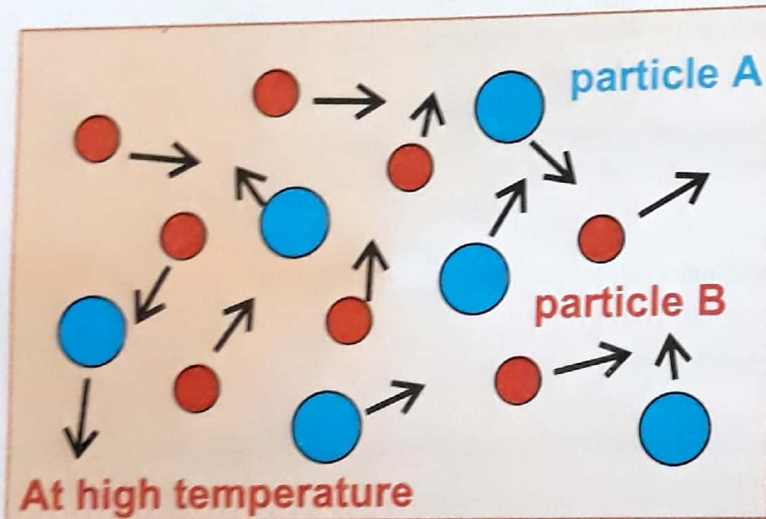


Transport Phenomena in Gases

3

AT A GLANCE

- Introduction
- Molecular Collision
- Mean Free Path (λ)
- Sphere of Influence
- Collision Cross-section
- Expression for Mean Free Path
- Variation of λ with Temperature and Pressure
- Transport Phenomena
- Viscosity (Coefficient η)
- Effect of Temperature on η
- Effect of Pressure on η
- Thermal Conductivity (Coefficient K)
- Relation Between η and K
- Effect of Temperature on K
- Effect of Pressure on K
- Largest Thermal Conductivity of Hydrogen
- Self Diffusion (Coefficient D)
- Effect of Temperature and Pressure on D
- Relation Between η and D



INTRODUCTION

In the kinetic theory of gases, it is assumed that the molecules of a gas are all identical and perfectly elastic spheres of negligible but finite size. Due to haphazard motion, the molecules constantly collide on each other. At room temperature, an air molecule suffers about 4×10^9 collisions per second and travels a mean free path about 10^{-7} m. When the gas is not in equilibrium, the random *i.e.*, haphazard motion of gas molecules give rise to viscosity, conductivity and diffusion, when it tries to attain an equilibrium state by transporting momentum, heat and mass respectively.

3.1 Molecular Collisions

According to kinetic theory of gases, the molecules are of finite size. During the random motion of gas molecules in all possible directions and with all possible velocities, they collide with each other. Between two successive collisions, a molecule moves with a constant speed, along a straight line as shown in Fig. 3.1. These collisions are known as molecular collisions.

3.2 Mean Free Path (λ)

At a given temperature, the molecules suffer continuous collisions with one another. Between any two collisions, the molecule travels freely a certain distance in a straight line. This distance is known as **free path**. Thus, the path covered by a gas molecule between any two consecutive collisions in a straight line is called the free path. The direction of the molecule is changed after every collision. After a number of collisions, the total path appears to be zig-zag and free path is not constant as shown in Fig. 3.1. Therefore, a term mean free path is used and is defined as the average distance travelled by a gas molecule between two successive collisions. It is denoted by λ . If the total distance travelled after N collisions is S , then mean free path (λ) is given by

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

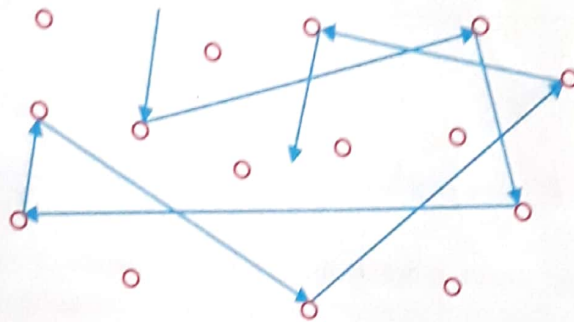


Fig. 3.1

Mean free time (τ): The average time taken by a gas molecule between two successive collisions is called mean free time (τ) and is given by

$$\tau = \frac{\lambda}{C}$$

where C is the average velocity of a gas molecule.

