UNIT II:

Viscosity:

Definition of Coefficient of viscosity with unit and dimension – expression for critical velocity– Poiseulli's formula for coefficient of viscosity and its correction – determination of coefficient of viscosity by capillary flow method (Poiseulli's method) – comparison of viscosities by Oswald's viscometer – viscosity of a highly viscous liquid –Stoke's formula–Stoke's method for the Coefficient of a highly viscous liquid

Diffusion:

Definition– Graham's laws of diffusion in liquids–Fick's laws of diffusion–Analogy with heat conduction– experimental determination of coefficient of diffusion (Diffusivity)–Graham's law of diffusion of gases–Effusion–transpiration

2 Viscosity

CHAPTER

2.1 INTRODUCTION

When two parallel layers of a liquid are moving with different velocities, they experience tangential forces which tend to retard the faster layer and accelerate the slower layer. These forces are called forces of viscosity. Consider two layers of liquid separated by a distance dz (Fig. 2.1). Let v and $v + dv$ be the velocities of two layers. So the velocity gradient is dv/dz. Let A be the surface area of the layer. The viscous force is directly proportional to the surface area A and velocity gradient dv/dz

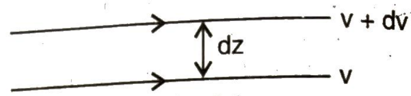

Fig. 2.1

i.e., $F \propto A\dfrac{dv}{dz}$ or $F = \eta A\dfrac{dv}{dz}$ ...(1)

where η is a constant for the liquid and called coefficient of viscosity. If $A = 1$ and $dv/dz = 1$, we have $F = \eta$.

The coefficient of viscosity is defined as the tangential force per unit area required to maintain a unit velocity gradient.

Unit of η is Nsm^{-2}. It is called the pascal second.

$$\text{Dimensions of } [\eta] = \frac{[F]}{[A]\,[(dv/dz)]} = \frac{MLT^{-2}}{L^2\,(LT^{-1}/L)} = ML^{-1}T^{-1}$$

2.2 STREAMLINE FLOW AND TURBULENT FLOW

Consider a liquid flowing in a pipe. Let the velocity of flow be v_1 at A, v_2 at B and v_3 at C (Fig. 2.2). If as time passes, the velocities at A, B, and C are constant in magnitude and direction, then the flow is said to be steady. In a steady flow, each particle follows exactly the same path and has exactly the same velocity as its predecessor. In such a case, the liquid is said to have an orderly or *streamline flow*.

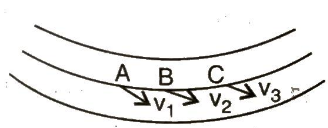

Fig. 2.2

The line ABC is called a streamline, which is the path followed by an orderly procession of particles. The tangent to the streamline at any point gives the velocity of the liquid at that point.

The flow is steady or streamlined only as long as the velocity of the liquid does not exceed a limiting value, called the *critical velocity*. When the external pressure causing the flow of the liquid is excessive, the motion of the liquid takes place with a velocity greater than the critical velocity and the motion becomes unsteady or *turbulent*. This causes eddies and whirlpools in the motion of the liquid. This turbulent motion is also known as *vortex motion*.

The distinction between streamline flow and turbulent flow can be demonstrated by injecting a jet of ink axially in a wider tube in which water is made to flow axially. When the velocity of the liquid is small, the ink will move in a straight line. As the speed of flow is increased beyond the critical velocity, the ink will spread out, showing that the motion has become turbulent.

