

DIFFUSION

In a mixture consisting of two or more components, if the concentrations of the components vary from point to point, then there is a natural tendency for each component to migrate/move from regions of high concentration to those of low concentration. The process of transfer of mass as a result of the concentration difference of a component in a mixture or two phases in contact is called **mass transfer**.

The operations carried out for separating the components of a mixture, involving the transfer of material from one homogeneous phase to another, utilising the difference in vapour pressure, solubility or diffusivity and in which the driving force for transfer is a concentration difference are called as **mass transfer operations**.

In case of evaporation of water from a pool of water into a stream of air flowing over the water surface, molecules of water vapour diffuse through those of the air at the surface into the main portion of air stream, as a result of which they are carried away with the air flowing. In this case, mass transfer is a result of a concentration difference or gradient, the diffusing substance (water) moving from a region of high concentration to a region of low concentration. Hence, the driving force for mass transfer is a concentration difference just as a temperature difference in heat transfer.

Fractional distillation (one of the methods of separation) depends on the difference in vapour pressures of different components at the same temperature (volatility), while gas absorption depends on the difference in solubility of gases in a selective solvent. Liquid-liquid extraction and leaching depend on the difference in solubility in a liquid solvent.

Mass transfer operations include separation techniques such as distillation, gas absorption, liquid extraction, drying, crystallisation, etc.

In mass transfer operations, mass transfer may occur :

- (a) In one direction, e.g., gas absorption.
- (b) In opposite directions (i.e., in both directions), e.g., distillation.
- (c) With simultaneous heat transfer, e.g., drying and crystallisation.
- (d) With a simultaneous chemical reaction, e.g., gas absorption accompanied by a chemical reaction (absorption of CO_2 in an aqueous solution of KOH)
- (e) With the exchange of one or more components.
- (f) Isothermally (i.e., at constant T) and non-isothermally.

The phenomena those must exist in a mass transfer operation are :

- (a) At least two phases must come in contact with each other.
- (b) Materials must flow from one phase to the other.
- (c) A part of the total flow of material from one phase to the other must occur by molecular diffusion.

Three states of aggregation of a substance are gas, liquid and solid and due to this we have six possibilities of the phase contact. Gas-gas (not practically realised), gas-liquid, gas-solid, liquid-liquid, liquid-solid and solid-solid (no industrial separation operation in this category is found).

Mass transfer operations have been classified according to the **phases in contact** as given in Table 7.1.

Table 7.1

Phases in contact	Mass transfer operation
Liquid-vapour (gas)	Distillation (Fractionation)
Liquid-gas	Gas absorption Stripping Humidification Dehumidification
Liquid-solid	Crystallisation Leaching Adsorption
Liquid-liquid	Extraction
Solid-vapour	Sublimation
Solid-gas	Adsorption
Solid (wet) gas (usually air)	Drying

Hence, distillation, gas absorption, stripping are gas-liquid operations, liquid extraction is a liquid-liquid operation, crystallisation is a liquid-solid operation and drying is a gas-solid operation.

As the basic mechanism is the same whether the phase is a gas, liquid or solid, there are some similarities among the various mass transfer operations and these are given below.

- Equilibrium between the phases is attained after a sufficiently long time of phase contact between them.
- Material transfer is caused by the combined effect of molecular diffusion and turbulence.
- There is no resistance to mass transfer at the phase interface (because of the existence of equilibrium at the interface).
- Rate of mass transfer is evaluated by deviation/departure from equilibrium concentration.

1. Distillation : Distillation is a gas-liquid operation. It is a method of separating the components of a liquid mixture using thermal energy. The difference in vapour pressures of different components is responsible for such a separation. It is also called as fractionation or fractional distillation. (The term fractionation is commonly used in petroleum refineries). The separation of a crude petroleum into gasoline, kerosene, etc. is a typical example of distillation.

Consider a binary liquid mixture. For this, we have : $C = 2$, $P = 2$.