3.3 Sphere of Influence

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 directions. In doing so, they are continuously colliding against each other. For the sake of simplicity of calculations, it is assumed that the molecule under consideration say A , is in motion, all other molecules are at rest Fig. (3.2). Let σ be the diameter of each gas molecule. Taking the centre of molecule A as a centre, if we draw a sphere of radius σ , then molecule A will collide with all those molecules whose centres lie within this sphere. Such a sphere is called 'sphere of influence'.

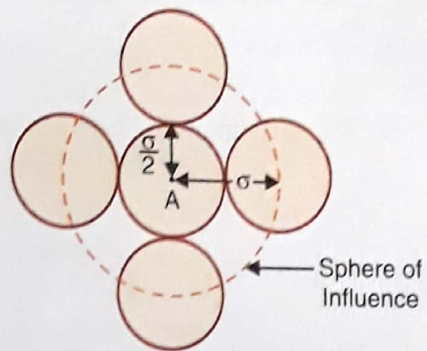


Fig. 3.2

3.4 Collision Cross-section

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 the collision cross-section as shown by dotted lines in Fig. 3.2. It is the effective area which determines the probability that a molecule of diameter σ will collide with another molecule of the same diameter.

3.5 Expression for Mean Free Path (Clausius' Expression)

Suppose the molecules of a gas are all identical perfectly elastic spheres, each of diameter σ . It is assumed that the molecules do not exert any force on each other. To simplify the calculations, we further assume that (1) only the molecule under consideration is in motion while all other molecules are at rest. The sphere of influence of the molecule has a radius σ i.e. equal to the diameter of the molecule Fig. 3.3.

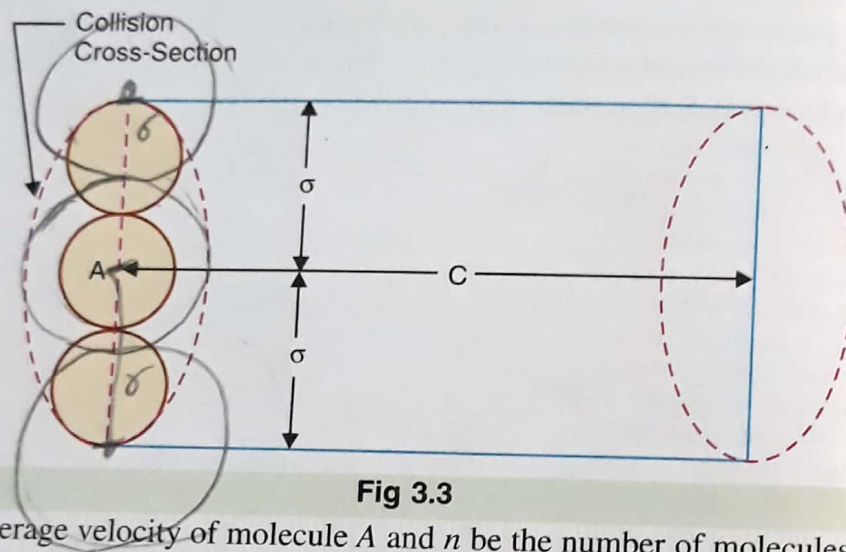


Fig 3.3

Let c be the average velocity of molecule A and n be the number of molecules per unit volume. Then in one second, A will collide with all the molecules whose centres lie within a cylinder of radius σ and length c .

No. of molecules in the cylinder

$$= \pi\sigma^2 cn$$

No. of collisions made by molecule A in 1 second

$$= \pi\sigma^2 cn$$

\therefore 1 Collision takes place in $\frac{1}{\pi\sigma^2 cn}$ seconds.

The time interval between two successive collisions

$$= \frac{1}{\pi\sigma^2 cn} \text{ seconds}$$

\therefore Distance travelled between two successive collisions

$$= \text{speed} \times \text{time}$$

$$= c \times \frac{1}{\pi\sigma^2 cn}$$

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

\therefore Mean free path, $\lambda = \frac{1}{\pi\sigma^2 n}$

This is Clausius' expression for the mean free path.

Maxwell's Formula

The above expression (3.1) is not exact because it is based on the assumption that only one molecule under consideration is in motion while all other are at rest. If the motion of all the molecules is taken into account and the Maxwell's law of distribution of molecular velocities is applied, which must hold in steady state, the corrected formula for mean free path is

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n} \quad \dots(3.2)$$

This is Maxwell's formula for the mean free path.