Definition of critical velocity. *Critical velocity of a liquid is the velocity below which the motion of the liquid is orderly and above which the motion of the liquid becomes turbulent.*

Expression for the critical velocity. *The critical velocity of a liquid may depend upon* (*i*) the coefficient of viscosity of the liquid (η), (*ii*) the density of the liquid (ρ) and (*iii*) the radius r of the tube through which the liquid is flowing. We may write

$$v_c = k\,\eta^a\,\rho^b\,r^c$$

where k is constant called *Reynold's number.*

Writing the dimensions of these quantities,

$$[LT^{-1}] = [ML^{-1}\,T^{-1}]^a\,[ML^{-3}]^b\,[L]^c$$

$$[LT^{-1}] = [M^{a+b}\,L^{-a-3b+c}\,T^{-a}]$$

$$\therefore \quad a+b=0\,;\ -a-3b+c=1 \text{ and } -a=-1$$

From these equations we have, $a = 1$, $b = -1$ and $c = -1$.

$$\therefore \quad v_c = \frac{k\,.\,\eta}{\rho\,r}$$

Significance of Reynold's number :

$$k = \frac{v_c\rho\,r}{\eta}$$

The significance of the Reynold's number k is that its value determines the nature of flow of a liquid through a tube. In the case of apparatus, geometrically similar, whatever their actual dimensions, turbulence sets in at the same constant value of Reynold's number in all cases of liquid flow. The flow will be steady and streamline in each individual case, until this number is not exceeded. After exceeding this number, the flow becomes turbulent. Even though the values of r, ρ and η may all vary from each other, but so long as k remains the same, the liquid flow will be similar in all the cases.

2.3. POISEUILLE'S FORMULA FOR THE FLOW OF A LIQUID THROUGH A CAPILLARY TUBE

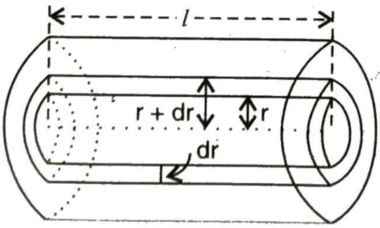

Fig. 2.3(*a*)

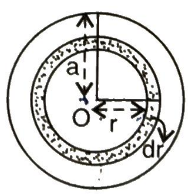

Fig. 2.3(*b*)

Suppose a constant pressure difference p is maintained between the two ends of the capillary tube of length l and radius a, as shown in Fig. 2.3 (*a*). Consider the steady flow of a liquid of coefficient of viscosity η through the tube. The velocity of the liquid is a maximum along the axis and is zero at the walls of the tube. Assume that there is no radial flow. Consider a cylindrical shell of the liquid co-axial with the tube of inner radius r and outer radius $r + dr$ [Fig. 2.3(*b*)]. Let the velocity of the liquid on the inner surface of the shell be v and that on the outer surface be $v - dv$. (dv/dr) is the velocity gradient.

The surface area of the shell $= A = 2\,\pi\,r\,l$.

According to Newton's law of viscous flow, the backward dragging tangential force exerted by the outer layer on the inner layer, opposite to the direction of motion

$$F_1 = -\eta A \frac{dv}{dr} = -\eta\, 2\pi r l \frac{dv}{dr}$$

The driving force on the liquid shell, accelerating it forward

$$F_2 = p\pi r^2$$

where, p = pressure difference across the two ends of the tube and

πr^2 = Area of cross-section of the inner cylinder.

When the motion is steady,

backward dragging force (F_1) = The driving force (F_2)

$$-\eta\, 2\pi r l \frac{dv}{dr} = p\,\pi r^2 \text{ or } dv = \frac{-p}{2\eta l} r\, dr.$$

Integrating, $$v = \frac{-p}{2\eta l}\frac{r^2}{2} + C.$$

where C is a constant of integration.

When $r = a$, $v = 0$. Hence, $0 = \frac{-p}{2\eta l}\frac{a^2}{2} + C$ or $C = \frac{pa^2}{4\eta l}$

$$\therefore \quad v = \frac{p}{4\eta l}(a^2 - r^2)$$

This gives us the average velocity of the liquid flowing through the cylindrical shell.