$\therefore F = 2$ (phase rule : $F = C - P + 2$). In this case there are four variables; temperature, pressure, composition of A in the liquid and vapour phases. If the pressure is fixed, then according to the phase rule only one variable, e.g., the liquid phase concentration can be varied and the temperature and vapour phase concentration follow and thus the system is defined completely. Here the equilibrium data are presented in temperature-composition diagrams at constant pressure or by plotting vapour phase composition against liquid phase composition. Such a plot is called the equilibrium curve.

2. Gas absorption : Gas absorption is a gas-liquid operation. It is a method of separating one or more constituents of a gas mixture by contacting it with a suitable liquid solvent. The necessary condition is the difference in solubility of the constituents in a given solvent. The washing of ammonia from an ammonia-air mixture by means of water is a typical example of gas absorption.

Consider that a gas mixture contains two components and one component is transferred. Thus, we have $C = 3$, $P = 2$ and $\therefore F = 3$. There are four variables : temperature, pressure, and the concentration of A in liquid and gas phases. If the temperature and pressure are fixed, one concentration may be chosen as the remaining independent variable that may be varied and the other concentration follows. A plot of equilibrium concentration in the gas phase v/s concentration in the liquid phase gives an equilibrium relationship between the phases.

3. Liquid extraction : Liquid extraction is a liquid-liquid operation. It is a method of separating the constituents of a liquid mixture by treating it with a suitable solvent that preferentially dissolves one or more of the constituents of the mixture. It is also called as solvent extraction. It is used as a separation technique only when distillation is ineffective and difficult. The separation of penicillin from fermentation mixtures is a typical example of application of liquid extraction.

4. Crystallisation : It is a liquid-solid operation and used to obtain materials in the form of attractive and uniform crystals of good purity. Crystallisation is the formation of solid particles within a homogeneous liquid phase.

5. Drying : Drying is a gas-solid operation. In general, it is the removal of moisture of a substance.

In case of drying, there are two phases and three components. $C = 3$, $P = 2$, $\therefore F = 3$.

The variables are : temperature, pressure, the concentration of water in the solid and the gas phases. If the temperature and pressure are fixed, one concentration may be taken as the remaining independent variable and the other concentration follows. These two concentrations can be plotted as the equilibrium curve.

DIFFUSION

It is the movement of an individual component through a mixture from a region of higher concentration to a region of lower concentration at fixed temperature and pressure with or without the help of an external force.

A mixture which is non-uniform initially will be ultimately brought to uniformity (a mixture is everywhere uniform in the concentration of its constituents) by diffusion since the concentration gradient which acts as a driving force for diffusion tends to move the component in such a direction as to equalise concentrations and destroy the gradient. If we maintain the concentration gradient by constantly supplying the diffusing component to the

high concentration end and removing it at the low concentration end, then the flow of diffusing component is continuous. This movement is utilised in mass transfer operations.

When diffusion results from the random movement/motion of the molecules, it is called **molecular diffusion**. As the molecular diffusion requires actual migration of molecules, the rate of mass transfer is higher in gases than liquids and very slow in solids. When the movement of the molecules occurs with the help of an external force (e.g., mechanical stirring and convective movement of the fluid), then it is called **eddy or turbulent diffusion**. The molecular diffusion is a slow process, whereas the eddy diffusion is a fast process. The molecular diffusion is the mechanism of a stationary fluid, i.e., a fluid at rest and fluids in laminar flow. In case of fluids in turbulent flow, the mechanism of mass transfer is by eddy diffusion. The transfer of material in the presence of a concentration gradient is classified as molecular transfer and eddy transfer. Molecular transfer of mass occurs in stationary fluids or fluids in laminar flow whereas eddy transfer occurs in fluids under turbulent conditions.

Role of diffusion in mass transfer :

Diffusion may occur in one phase or in both phases in all the mass transfer operations. In case of distillation, the more volatile component diffuses through the liquid phase to the interface between the phases (liquid and vapour phases) and away from the interface into the vapour phase. The less volatile component diffuses in the opposite direction and passes from the vapour phase to the liquid phase. In case of gas absorption, the solute gas diffuses through the gas phase to the interface and then through the liquid phase (liquid solvent phase) from the interface between the phases. In case of crystallisation, the solid solute diffuses through the mother liquor (liquid phase) to the crystals and deposit on the solid surfaces. In case of drying operation, liquid water (moisture) diffuses through the solid towards the surface of the solid, evaporates and diffuses as a vapour into the gas phase (drying medium). In case of liquid-liquid extraction, the liquid solute diffuses through the raffinate phase and then into the extract phase (solvent phase) from the interface between the phases.

