

Study Material - Sem. 3 - CGT -

Kinetic Theory of Gases - Dr. T. Ker-

Class 4

Diffusion: Diffusion is the phenomenon arising out of transference of mass due to difference in concentration and results finally in equilibrium distribution in concentration.

Diffusion may be of two types: one is self-diffusion  $\rightarrow$  when it occurs in a single gaseous system, and the other is interdiffusion  $\rightarrow$  when two different gases communicate with each other. Here, we discuss self-diffusion only.

Let us consider the fig. 1, and assume that the concentration of molecules in the reference plane is  $n$ . Let the elementary volume  $dv$  is at a distance  $r$  from an area  $dA$  of the reference plane. Then it is a vertical height

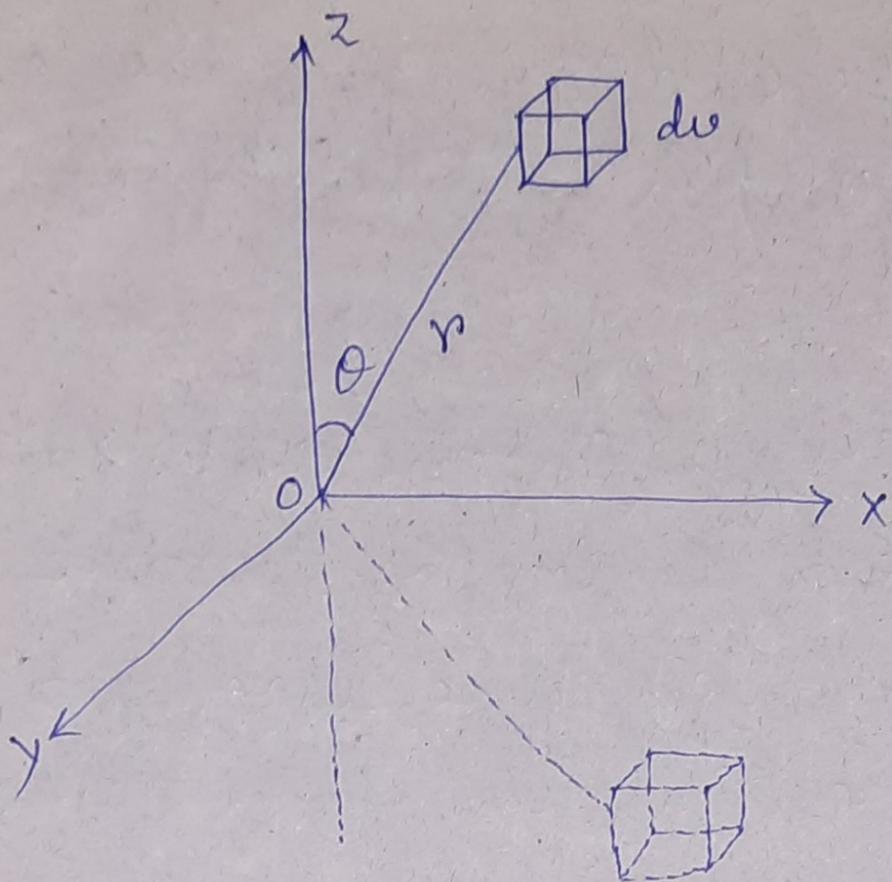


Fig. 1.

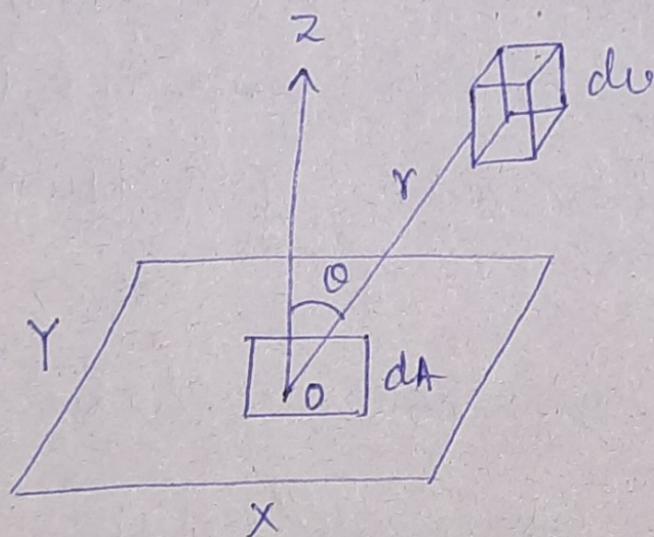


Fig. 2.