Hence the volume of the liquid that flows out per second through this shell

$$dV = \begin{pmatrix}\text{Area of cross-section of the shell} \\ \text{of radius } r \text{ and thickness } dr\end{pmatrix} \times \text{Velocity of flow}$$

$$= 2\pi r\, dr \frac{p}{4\eta l}(a^2 - r^2) = \frac{\pi p}{2\eta l}(a^2 r - r^3)\, dr$$

The volume of the liquid that flows out per second is obtained by integrating the expression for dV between the limits $r = 0$ to $r = a$.

$$V = \int_0^a \frac{\pi p}{2\eta l}(a^2 r - r^3)\, dr = \frac{\pi p}{2\eta l}\left[a^2\frac{r^2}{2} - \frac{r^4}{4}\right]_0^a$$

$$= \frac{\pi p}{2\eta l} \cdot \frac{a^4}{4}$$

or $$V = \frac{\pi p a^4}{8\eta l}$$

2.4. CORRECTIONS TO POISEUILLE'S FORMULA

Two important corrections are to be applied in the Poiseuille's equation :

(*i*) **Correction for pressure head :** The outgoing liquid acquires K.E. due to its velocity after passing through the tube. Hence the pressure-head maintained is utilized not only for overcoming viscous resistance but also in imparting considerable K.E. to emergent liquid. So the effective pressure is less and is given by

$$p_1 = p - \frac{V^2 \rho}{\pi^2 a^4}.$$

This can be deduced as follows :

The K.E. given to the liquid of density ρ per second

$$E' = \int_0^a \frac{1}{2}(2\pi r\, dr v\rho)\, v^2 = \pi\rho \int_0^a r v^3\, dr$$

But

$$v = \frac{p}{4\eta l}(a^2 - r^2)$$

∴

$$E' = \pi\rho \int_0^a r \left(\frac{p}{4\eta l}\right)^3 (a^2 - r^2)^3\, dr$$

$$= \pi\rho \left(\frac{p}{4\eta l}\right)^3 \frac{a^8}{8} = \left(\frac{\pi p a^4}{8\eta l}\right)^3 \frac{\rho}{\pi^2 a^4}$$

$$= \frac{V^3 \rho}{\pi^2 a^4}$$

The work done in overcoming viscosity is $p_1 V$ whereas total work done per unit volume is pV. Here p_1 is the effective pressure.

∴

$$pV = p_1 V + \frac{V^3 \rho}{\pi^2 a^4}$$

or

$$p_1 = p - \frac{V^2 \rho}{\pi^2 a^4}$$

∴

$$p_1 = g\rho \left(h - \frac{V^2}{\pi^2 a^4 g}\right)$$

Thus $[V^2/(\pi^2 a^4 g)]$ is the correction factor to the pressure head for gain of kinetic energy by the emergent liquid.

(*ii*) **Correction for length of tube:** At the inlet end of the tube, the flow of the liquid is not streamline for some distance. Consequently the liquid is accelerated. The effective length of the tube is thus increased from l to $l + 1.64\, a$. Thus, the corrected relation for η becomes

$$\eta = \frac{\pi a^4}{8V(l + 1.64\, a)} \left(h - \frac{V^2}{\pi^2 a^4 g}\right) g\rho$$

2.5. POISEUILLE'S METHOD FOR DETERMINING COEFFICIENT OF VISCOSITY OF A LIQUID

The liquid is taken in the constant level tank up to a height h (Fig. 2.4). A capillary tube AB is fixed to the bottom of the tank. A weighed beaker is placed below the free end B of the capillary tube. The mass m of the liquid collected in it in time t is found out.

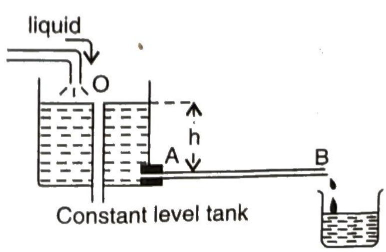

Fig. 2.4

Volume of liquid flowing per second $= V = m/(\rho\, .\, t)$ where ρ is the density of the liquid. The length l of the capillary tube is measured by a metre rod. The radius a of the capillary tube is determined very accurately, using the travelling microscope. Then from the relation

$$\eta = \frac{\pi p a^4}{8 V l} \qquad \text{(where } p = h\rho g)$$

the value of η for the liquid can be easily calculated.