If λ and n are known, the molecular diameter σ can be calculated. Collision frequency is $f = \frac{c}{\lambda}$ where c is average velocity of the gas molecule.

3.6 Variation of λ with Temperature and Pressure

Consider 1 mole of an ideal gas. Then

$$PV = RT$$

Dividing both sides by N , the Avogadro's number, we have,

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

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

\therefore The pressure P of a gas is given by

$$P = n k T \quad \dots(3.3)$$

Where, $n = \frac{N}{V}$, the no. of molecules per unit volume and $k = \frac{R}{N}$, the Boltzmann's constant.

Equation (3.3) gives, $n = \frac{P}{kT}$

Substituting for n in equation (3.2), the mean free path

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

$$\lambda = \frac{kT}{\sqrt{2} \pi \sigma^2 P} \quad \dots(3.4)$$

or

Thus, the mean free path varies directly as the absolute temperature (T) and inversely as the pressure.

3.7 Transport Phenomena

According to the kinetic theory of gases, the molecules of a gas are in a state of thermal agitation. The gas, therefore, attains a steady state or equilibrium state by transporting momentum, heat (thermal energy) and mass from one layer of a gas to another layer, giving rise to the viscosity, conductivity and diffusion respectively and the phenomena is called transport phenomena.

The transport phenomena occur only in the non-equilibrium state of a gas.

3.8 Viscosity: Transport of Momentum

The different layers of a non-equilibrium gas may have different velocities. This will result in the relative motion of the different layers with respect to one another. In such a case, the layer moving faster will impart momentum to the layer moving slower to bring about an equilibrium state. Thus, the transport of momentum gives rise to the phenomenon of viscosity.

86 • Heat, Thermodynamics and Statistical Physics

Consider a gas flowing over a horizontal surface OX from left to right. The velocity of the layer in contact with the surface OX is zero and goes on increasing along OZ at a uniform rate $\frac{dv}{dz}$, known as velocity gradient (Fig 3.4).

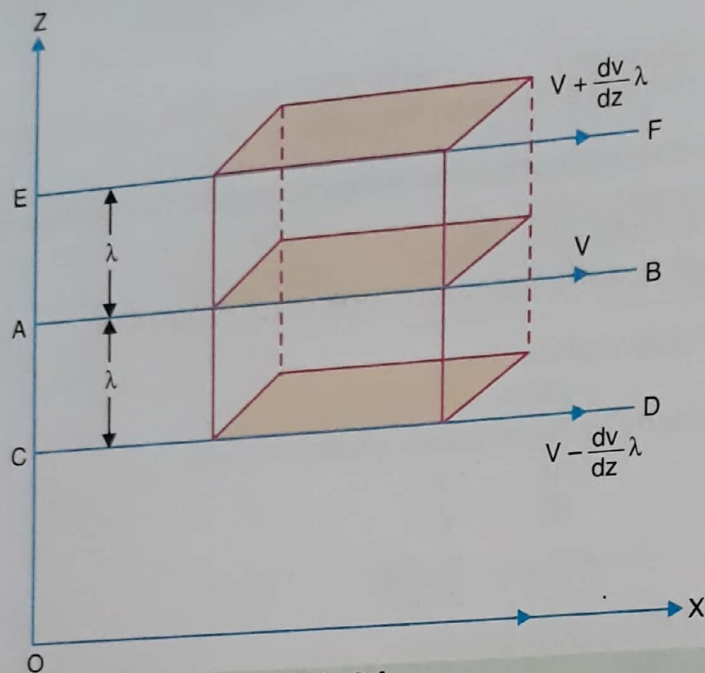


Fig 3.4

Let us consider a layer AB moving with a drift velocity V , situated at a distance Z from O . All the molecules in this layer have the same drift velocity. Consider two more layers EF and CD just above and below AB respectively at a distance λ equal to the mean free path of the molecules, so that the molecules moving vertically up or down do not suffer any collision while moving between the two layers.

$$\text{The velocity of the gas in the layer } EF = V + \frac{dv}{dz} \lambda$$

$$\text{and the velocity of the gas in the layer } CD = V - \frac{dv}{dz} \lambda$$

Due to thermal agitation, the gas molecules are moving in all directions, thus, the average number of molecules along any one (+ve or -ve) axis will be $\frac{1}{6}$ th of the total number of molecules in the gas.