$z = r \cos \theta$ . Number of molecules/volume at the specified layer is  $\left[ n + r \cos \theta \frac{dn}{dz} \right]$  and that at a similar layer below the reference plane is  $\left[ n - r \cos \theta \frac{dn}{dz} \right]$ .

The number of molecules moving with velocities between  $c$  and  $c+dc$  and contained in the volume  $dv$  is given by —

$$4\pi \left[ n + \frac{dn}{dz} r \cos \theta \right] a^3 e^{-bc^2} c^2 dc dv$$

If  $P_c$  be the collision probability then no. of collisions in time  $dt$  is —

$$\left( \frac{1}{2} P_c \right) 4\pi \left[ n + \frac{dn}{dz} r \cos \theta \right] a^3 e^{-bc^2} c^2 dc dv dt$$

As a result of collisions, no. of new paths emanating or the no. of molecules coming out of the volume  $dv$  in time  $dt$  is —

$$\left( \frac{c}{\lambda} \right) 4\pi \left[ n + \frac{dn}{dz} r \cos \theta \right] a^3 e^{-bc^2} c^2 dc dv dt$$

The molecules come out in all possible directions <sup>from</sup> <sub>and</sub> contained within a solid angle equal to  $4\pi$ . How many of them will be heading towards the area  $dA$  of the reference plane will be determined by the solid angle subtended by  $dA$  at the elementary

volume. This solid angle is  $\frac{dA \cos \theta}{r^2}$ .  
 The number of molecules heading towards the area  $dA$  is given by —

$$\left(\frac{dA \cos \theta}{4\pi r^2}\right) \left(\frac{c}{\lambda}\right) 4\pi \left[n + \frac{dn}{dz} r \cos \theta\right] a^3 e^{-bc^2} c^2 dc d\theta dt$$

Out of them, some will suffer collisions in their journey to the destination (i.e.,  $dA$ ) and will be wiped out.

The number of molecules which come out of the volume  $dv$  as a result of collision in time  $dt$  and reach the area  $dA$  is —

$$\begin{aligned} & \left(\frac{dA \cos \theta}{4\pi r^2}\right) \left(\frac{c}{\lambda}\right) 4\pi \left[n + \frac{dn}{dz} r \cos \theta\right] a^3 e^{-bc^2} c^2 dc dt \\ & (r^2 dr \sin \theta d\theta d\phi) e^{-r/\lambda} \\ & = a^3 dA dt \left[n + \frac{dn}{dz} r \cos \theta\right] (c^3 e^{-bc^2} dc) \left(\frac{e^{-r/\lambda}}{\lambda} dr\right) \\ & (\sin \theta \cos \theta d\theta) d\phi \end{aligned}$$

$\therefore$  Total number of molecules crossing the area  $dA$  in time  $dt$  downwards is given by —

$$N_{\downarrow} = a^3 dA dt \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \left[n + \frac{dn}{dz} r \cos \theta\right] [c^3 e^{-bc^2} dc] \left[\frac{e^{-r/\lambda}}{\lambda} dr\right] [\sin \theta \cos \theta d\theta] d\phi$$

Similarly,

Total no. molecules crossing the area  $dA$  in time  $dt$  upwards is given by —

$$N \uparrow = a^3 dA dt \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \left[ n - \frac{dn}{dz} r \cos \theta \right] \left[ c^3 e^{-bc^2} dc \right] \left[ \frac{e^{-r/\lambda}}{\lambda} dr \right] \left[ \sin \theta \cos \theta d\theta \right] d\phi$$