Comparison of viscosities : The liquid whose viscosity is η_1 is first used in the constant level tank and the volume of liquid flowing per second $= V_1 = m_1/\rho_1 . t$ is determined with a capillary tube. The tube is then taken out and cleaned well. The experiment is repeated for the other liquid whose viscosity is η_2 and the volume of liquid flowing per second $= V_2 = m_2/\rho_2 . t$ is determined for the same pressure head and with the same capillary tube. If l is the length of the tube, a its radius and ρ_1 and ρ_2 the densities of the two liquids,

$$\eta_1 = \frac{\pi h \rho_1 g a^4}{8 V_1 l} \text{ and } \eta_2 = \frac{\pi h \rho_2 g a^4}{8 V_2 l} \quad \therefore \quad \frac{\eta_1}{\eta_2} = \frac{\rho_1 V_2}{\rho_2 V_1}$$

ρ_1/ρ_2 can be determined with a Hare's apparatus. Thus the viscosities of two liquids can be compared.

2.6 OSTWALD'S VISCOMETER

This instrument is used to compare the viscosities of two liquids. It is also used to study the variation of viscosity of a liquid with temperature.

The apparatus consists of two glass bulbs A and B joined by a capillary tube DE bent into a U-form (Fig. 2.5). The bulb A is connected to a funnel F. The bulb B is connected to an exhaust pump through a stop-cock S. K, L, and M are fixed marks, as shown in the figure. The whole apparatus is placed inside a constant temperature bath.

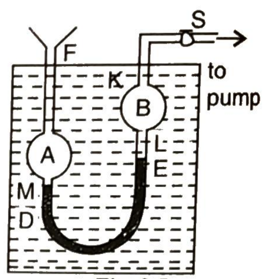

Fig. 2.5

The liquid is then introduced into the apparatus through the funnel and its volume is adjusted, so that the liquid occupies the portion between the marks K and M, when the stop-cock is closed. The stop-cock is now opened and with the help of the exhaust pump the liquid is sucked up above the mark K. The stop-cock is closed and the exhaust pump is removed. The stop-cock is again opened. The liquid is allowed to flow through the capillary tube.

The time (t_1) taken by the liquid to fall from the mark K to the mark L is noted. The experiment is then repeated with the second liquid and the time (t_2) taken by it to fall from K to L is noted.

Theory : Let η_1 and η_2 be the coefficients of viscosity and ρ_1 and ρ_2 the densities of the two liquids respectively. Let the volume of liquid between K and L be V. Then,

the rate of flow of the first liquid $= V_1 = V/t_1$ ...(1)

and the rate of flow of the second liquid $= V_2 = V/t_2$ ...(2)

Now, $\eta_1 = \dfrac{\pi . P_1 . a^4}{8 V_1 . l}$ and $\eta_2 = \dfrac{\pi . P_2 . a^4}{8 V_2 . l}$

or $$\frac{\eta_1}{\eta_2} = \frac{V_2}{V_1} \times \frac{P_1}{P_2} \quad ...(3)$$

But the pressure P is proportional to the density of the liquid used ($P = h\rho g$)

Hence, $$\frac{P_1}{P_2} = \frac{\rho_1}{\rho_2} \quad ...(4)$$

Also, dividing (2) by (1), $$\frac{V_2}{V_1} = \frac{t_1}{t_2} \quad ...(5)$$

Hence, $\frac{\eta_1}{\eta_2} = \frac{t_1 \cdot \rho_1}{t_2 \cdot \rho_2}$ ...(6)

From equation (6), η_1/η_2 can be calculated.

