d^2}$$

Maxwell Expression

Maxwell has derived the mean free path by considering the probability of occurrence of the velocities gas molecules to find average velocity.

Introducing probability occurrence v_2 , we get an intermediate average relative velocity \bar{v}_1

$$\bar{v}_1 = \frac{\int_0^\infty \bar{v} dN_2}{N}$$

Where dN_2 is the number of molecules whose velocity ranging from v_2 to $v_2 + dv_2$

$$\therefore \ \bar{v}_1 = \frac{\int_0^\infty \bar{v} \, 4\pi N \left(\frac{b}{\pi}\right)^{\frac{3}{2}} e^{-bv_2^2} \, v_2^2 dv_2}{N}$$

$$\therefore \ \bar{v}_{1} = \frac{4\pi N \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \int_{0}^{\infty} \bar{v} \ e^{-bv_{2}^{2}} \ v_{2}^{2} dv_{2}}{N}$$

$$\therefore \ \bar{v}_1 = 4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \int_{0}^{\infty} \bar{v} \ e^{-bv_2^2} v_2^2 dv_2$$

Since \bar{v} takes different values in for $v_1 > v_2 \left(\frac{v_2^2 + 3v_1^2}{3v_1}\right)$ and $v_2 > v_2 \left(\frac{v_2^2 + 3v_1^2}{3v_1}\right)$

$$v_{1}\left(\frac{v_{1}^{2}+3v_{2}^{2}}{3v_{2}}\right)$$

$$\therefore \ \bar{v}_{1} = 4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \left\{ \int_{0}^{c_{1}} \left(\frac{v_{2}^{2}+3v_{1}^{2}}{3v_{1}}\right) e^{-bv_{2}^{2}} v_{2}^{2} dv_{2} + \int_{c_{1}}^{\infty} \left(\frac{v_{1}^{2}+3v_{2}^{2}}{3v_{2}}\right) e^{-bv_{2}^{2}} v_{2}^{2} dv_{2} \right\}$$

Introducing the probabilities of occurrence of v_1 , we get the final average \bar{v}_2 for relative velocity

$$\begin{split} \bar{v}_{2} &= 4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \int_{0}^{\infty} \bar{v}_{1} \ e^{-bv_{1}^{2}} \ v_{1}^{2} dv_{1} \\ \therefore \ \bar{v}_{2} &= 4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \int_{0}^{\infty} \left[4\pi \left(\frac{b}{\pi}\right)^{\frac{3}{2}} \left\{ \int_{0}^{c_{1}} \left(\frac{v_{2}^{2} + 3v_{1}^{2}}{3v_{1}}\right) \ e^{-bv_{2}^{2}} \ v_{2}^{2} dv_{2} \\ &+ \int_{c_{1}}^{\infty} \left(\frac{v_{1}^{2} + 3v_{2}^{2}}{3v_{2}}\right) \ e^{-bv_{2}^{2}} \ v_{2}^{2} dv_{2} \\ \right\} \right] \ e^{-bv_{1}^{2}} \ v_{1}^{2} dv_{1} \\ \therefore \ \bar{v}_{2} &= \frac{16b^{3}}{\pi} \int_{0}^{\infty} \left[\left\{ \int_{0}^{c_{1}} \left(\frac{v_{2}^{2} + 3v_{1}^{2}}{3v_{1}}\right) \ e^{-bv_{2}^{2}} \ v_{2}^{2} dv_{2} \\ &+ \int_{c_{1}}^{\infty} \left(\frac{v_{1}^{2} + 3v_{2}^{2}}{3v_{2}}\right) \ e^{-bv_{2}^{2}} \ v_{2}^{2} dv_{2} \\ \end{bmatrix} \right] \ e^{-bv_{1}^{2}} \ v_{1}^{2} dv_{1} \end{split}$$

$$\therefore \bar{v}_2 = \frac{16b^3}{\pi} [J_1 + J_2]$$

Where

$$J_{1} = \int_{0}^{\infty} \left\{ \int_{0}^{c_{1}} \left(\frac{v_{2}^{2} + 3v_{1}^{2}}{3v_{1}} \right) e^{-bv_{2}^{2}} v_{2}^{2} dv_{2} \right\} e^{-bv_{1}^{2}} v_{1}^{2} dv_{1}$$

&

$$J_{2} = \int_{0}^{\infty} \left\{ \int_{c_{1}}^{\infty} \left(\frac{v_{1}^{2} + 3v_{2}^{2}}{3v_{2}} \right) e^{-bv_{2}^{2}} v_{2}^{2} dv_{2} \right\} e^{-bv_{1}^{2}} v_{1}^{2} dv_{1}$$