$\therefore$  The net number of molecules crossing  $\frac{dA}{\lambda}$  <sup>The area</sup> downwards in time  $dt$  is —

$$N = 2a^3 dA dt \int_0^{\infty} c^3 e^{-bc^2} dc \int_0^{\infty} \frac{r e^{-r/\lambda}}{\lambda} dr \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin \theta \cos^2 \theta d\theta \left( \frac{dn}{dz} \right)$$

$$= 2a^3 dA dt \left( \frac{dn}{dz} \right) (2\pi) \int_0^{\infty} c^3 e^{-bc^2} dc \int_0^{\infty} \frac{r e^{-r/\lambda}}{\lambda} dr \int_0^{\pi/2} \sin \theta \cos^2 \theta d\theta$$

↳ (1)

Now,  $\int_0^{\infty} \frac{r e^{-r/\lambda}}{\lambda} dr = \lambda$

$$\int_0^{\pi/2} \sin \theta \cos^2 \theta d\theta = \frac{1}{3}$$

$$\begin{aligned} \int_0^{\infty} c^3 e^{-bc^2} dc &= \int_0^{\infty} \left( \frac{z}{b} \right) e^{-z} \frac{dz}{2b} \\ &= \frac{1}{2b^2} \int_0^{\infty} z^{2-1} e^{-z} dz = \frac{1}{2b^2} \Gamma(2) \\ &= \frac{1}{2b^2} \end{aligned}$$

$$\left[ \begin{array}{l} \text{Let, } bc^2 = z \\ \therefore 2bc dc = dz \\ \therefore \frac{dz}{2b} = c dc \\ c^2 = \frac{z}{b} \quad \left| \begin{array}{l} c=0 \rightarrow z=0 \\ c=d \rightarrow z=d \end{array} \right. \end{array} \right.$$

From (1),

$$N = 2a^3 dA dt \left( \frac{dn}{dz} \right) (2\pi) \left( \frac{1}{2b^2} \right) \lambda \left( \frac{1}{3} \right)$$

$$= \left(\frac{2}{3}\right) \pi \lambda \frac{a^3}{b^2} dA dt \left(\frac{dn}{dz}\right)$$

$$= \left(\frac{2}{3}\right) \frac{\pi \lambda}{\pi} \sqrt{\frac{2RT}{m\pi}} dA dt \left(\frac{dn}{dz}\right)$$

$$= \left(\frac{2}{3}\right) \sqrt{\frac{8RT}{m\pi}} dA dt \left(\frac{dn}{dz}\right)$$

$$= \frac{\lambda}{3} \bar{c} dA dt \left(\frac{dn}{dz}\right) \rightarrow (2)$$

Now,

$$a^3 = \left(\frac{m}{2\pi KT}\right)^{3/2} = \left(\frac{b}{\pi}\right)^{3/2}$$

$$b^2 = \left(\frac{m}{2RT}\right)^2, \quad b = \frac{m}{2RT}$$

$$\frac{a^3}{b^2} = \frac{b^{3/2}}{b^2 \pi^{3/2}} = \frac{1}{\sqrt{b} \pi^{3/2}}$$

$$= \sqrt{\frac{2RT}{m}} \times \frac{1}{\sqrt{\pi^3}}$$

$$= \sqrt{\frac{2RT}{m\pi}} \left(\frac{1}{\pi}\right)$$

$$\bar{c} = \text{average velocity}$$

$$= \sqrt{\frac{8RT}{m\pi}}$$

Now, The coefficient of diffusion,  $D$ , is defined as the

number crossing unit area in unit time for unit concentration gradient, i.e.,  $\frac{dn}{dz} = 1$ .