2.7. POISEUILLE'S METHOD FOR DETERMINING COEFFICIENT OF VISCOSITY OF A LIQUID [VARIABLE PRESSURE HEAD]

The given liquid is poured into a graduated burette. The capillary tube is fixed as shown in figure (Fig. 2.6). The clip is opened fully. The liquid is allowed to flow slowly through the capillary tube. When the liquid level in the burette crosses the zero marking, a stop-clock is started. The readings of the stop clock are noted when the liquid level crosses the 10cc, 20cc, 30cc. etc., markings. The vertical height h between the capillary tube and midpoints of the range 0–10cc, 10–20cc, 20–30cc etc., are measured.

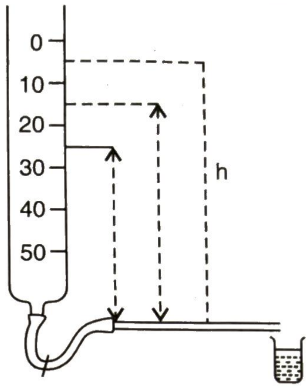

Fig. 2.6

The length of the capillary tube (l) is measured. The radius a of the capillary tube is measured using mercury thread or microscope. The density of the liquid ρ is determined using Hare's apparatus. The readings are tabulated as follows :

Burette Reading cc	*Stop-clock reading seconds*	*Burette reading range*	*Volume of liquid flowing m³*	*Mean pressure head h m*	*Time of flow t seconds*	$\frac{h.t}{V}$
0						
10		0 to 10 cc	10×10^{-6}			
20		10 to 20 cc	”			
30		20 to 30 cc	”			

Mean $h \cdot t/V =$

The coefficient of viscosity is calculated using the formula,

$$\eta = \frac{\pi \rho g a^4}{8l}\left(\frac{h.t}{V}\right)$$

Example 1 : *Water flows through a horizontal tube of length 0.2 metres and internal radius 8.1×10^{-4} metre under a constant head of the liquid 0.2 metres high. In 12 minutes 8.64×10^{-4} m³ of liquid issues from the tube. Calculate the coefficient of viscosity of water. (The density of water = 1000 kg m⁻³ and g = 9.81 ms⁻²).*

From Poiseuille's formula, $V = \frac{\pi p . a^4}{8\eta . l}$

Here, $p = h \cdot \rho \cdot g = 0.2 \times 1000 \times 9.8$ Nm⁻² ; $a = 8.1 \times 10^{-4}$ m

$$l = 0.2\ m,\ V = \frac{8.64 \times 10^{-4}}{12 \times 60} = 1.2 \times 10^{-6}\ m^3 ;\ \eta = ?$$

Now,
$$\eta = \frac{\pi p . a^4}{8 V . l} = \frac{(3.14)(0.2 \times 1000 \times 9.8)(8.1 \times 10^{-4})^4}{8(1.2 \times 10^{-6})\,0.2}$$

$$= 1.38 \times 10^{-3}\ Nsm^{-2}$$

Example 2 : *A vessel of cross-section 0.002m² has at the bottom a horizontal capillary tube of length 0.1m and internal radius 0.0005m. It is initially filled with water up to a height of 0.2m above the capillary tube. Find the time taken by the vessel to empty one-half of its contents, given the viscosity of water = 10^{-3} Nsm⁻².*

2.8. TERMINAL VELOCITY AND STOKES' FORMULA

Let us consider an infinite column of a highly viscous liquid like castor oil contained in a tall jar. If a steel ball is dropped into the liquid, it begins to move down with acceleration under gravitational pull. But its motion in the liquid is opposed by viscous forces in the liquid. These viscous forces increase as the velocity of the ball increases. Finally a velocity will be attained when the apparent weight of the ball becomes equal to the retarding viscous forces acting on it. At this stage, the resultant force on the ball is zero. Therefore the ball continues to move down with the same velocity thereafter. This uniform velocity is called the *terminal velocity.*