Molecular Diffusion :

Concentrations, velocities and fluxes :

Let us consider two chemical species A and B are placed in two compartments that are separated by a impermeable partition. Now, assume that the partition is suddenly removed so that the species A will diffuse into B and the species B will diffuse in A and this will continue at a constantly decreasing rate until the mixture becomes everywhere uniform in the concentration of its constituents, i.e., of A and B. The process is one of molecular diffusion in which the species are diffused in one another as a result of the random motion of molecules. The rate of diffusion is governed by Fick's law and before dealing with this law, we will define the above mentioned terms based on the combination of such species. We make it clear here that by the word *solution* we mean a mixture of species of the same phase – gas in gas, liquid in liquid, etc., i.e., one phase - a gaseous, a liquid or a solid mixture.

Concentration :

There are various ways to express the concentration of the various species in a multicomponent system/mixture. We limit our discussion to mass concentration, molar concentration, mass fraction and mole fraction.

Mass concentration : The mass concentration of a species A in a solution is the mass of species A per unit volume of the solution (mixture). It is equivalent to the density of A and denoted by the symbol ρ_A .

For a binary mixture/solution of A and B,

$$\rho_A + \rho_B = \rho \quad \dots (7.1)$$

where ρ is the mass density of the solution.

Molar concentration : The molar concentration of a species A in a solution is the number of moles of species A per unit volume of the solution.

$$C_A = \frac{\rho_A}{M_A} \quad \dots (7.2)$$

where M_A is the molecular weight of component A. The unit of molar concentration in the SI system is kmol/m^3 .

Hence, for a binary mixture of A and B, the total molar concentration of the mixture is given by

$$C = C_A + C_B \quad \dots (7.3)$$

Mass fraction : The mass fraction x_A of a species A in a solution may be defined as the ratio of the mass concentration of species A to the mass density of the solution.

$$x_A = \frac{\rho_A}{\rho} \quad \dots (7.4)$$

Mole fraction : The mole fraction (x_A) of a species A in a solution may be defined as the ratio of the molar concentration of A to the molar concentration of the solution.

$$x_A = \frac{C_A}{C} \quad \dots (7.5)$$

For a binary system of A and B, we have

$$x_A + x_B = 1$$

and

$$x_A + x_B = 1$$

In the gas phase, concentrations are usually expressed in terms of partial pressures.

For an ideal gas A, $p_A V = n_A R T$

$$C_A = \frac{n_A}{V} = \frac{p_A}{RT} \quad \dots (7.6)$$

where p_A is the partial pressure of species A in the mixture, n_A is the number of moles of A in the mixture, V is the molar volume of the mixture, T is the temperature (absolute), and R is the universal gas constant.

x_A in terms of p_A is given as :

$$x_A = \frac{C_A}{C} = \frac{p_A/RT}{P/RT} = \frac{p_A}{P} \quad \dots (7.7)$$

where P is the total pressure exerted by the gas mixture.

Also, we have

$$C = C_A + C_B = \frac{p_A}{RT} + \frac{p_B}{RT} = \frac{P}{RT} \quad \dots (7.8)$$

Velocities :

In a diffusing mixture, various chemical species are moving at different velocities as they may have different mobilities. The bulk velocity of the mixture would be some sort of an average velocity. Let u_i be the velocity of the i^{th} species with respect to the stationary coordinate system. Then, for a mixture of n species, the local mass average velocity u is defined by

$$u = \frac{\sum_{i=1}^n \rho_i u_i}{\sum_{i=1}^n \rho_i} \quad \dots (7.9)$$

ρu is the local rate at which mass passes through a unit cross-section when it is placed perpendicular to u .