Therefore, from (2),  $D = \frac{1}{3} \lambda \bar{c}$

Now,  $\eta = \frac{1}{3} \rho \bar{c} \lambda \Rightarrow D = \eta / \rho$

### Discussions:

A. Expression for coefficient of viscosity:—

$$\eta = \frac{1}{3} \rho \bar{c} \lambda, \quad \lambda = \frac{1}{\sqrt{2} n \pi \sigma^2} \quad (\text{Maxwell's mean free path})$$

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

$$\therefore \eta = \frac{1}{3} \rho \sqrt{\frac{8RT}{m\pi}} \left(\frac{1}{\sqrt{2} n \pi \sigma^2}\right) \rightarrow (3)$$

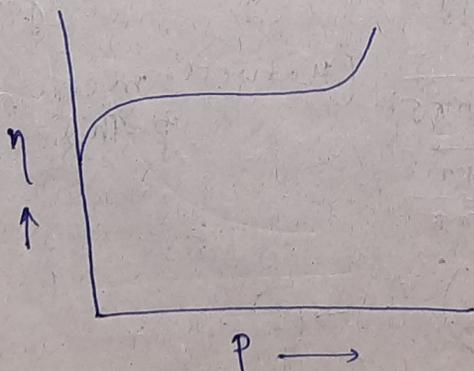
From eq. (3), a few informations are readily available.

i)  ~~$\eta$  is~~, ~~so it can say~~  ~~$\eta$  is~~ independent of pressure, because none of  $m$ ,  $\bar{c}$ ,  $\sigma$  is a function of pressure.

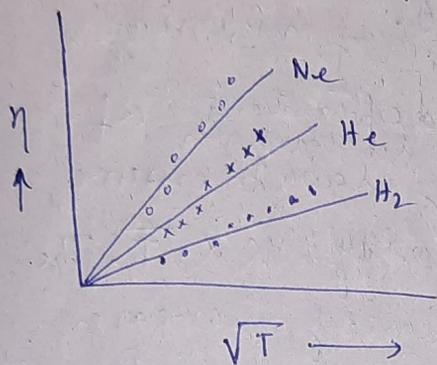
But at extremely low pressure, this information falls short of truth, because

Then the mean free path becomes comparable to the dimension of the apparatus and as a result, the collisions are few and far between, so that our assumption in the deduction of  $\eta$  no longer holds.

At extremely high pressure also, this inference is found to be at invariance. This departure may be due to the fact that the mean free path becomes equal to the molecular diameter, so the transport is not through.



(ii) Effect of temperature: Since  $\bar{c} \propto \sqrt{T}$ ,  $\eta$  is found to be proportional to  $\sqrt{T}$  i.e., square root of absolute temperature. So, unlike most of the



liquids, the viscosity of gases increases with  $T$ . The agreement with predicted  $\sqrt{T}$  is rather satisfactory but the experiments show that

the variation is much more rapid. This is because we considered the molecules as rigid elastic spheres with no mutual interaction between them. In fact, they are surrounded by a force field repulsive in nature. When the temperature increases, so does the velocity of molecules and they penetrate into each other's force field to some extent. As a result of interpenetration, the effective size of molecules decreases at higher temperatures resulting in an increase in the value of  $\eta$  [eq. (3)].

B. Expression for Thermal conductivity,

$$K = \eta c_v = \frac{1}{3} \rho c_v \sqrt{\frac{8KT}{m\pi}} \left( \frac{1}{\sqrt{2} n \pi \sigma^2} \right) \rightarrow (4)$$

Now, variation of  $\lambda$  is small, therefore the variation of  $K$  with pressure and temperature follows, in general, the same course as the variation of viscosity.

Thus conductivity is independent of pressure, <sup>except at very high and low pressures</sup> At extremely low pressure,  $K$  decreases. As in viscosity,  $K \propto \sqrt{T}$ . The conductivity, like viscosity, increases for all gases more rapidly than <sup>the</sup> square root of absolute temperature.

C. Expression for Diffusion,

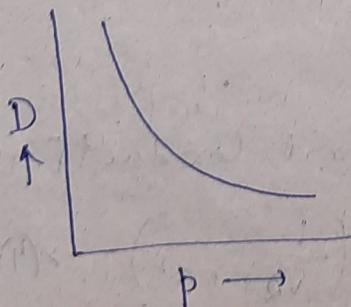
$$D = \frac{1}{3} \bar{c} \lambda = \frac{\bar{c}}{3\sqrt{2} \pi n \sigma^2}$$

Effect of temperature & pressure:

Now,  $D \propto \frac{1}{n}$  i.e.,  $D \propto \frac{T}{p}$  (as  $p = nkT$ )

and  $D \propto \bar{c}$  i.e.,  $D \propto \sqrt{T}$

Therefore,  $D \propto p^{-1} T^{3/2}$



At a fixed temperature,  $D$  is inversely proportional to pressure. It holds quite well with experiment.