Let n be number of molecules per unit volume,

m be the mass of each gas molecule,

c be the average velocity of a molecule at a given temperature of the gas, then

Number of molecules passing downwards from EF to CD per unit area of the AB in one second

$$= \frac{nc}{6}$$

\therefore Forward momentum lost per unit area per second by the layer EF

$$= m \times \frac{nc}{6} \times \left(V + \frac{dv}{dz} \lambda \right)$$

Similarly, the number of molecules passing upwards from CD to EF per unit area of the layer AB in one second is also

$$= \frac{nc}{6}$$

∴ Forward momentum gained per unit area per second by the layer EF

$$= m \times \frac{nc}{6} \times \left(v - \frac{dv}{dz} \lambda \right)$$

∴ Net momentum lost by the layer EF per unit area per second

$$= \frac{mnc}{6} \left\{ \left(v + \frac{dv}{dz} \lambda \right) - \left(v - \frac{dv}{dz} \lambda \right) \right\}$$

$$= \frac{1}{3} mnc \lambda \frac{dv}{dz}$$

The layer CD below AB gains the same amount of momentum. Hence, the layer EF above AB tends to accelerate its motion and the layer CD below AB tends to retard its motion.

The backward dragging force per unit area = gain or loss of momentum per unit area per second.

$$\therefore F = \frac{1}{3} mnc \lambda \frac{dv}{dz} \quad \dots(3.5)$$

This must be equal to the viscous or tangential force $\left(\eta \frac{dv}{dz} \right)$ acting per unit area of the layer AB , η being the coefficient of viscosity of the gas.

$$\therefore \eta \frac{dv}{dz} = \frac{1}{3} mnc \lambda \frac{dv}{dz}$$

$$F = -\eta A \frac{dv}{dz}$$

or $\eta = \frac{1}{3} mnc \lambda$

or $\eta = \frac{1}{3} \rho c \lambda \quad \dots(3.6)$

where $\rho = mn$, the density of the gas

3.9 Effect of Temperature on η

The density (ρ) of the gas decreases with increase in temperature but λ , the mean free path increases in the same proportion so that $\rho\lambda$ remains constant. Since the average molecular speed c is directly proportional to the square root of its absolute temperature ($c \propto \sqrt{T}$), the coefficient of viscosity (η) will also be proportional to \sqrt{T} .

Therefore,

$$\eta \propto \sqrt{T} \quad \dots(3.7)$$

In other words, the coefficient of viscosity of a gas increases with increase in temperature.

3.10 Effect of Pressure on η

The density (ρ) of a gas increases with increase in pressure but λ , the mean free path decreases in the same proportion, so that $\rho\lambda$ remains constant. Moreover, the average molecular speed c is independent of pressure. Thus, using relation

$$\eta = \frac{1}{3} \rho c \lambda$$

η , the coefficient of viscosity is independent of pressure.

3.11 Thermal Conductivity: Transport of Thermal Energy ✓

The different layers of a gas may have different temperatures. The molecules will carry kinetic energy (heat) from regions of higher temperature to the region of lower temperature to bring about an

equilibrium state. Thus, the transport of thermal energy (thermal) gives rise to the phenomenon of thermal conductivity.

Consider a fixed mass of a gas at rest as shown in Fig. 3.5. Suppose there is a uniform temperature gradient $\frac{d\theta}{dz}$ along OZ . In the steady state, the temperature of each horizontal layer parallel to the OX axis is constant. Let θ be the temperature of layer AB . The temperature of the layer EF which is at a distance λ (the mean free path) above AB is $\left(\theta + \lambda \frac{d\theta}{dz}\right)$ and the layer CD at the distance λ below AB will be $\left(\theta - \lambda \frac{d\theta}{dz}\right)$. This means the gas above the layer AB is at higher temperature than the gas below AB . Hence, molecules of gas coming from EF and passing downward across AB possess more K.E. than the molecules coming from CD and passing upward across AB . Thus, the average energy of molecules below AB is continuously increasing and that of molecules above AB is continuously decreasing, till the equilibrium is reached.