Stokes' Formula : The viscous force F experienced by a falling sphere must depend on (*i*) the terminal velocity v of the ball, (*ii*) the radius (r) of the ball and (*iii*) the coefficient of viscosity (η) of the liquid. We can write $F = k\, v^a\, r^b\, \eta^c$ where k is a dimensionless constant. The dimensions of these quantities are $F = MLT^{-2}$; $v = LT^{-1}$; $r = L$; $\eta = ML^{-1}\,T^{-1}$; (k is a number; it has no dimensions).

$$\therefore \qquad MLT^{-2} = (LT^{-1})^a\, L^b\, (ML^{-1}\,T^{-1})^c$$

$$MLT^{-2} = M^c\, L^{a+b-c}\, T^{-a-c}$$

Equating the powers of M, L and T on either side,

$c = 1$; $a + b - c = 1$ and $-a - c = -2$.

Solving, $a = 1$; $b = 1$ and $c = 1$. $\therefore\ F = k\, v\, r\, \eta$.

Stokes experimentally found the value of k to be $6\,\pi$.

$$\therefore \qquad F = 6\,\pi\, v\, r\, \eta.$$

Expression for terminal velocity. Let ρ be the density of the ball and ρ' the density of the liquid. Then,

the weight of the ball $= \frac{4}{3}\pi\, r^3\, \rho g$.

The weight of the displaced liquid or the upthrust on the ball $= \frac{4}{3}\pi\, r^3\, \rho' g$

The apparent weight of the ball $= \frac{4}{3}\pi r^3\, \rho g - \frac{4}{3}\pi\, r^3\, \rho' g = \frac{4}{3}\pi\, r^3\, (\rho - \rho')\, g$.

When the ball attains its terminal velocity v, the apparent weight of the ball = viscous force F.

$$\therefore \qquad 6\pi v r \eta = \frac{4}{3}\pi r^3 (\rho - \rho')g$$

or

$$v = \frac{2}{9}\frac{r^2}{\eta}(\rho - \rho')g$$

Assumptions made by Stokes while deriving the formula:

(1) The medium through which the body falls is *infinite in extent.*

(2) The moving body is *perfectly rigid* and *smooth.*

(3) There is *no slip between the moving body and the medium.*

(4) There are no eddy currents or waves set up in the medium due to the motion of the body through it. In other words, the body is moving very slowly through it.

2.9. STOKES' METHOD FOR THE COEFFICIENT OF VISCOSITY OF A VISCOUS LIQUID

Stokes' method is suitable for highly viscous liquids like castor oil and glycerine. The experimental liquid is taken in a tall and wide jar (Fig. 2.7). Four or five marks A, B, C, D... are drawn on the outside of the jar at intervals of 5 cm. A steel ball is gently dropped centrally into the jar. The time taken by the ball to move through the distances AB, BC, CD, ... are noted. When the times for two consecutive transits are equal, the ball has reached terminal velocity. Now another ball is gently dropped into the jar. When the ball just reaches a mark below the terminal stage, the time (t) taken by the ball to move through a definite distance (x) is noted.

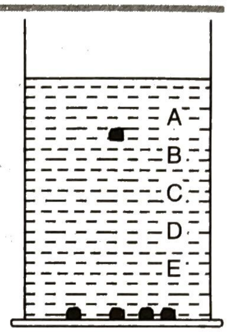

Fig. 2.7

$\therefore$ Terminal velocity $= v = x/t$.

The experiment is repeated for varying distances and the mean value of v is found.

The radius of the ball is measured accurately with a screw gauge. The density of the ball ρ and the density of the liquid ρ' are found by the principle of Archimedes. η is calculated using the formula

$$\eta = \frac{2}{9}\frac{r^2}{v}(\rho - \rho')g$$

Example 1 : *Assuming that when a spherical body moves in a viscous fluid under the action of a force F, the resultant force is given by ma = F – 6 πr η v, calculate the terminal velocity of a rain drop of diameter* 10^{-3} *m. Density of air relative to water is* 1.3×10^{-3}; $\eta = 1.81 \times 10^{-5}$ *N* sm^{-2}.