Integral $J_1 \& J_2$ can be calculated and given by

$$\begin{aligned} \mathbf{2} \quad J_1 &= J_2 = \frac{1}{8\sqrt{2}} \left(\frac{\pi}{b^7}\right)^{\frac{1}{2}} \\ \therefore \ \bar{v}_2 &= \frac{16b^3}{\pi} [J_1 + J_2] \\ \therefore \ \bar{v}_2 &= \frac{16b^3}{\pi} \left[2 X \frac{1}{8\sqrt{2}} \left(\frac{\pi}{b^7}\right)^{\frac{1}{2}} \right] \\ \therefore \ \bar{v}_2 &= \frac{4}{\sqrt{2\pi b}} = \sqrt{\frac{8}{\pi b}} \\ \therefore \ \bar{v}_2 &= \sqrt{\frac{8}{\pi \left(\frac{m}{2kT}\right)}} \\ \therefore \ \bar{v}_2 &= \sqrt{\frac{2X \ 8kT}{\pi m}} \end{aligned}$$

$$\therefore \bar{v}_2 = \sqrt{2} \sqrt{\frac{8kT}{\pi m}}$$
$$\therefore \bar{v}_2 = \sqrt{2} \sqrt{\frac{8kT}{\pi m}}$$
$$\therefore \bar{v}_2 = \sqrt{2}v$$

Where v is the average velocity of molecule having mass m

Therefore the mean free path, λ becomes

$$\lambda = \frac{v}{\pi n d^2(\sqrt{2}v)}$$
$$\lambda = \frac{1}{\sqrt{2}\pi n d^2}$$

Brownian Motion

Botanist Brown observed under a high power microscope that when pollen grains suspended in liquid were moving rapidly and constantly in random fashion in all direction. This irregular motion of particles suspended in liquid is called Brownian motion.

Salient features of Brownian motion

- i) The motion is continuous , irregular and random,
- ii) The motion is independent of mechanical vibration.
- iii) The smaller the size of the particle, greater is the motion and vice-versa.

- iv) The lower is the viscosity of the liquid, greater is the motion and vice-versa.
- v) The higher is the temperature, greater is the motion and viceversa.

Einstein's theory of Brownian motion

Brownian motion is acted upon three kind of forces

- 1) The unbalanced force due to collision of unbalanced molecules in the opposite direction.
- 2) The viscous drag which opposes the Brownian motion.
- 3) Force due to difference in the osmotic pressure(ie. due to the difference in the concentration)



Imagine a cylinder with its axis along X axis whose surfaces P and Q are separated by a distance $\Delta(\Delta \text{ is root mean square} \text{ distance})$. Let A be the cross section area of the cylinder. Let n₁ and n₂ be the concentration of the particles per unit volume at the surfaces P and Q respectively.

Imagine two more cylinders on both sides of P and Q as shown in the figure.

The number of Brownian particles in the cylinder on the P side = $n_1 \Delta A$ The number of Brownian particles crossing at P side

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

The number of Brownian particles in the cylinder on the Q side = $n_2 \Delta A$

The number of Brownian particles crossing at Q side $=\frac{1}{2}n_2\Delta A$

So the total number of particles crossing the middle section R from left to right $=\frac{1}{2}(n_1 - n_2) \Delta A \dots (1)$

³ By the definition of diffusion co-efficient, the number of particles crossing the middle section R from left to right = $-D \frac{dn}{dx} A t \dots \dots (2)$

Where D = diffusion coefficient, $\frac{dn}{dx}$ concentration grdient and t is the time taken for diffusion.

From equation (1)&(2)

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

$$\therefore -\frac{1}{2}\frac{dn}{dx} \Delta^2 A = -D\frac{dn}{dx}A t$$

$$\therefore D = \frac{\Delta^2}{2t}\dots(3)$$

4 Let P₁ and P₂ be the osmotic pressure acting on the surfaces P and Q respectively.

Then $P_1 = n_1 kT \& P_2 = n_2 kT$

 \therefore Pressure difference = $P_1 - P_2 = (n_1 - n_2)kT$

The force exerted due to this pressure difference

 $= (n_1 - n_2)kTA$

This force acts on all the particles in the cylinder PQ in which the number of particles, where $n = \frac{n_1 + n_2}{2}$

: Force experience by each particle, $F = \frac{(n_1 - n_2)kTA}{n\Delta A}$

$$\therefore F = \frac{(n_1 - n_2)kT}{n\Delta}$$
$$\therefore \frac{(n_1 - n_2)}{\Delta} = -\frac{dn}{dx}$$
$$\therefore F = -\frac{kT}{n}\frac{dn}{dx}\dots\dots(4)$$

Simultaneously particle also experience viscous drag (stokes law) , which is given by

 $F = 6\pi\eta r\nu \dots (5)$

Where η is the coefficient of viscosity

r is the radius of particles

v is the velocity of the particles

From equation (4) & (5)

$$F = -\frac{kT}{n}\frac{dn}{dx} = 6\pi\eta rv$$
$$\frac{nv}{\frac{dn}{dx}} = -\frac{kT}{6\pi\eta r}$$

Where nv is number of particles moving from left to right through unit area in unit time and hence $\frac{nv}{-\frac{dn}{dx}}$ gives diffusion coefficient D

coefficient D

$$\therefore D = \frac{kT}{6\pi\eta r}\dots(6)$$

From equation (3) & (6)

$$\frac{\Delta^2}{2t} = \frac{kT}{6\pi\eta r}$$
$$\therefore k = \frac{R}{N_A}$$
$$\therefore \frac{\Delta^2}{2t} = \frac{RT}{6\pi N\eta r}$$
$$\therefore \Delta^2 = \frac{RT}{N} \frac{t}{3\pi\eta r}$$

The above equation is Einstein's equation which gives the value of square of rms displacement of Brownian particles.