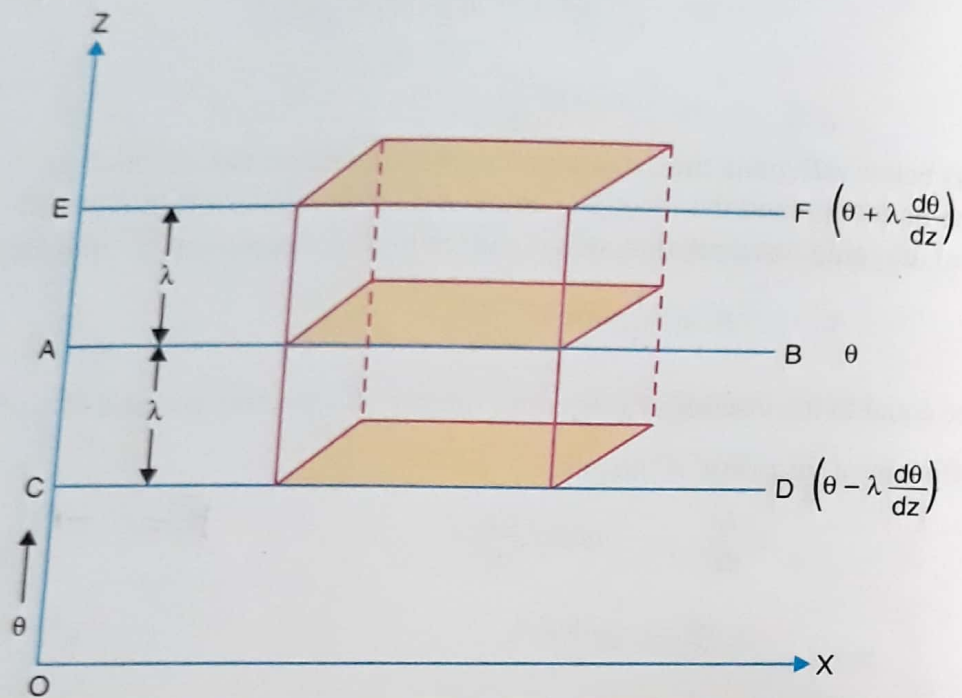


Fig. 3.5

OX is constant. Let θ be the temperature of layer AB . The temperature of the layer EF which is at a distance λ (the mean free path) above AB is $\left(\theta + \lambda \frac{d\theta}{dz}\right)$ and the layer CD at the distance λ below AB will be $\left(\theta - \lambda \frac{d\theta}{dz}\right)$. This means the gas above the layer AB is at higher temperature than the gas below AB . Hence, molecules of gas coming from EF and passing downward across AB possess more K.E. than the molecules coming from CD and passing upward across AB . Thus, the average energy of molecules below AB is continuously increasing and that of molecules above AB is continuously decreasing, till the equilibrium is reached.

Number of molecules crossing unit area of the layer AB upward or downward per second $\frac{nc}{6}$, where n is the number of gas molecules per unit volume and c is the average molecular velocity.

If m is the mass of each gas molecule, then the mass of gas crossing unit area of layer AB upward or downward per second $= \frac{mnc}{6}$.

If C_v be the specific heat of the gas at constant volume, then

Heat energy carried by the molecules in crossing unit area of the layer AB in the downward direction per second

$$= \text{mass} \times \text{specific heat} \times \text{temperature}$$

$$= \frac{mnc}{6} \times C_v \times \left(\theta + \lambda \frac{d\theta}{dz}\right)$$

Similarly, heat energy carried by the molecules crossing in unit area of the layer AB in the upward direction per second

$$= \frac{mnc}{6} \times C_v \times \left(\theta - \lambda \frac{d\theta}{dz}\right)$$

∴ Net transfer of heat energy per unit area of layer AB in the downward direction per second

$$Q = \frac{mnc}{6} \times C_v \times \left(\theta + \lambda \frac{d\theta}{dz} \right) - \frac{mnc}{6} \times C_v \times \left(\theta - \lambda \frac{d\theta}{dz} \right)$$

$$= \frac{mnc}{6} \times C_v \times 2\lambda \frac{d\theta}{dz} = \frac{1}{3} mnc \times C_v \lambda \frac{d\theta}{dz}$$

Since $mn = \rho$, the density of the gas,

$$Q = \frac{1}{3} \rho c \lambda C_v \frac{d\theta}{dz} \quad \dots(3.8)$$

The coefficient of thermal conductivity (K) of the gas is defined as the quantity of heat that flows per unit area per second per unit temperature gradient.