When the body attains the terminal velocity, the acceleration of the body is zero. The body continues moving in the direction of the force with a constant velocity (v).

$$v = \frac{2}{9}\frac{r^2(\rho - \rho')g}{\eta};$$

Here

$$r = \frac{10^{-3}}{2} = 5 \times 10^{-4}\text{ m}$$

ρ = Density of water = 1000 kg m^{-3}.

ρ' = Density of air = Density of air relative to water × Density of water = $(1.3 \times 10^{-3}) \times 1000$ = 1.3 kg m^{-3}; $\eta = 1.81 \times 10^{-5}$ N sm^{-2} and $g = 9.8$ ms^{-2}.

$$\therefore \qquad v = \frac{2}{9}\frac{(5\times10^{-4})^2(1000 - 1.3)\,9.8}{1.81\times10^{-5}} = 30\text{ ms}^{-1}$$

4.1 Introduction

A strong copper sulphate solution is placed at the bottom of a tall jar. The rest of the jar is filled with water, without disturbing the solution. It is found that the coloured solution gradually moves upwards. After a long time, the entire solution is uniformly coloured.

The process by which the molecules of a solute spontaneously move from regions of greater concentration to regions of lower concentration in a solution, unaided by external pressure and against the force of gravity, is called diffusion.

Graham's laws of diffusion in liquids:

1. The same solute diffuses at different rates through different solvents.
2. Different solutes diffuse at different rates through the same solvent.
3. When the temperature increases, the rate of diffusion also increases.
4. Crystalloids diffuse faster than colloids.
5. For a given solution, the rate of diffusion is directly proportional to its concentration.

4.2 Fick's laws of diffusion

Fick stated the law of diffusion in analogy with the law of conduction of heat through a solid.

Consider two parallel layers in a solution at rest. Then, the mass of the substance moving across the layers by diffusion is —

(*i*) *directly proportional to the area of the layers*
(*ii*) *directly proportional to the difference in concentration between the layers*
(*iii*) *inversely proportional to the distance between the layers*
(*iv*) *directly proportional to the time.*

Let A be the area of the layers, and d the distance between them. Let the concentration at these layers be C_1 and C_2. Then the mass (m) of the substance diffusing in t seconds is

$$m \propto \frac{A(C_1 - C_2)t}{d} \quad \text{or} \quad m = K\frac{A(C_1 - C_2)t}{d}$$

K is a constant known as *coefficient of diffusion* or *diffusivity* of the solution . $(C_1 - C_2)/d$ is called concentration gradient.

If $A = 1$, $(C_2 - C_2)/d = 1$ and $t = 1$, then $m = K$.

Therefore *the coefficient of diffusion can be defined as the mass of substance diffusing per second across unit area of cross-section, where the concentration gradient is unity.*

Unit of K is kg $\sec^{-1}$ m^{-2} per unit concentration gradient.

Its dimensions are $[K] = [L^2 T^{-1}]$.

Analogy with Heat Conduction : Heat conduction in solids and diffusion is liquids are similar phenomena.

The quantity of heat (Q) flowing in t seconds across two layers of a conductor of area A, separated by a distance d, when the temperatures at these layers are T_1 and T_2, is given by

$$Q = \lambda \frac{A(T_1 - T_2)t}{d}$$

where λ is the coefficient of thermal conductivity.

Fick's law states that the mass m of a substance diffusing in t seconds across two layers of a solvent of area A, separated by a distance d, when the concentrations of the substance at these layers are C_1 and C_2, is given by

$$m = K\frac{A(C_1 - C_2)t}{d}$$

where K is the coefficient of diffusion of the substance. Thus Fick's law of diffusion is similar to the law of heat conduction.