But the variation of

D with temperature is not as  $T^{3/2}$  or  $T^{1.5}$ . The power of T actually lies between 1.75 and 2. This more rapid variation of D with temperature is due to the attractive forces between the molecules.

## Brownian Motion

British botanist Robert Brown observed in 1827 a peculiar phenomenon while working with pollen grains. He observed that when pollen grains are suspended in water and viewed under a high power microscope, they show a continuous, random, erratic motion, consisting of translations and rotations, and performing, as it were, a wild fantastic dance with no sign of abatement or stoppage. Subsequently, it transpired that the phenomenon is not restricted to pollen grains alone; neither is it connected with the biological origin of the particles, nor specifically with water has anything to do with it. For instance, such chaotic movements are performed

by particles of smoke in still air.

In fact, if any colloidal solution is observed under high power microscope (better, ultramicroscope), the suspended particles exhibit such an eternal, irregular, to-and-fro-motion. In the field of view of the microscope, each particle is seen to spin, rise, sink and rise again. This phenomenon of chaotic motion of colloidal particles suspended in a liquid or a gas was termed Brownian motion, after Brown who was neither the first to observe it, nor could interpret it.

### Salient Features of Brownian Motion

The following salient features of Brownian motion are the outcome of special investigations carried out painstakingly by a number of workers over a number years:

- i) The motion is continuous, eternal, irregular and random. No two particles in close vicinity move in the same direction at the same time.

This shows that the cause does not lie in eddies, convection or streaming motion of the fluid.

- ii) The motion is independent of the mechanical vibration, say the shaking of the container.
- iii) The smaller the particle size, greater is the motion.
- iv) The lower the viscosity of the liquid (or gas), greater <sup>is</sup> the motion and conversely.
- v) The higher the temperature, greater is the motion and conversely. Two particles of the same size move equally fast at the same temperature.

Explanation: It is thus established that the Brownian motion cannot but be due to the continuous impact received by the suspended particles from moving molecules of the liquid or gas due to their ever-existing heat motion. Naturally every particle is subjected to such impacts from all sides every instant and due to the complete disorder of

molecular movements, it is expected that the number of impacts received by a particle from one direction should, on the average, equal to the number of impacts from opposite direction. The particles should therefore remain stationary. This is exactly what will occur if the particles are too large. But if the particle-size be small enough ( $\sim 10^{-4}$  to  $10^{-5}$  cm) - colloidal particles - matters are different.

Since the molecular motion is chaotic, the number of impacts averaged over a sufficiently long time from different directions is the same.

However, deviations from average values are inevitable in a statistical system such as fluid. Such deviations from mean values which occur in a small volume or during a small time-interval are called fluctuations.

For a body of ordinary size in a fluid, the number of impacts received is too large to note

either separate impacts or a random prominence of impact in one direction over another. For too small particles, the total number of impacts is comparatively small and the prevalence first in one direction and then in another becomes noticeable. It is exactly such fluctuations that give the particles a perceptible motion, opposed only by the viscous drag of the fluid. But the molecular motion is chaotic; so the prominence in one direction would be randomised. This therefore is the motion of a Brownian particle.

The importance of the Brownian motion is that it provides the direct proof of the motion of molecules - the corner stone of kinetic theory.

Brownian movement is not the movement of the molecules. What we observe is not the result of impact of one molecule, but rather the result of a number of impacts in one direction prevailing over those in the opposite direction.

Brownian movement is explained by a resultant force in a direction owing to a chance difference between the number of impacts against a particle from different directions. Since fluctuations usually last for only a short while, the direction of the resultant will change very rapidly, and along with <sup>it</sup> the direction of motion of the particle. This gives the chaotic nature of the Brownian movement which in <sup>its</sup> turn reflects the chaotic nature of molecular motion.