or
$$Q = K \frac{d\theta}{dz} \quad \dots(3.9)$$

Equating equation (3.8) and (3.9),

$$K \frac{d\theta}{dz} = \frac{1}{3} \rho c \lambda C_v \frac{d\theta}{dz}$$

or,
$$K = \frac{1}{3} \rho c \lambda C_v \quad \dots(3.10)$$

3.12 Relation between η and K ✓

The coefficient of viscosity of a gas is given by

$$\eta = \frac{1}{3} \rho c \lambda$$

and, the coefficient of thermal conductivity is

$$K = \frac{1}{3} \rho c \lambda C_v$$

∴
$$K = \eta C_v \quad \dots(3.11)$$

The relation is, however, does not hold good with the experimental values since it is true only if all the heat supplied is converted into kinetic energy of translation.

According to Chapman and Enskog, the corrected value is

$$K = \epsilon \eta C_v$$

where $\epsilon = \frac{1}{4} (9\gamma - 5)$, where γ is ratio of two specific heats of the gas.

$$K = \frac{1}{3} \epsilon \rho c \lambda C_v \quad \dots(3.12)$$

3.13 Effect of Temperature on K

The coefficient of thermal conductivity (K) is given by equation (3.10) as

$$K = \frac{1}{3} \rho c \lambda C_v$$

$$= \frac{1}{3} mnc \cdot C_v \lambda \quad (\because \rho = mn)$$

$$K = \frac{1}{3} mnc \cdot C_v \times \frac{1}{\sqrt{2} \pi \sigma^2 n}$$

$$K = \frac{mcC_V}{3\sqrt{2}\pi\sigma^2}$$

But

$$C \propto \sqrt{T}$$

∴

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

Thus, the coefficient of thermal conductivity of a gas is directly proportional to the square root of its absolute temperature. In other words, coefficient of thermal conductivity increases with increase in the temperature.

3.14 Effect of Pressure on K

In the relation, $K = \epsilon \eta C_V$, all the quantities ϵ , η and C_V are independent of pressure. Hence the coefficient of conductivity K is also independent of pressure.

3.15 Largest Thermal Conductivity of Hydrogen

The coefficient of thermal conductivity of a gas is given by

$$K = \frac{1}{3} \rho c \lambda C_V$$

Substituting for

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

we have,

$$K = \frac{1}{3\sqrt{2}} \frac{mcC_V}{\pi\sigma^2} \quad (\because \rho = mn)$$

If M is the molecular weight and N , the Avogadro's number, then $m = \frac{M}{N}$ and C_V its molar specific heat, then

$$\begin{aligned} K &= \frac{1}{3\sqrt{2}} \cdot \frac{c}{\pi\sigma^2} \left(\frac{M}{N}\right) \frac{C_V}{M} \\ &= \frac{1}{3\sqrt{2}} \cdot \frac{C_V}{\pi N \sigma^2} c \end{aligned} \quad \dots(3.14)$$

In this relation, N is constant, being Avogadro's number. For a diatomic gas, the value of gram molecular specific heat C_V is the same for all gases being equal to $\frac{5}{2}R$. Assuming equal molecular diameters (σ) for all gases

$$K \propto c$$

But

$$c = \text{average speed of the molecules}$$

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

Where k is Boltzmann's constant.

$$K \propto \frac{1}{\sqrt{m}}$$

Thus, coefficient of thermal conductivity (K) is inversely proportional to the square root of the mass of the molecule of the gas.

As the mass of molecule of hydrogen is the least among diatomic gases, the thermal conductivity (K) of hydrogen gas will be greatest at a given temperature.

3.16 Self Diffusion: Transport of Mass

The phenomenon of self diffusion is due to the transport of mass from a region of higher concentration to a region of lower concentration to bring about an equilibrium.

Consider a gas having a concentration gradient $\frac{dn}{dz}$ along OZ . Let n be the concentration of layer AB .

Consider two more layers EF and CD above and below that of AB at a distance λ equal to the mean free path of the molecules of the gas, so that the molecules moving vertically upward or downward do not collide between these two layers (Fig. 3.6).