Mass of the diffusing substance plays the role of "quantity of heat"

Concentration gradient $(C_1 - C_2)/d$ plays the role of temperature gradient $(T_1 - T_2)/d$.

Coefficient of diffusion plays the role of coefficient of thermal conductivity.

4.3. Experimental determination of Coefficient of Diffusion [Diffusivity]

A strong solution of the given solute in water is placed at the bottom of a tall jar [Fig. 4.1]. Water is poured gently above the solution without disturbing the solution. Water is allowed to flow at the top slowly through the inlet L and outlet N. The stream of the solvent through the tube, carries with it the salt arriving at the opening M. After a time, steady conditions will be obtained, when the amount of the salt arriving at M becomes constant.

The solution passing out at N is collected for a known time t. The mass (m) of the salt present is found out. By taking out a small amount of solution out of the taps P and Q, the concentrations C_1 and C_2 are found out. Let x be the distance between the taps. Then, concentration gradient $= (C_1 - C_2)/x$. The area of opening M gives the area of the layer across which diffusion into M has taken place. K is calculated using the formula,

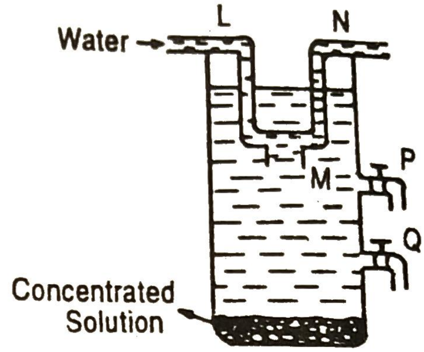

Fig. 4.1

$$m = K \cdot A \left(\frac{C_1 - C_2}{x} \right) t$$

4.4 Graham's Law of Diffusion of Gases

The rate of diffusion of a gas is inversely proportional to the square root of its density.

The law can be deduced from kinetic theory of gases. Let two gases diffuse one into the other, till a steady state of diffusion is reached. Under this condition, their pressures and temperatures are equal. Let ρ_1 and ρ_2 be the densities and C_1 and C_2 the r.m.s. velocities of the molecules of the two gases. Then

$$p = \frac{1}{3} \rho_1 C_1^2 = \frac{1}{3} \rho_2 C_2^2$$

$$\therefore \quad \frac{C_1}{C_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Now rate of diffusion of a gas is directly proportional to the mean velocity of molecules.

$$\frac{R_1}{R_2} = \frac{C_1}{C_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

The rates of diffusion of two gases are inversely proportional to the square roots of their densities.

or $$R \propto 1/\sqrt{\rho}.$$

On account of their higher molecular velocities, the gases diffuse at a much quicker rate than the liquids.

4.5. Effusion of Gases

Effusion is the process whereby a gas escapes into vacuum, from a thin walled vessel through a small hole in it. Graham showed that the rate of effusion varies directly as the square root of the difference of pressure on the two sides of the hole, and inversely as the square root of its density.

$$\text{Velocity of effusion} \propto \sqrt{\frac{\text{pressure difference}}{\text{density of the gas}}}$$

In a mixture of gases, each gas effuses out in proportion to its partial pressure. So the proportion of the gases remains unaltered, even after effusion. Thus there is no separation of a mixture of gases into its constituents .

4.6. Transpiration

If the hole in a plate is not too fine, and the thickness of the plate is greater than the diameter of the hole, the process of escape of the gas through it is called 'transpiration'. Here, the flow of the gas is controlled by viscosity alone.

EXERCISE IV

1. Explain what you understand by diffusion.
2. State Fick's laws of diffusion and explain their analogy to laws of heat conduction.
3. Define 'diffusivity'. Explain how the diffusivity of a salt can be determined experimentally.
4. Write notes on : 'effusion' and 'transpiration'.