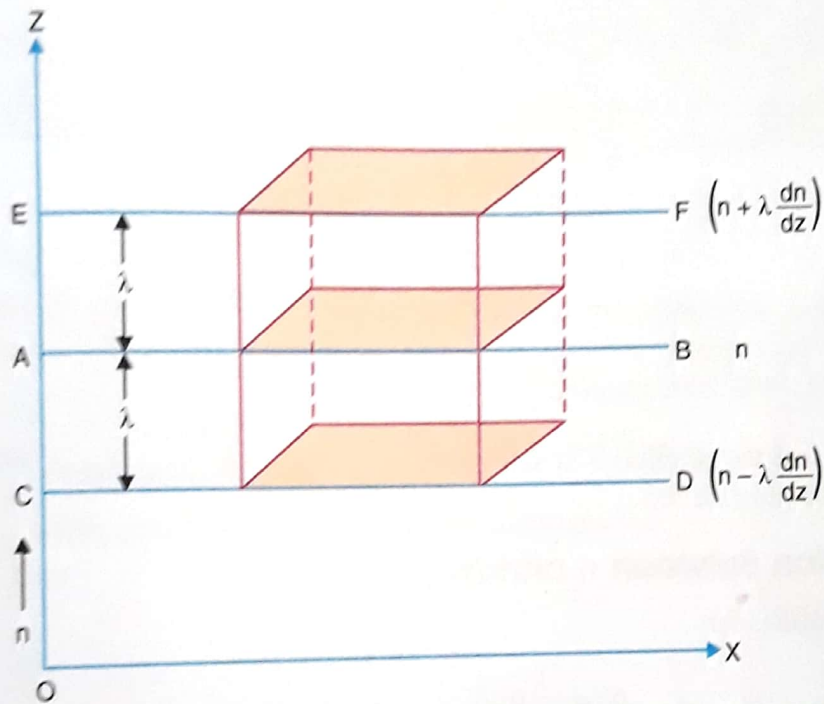


Fig 3.6

Concentration at the layer $EF = n + \lambda \frac{dn}{dz}$

and concentration at the layer $CD = n - \lambda \frac{dn}{dz}$

Therefore, the number of molecules coming from layer EF and crossing AB downward per unit area per second

$$= \frac{1}{6} c \left(n + \lambda \frac{dn}{dz} \right)$$

and number of molecules coming from layer CD and crossing AB upward per unit area per second

$$= \frac{1}{6} c \left(n - \lambda \frac{dn}{dz} \right)$$

\therefore Net number of molecules crossing per unit area per second of layer AB in downward direction

$$\begin{aligned} &= \frac{1}{6} c \left(n + \lambda \frac{dn}{dz} \right) - \frac{1}{6} c \left(n - \lambda \frac{dn}{dz} \right) \\ &= \frac{1}{6} c \lambda \frac{dn}{dz} \end{aligned}$$

92 • Heat, Thermodynamics and Statistical Physics

The coefficient of diffusion is defined as the ratio of the number of molecules crossing per area in one second to the rate of change of concentration with distance.

$$\therefore \text{Coefficient of diffusion } D = \frac{\frac{1}{3} c \lambda \frac{dn}{dz}}{\frac{dn}{dz}}$$

$$D = \frac{1}{3} c \lambda$$

3.17 Effect of Temperature and Pressure

We have

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

and

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

$$D = \frac{1}{3} \cdot \frac{kT}{\sqrt{2} \pi \sigma^2 P} \cdot \sqrt{\frac{8kT}{\pi m}}$$

$$= \frac{2}{3} \frac{1}{\sigma^2 P \sqrt{m}} \cdot \left(\frac{kT}{\pi}\right)^{\frac{3}{2}}$$

This shows that the coefficient of self diffusion is directly proportional to $T^{3/2}$ and inverse proportional to the pressure P .

3.18 Relation Between η and D

From the relations for

$$\eta = \frac{1}{3} \rho c \lambda$$

and

$$D = \frac{1}{3} c \lambda$$

we have

$$D = \frac{\eta}{\rho}$$

This relation between D and η does not agree well with the experimental values for a gas. A more detailed analysis yields the relation

$$D = f' \frac{\eta}{\rho}$$

where f' is a numerical factor whose value is nearly 1.4.

The values of Table 3.1 the density (ρ), average speed (C), molecular diameter (σ), mean free path (λ), coefficient of viscosity (η), coefficient of viscosity (K) at N.T.P. and specific heat capacity at constant volume (C_V) for some gases are given in the following table. All the quantities are in SI units.