For a binary system of A and B components, we can write

$$u = \frac{\rho_A u_A + \rho_B u_B}{\rho} \quad \dots (7.10)$$

The local molar average velocity of the mixture, U , is defined by

$$U = \frac{\sum_{i=1}^n C_i u_i}{\sum_{i=1}^n C_i} \quad \dots (7.11)$$

Cu is the local rate at which moles pass through a unit cross-section which is placed perpendicular to U .

For a binary system of A and B, we can write

$$U = \frac{C_A u_A + C_B u_B}{C} \quad \dots (7.12)$$

Let us define two diffusion velocities relative to/with respect to the two bulk velocities (mass and molar average velocities of the mixture).

The mass diffusion velocity of a species is the velocity of that species relative to the local mass average velocity of the mixture.

Mass diffusion velocity of species i w.r.t. $u = u_i - u$

Mass diffusion velocity of species A w.r.t. $u = u_A - u$.

The molar diffusion velocity of a species is the velocity of species with respect to/relative to the local molar average velocity of the mixture.

Molar diffusion velocity of species i w.r.t. $U = u_i - U$... (7.13)

Molar diffusion velocity of species A w.r.t. $U = u_A - U$... (7.14)

Mass flow rate : It is the quantity of material flow in mass units per unit time (e.g., kg/s)

Molar flow rate : It is the quantity of material flow in molar units per unit time (e.g., kmol/s).

Flux : The mass transfer flux of a given species (vector quantity) is defined as the amount of that species, in either mass or, molar units, that crosses a unit area per unit time. We will define four types of fluxes, two with reference to fixed coordinates in space and two with respect to local mass average velocity and local molar average velocity (w.r.t. coordinates moving with mass average velocity and molar average velocity).

Mass flux : The mass flux of a species i is defined as the mass of species i that passes through a unit area per unit time.

The mass flux relative to stationary/fixed coordinates is given by

$$n_i = \rho_i u_i \quad \dots (7.15)$$

The mass flux relative to the mass average velocity u is given by

$$j_i = \rho_i (u_i - u) \quad \dots (7.16)$$

Molar flux : It is defined as the moles of species i that passes through a unit area per unit time.

The molar flux relative to stationary coordinates is given by

$$N_i = C_i u_i \quad \dots (7.17)$$

The molar flux relative to the molar average velocity U is given by

$$J_i = C_i (u_i - U) \quad \dots (7.18)$$

It is true that any one of the above mentioned notation used for the flux is adequate for all diffusion problems, but each has certain advantages. In process calculations, it is usually desirable to refer to a coordinate system fixed in an equipment so the flux N_i is used in engineering. The fluxes j_i and J_i are the usual measures of rates of diffusion and are useful in formulating the equations of change for multicomponent systems.

For a binary system of A and B :

The mass fluxes of A and B relative to stationary coordinates are :

$$n_A = \rho_A u_A \quad \dots (7.19)$$

$$n_B = \rho_B u_B \quad \dots (7.20)$$

The mass fluxes of A and B relative to mass average velocity are :

$$j_A = \rho_A (u_A - u) \quad \dots (7.21)$$

$$j_B = \rho_B (u_B - u) \quad \dots (7.22)$$

The molar fluxes of A and B with respect to stationary coordinates are :

$$N_A = C_A u_A \quad \dots (7.23)$$

$$N_B = C_B u_B \quad \dots (7.24)$$

The molar fluxes of A and B relative to molar average velocity U are :

$$J_A = C_A (u_A - U) \quad \dots (7.25)$$

$$J_B = C_B (u_B - U) \quad \dots (7.26)$$

J_A and J_B are the diffusion flux of components A and B. The various fluxes can be interrelated as,

$$\begin{aligned} n_A &= \rho_A u_A \\ &= \rho_A (u + u_A - u) \\ &= \rho_A u + \rho_A (u_A - u) \\ &= \rho_A u + j_A \end{aligned} \quad \dots (7.27)$$

We have,

$$x_A = \frac{\rho_A}{\rho} \quad \therefore \quad \rho_A = x_A \rho$$

Since,

$$n_A = x_A (\rho u) + j_A$$

$$\sum n_i = \sum \rho_i u_i = \rho u$$

\therefore

$$n_A = x_A \sum n_i + j_A \quad \dots (7.28)$$

Similarly,

$$\begin{aligned} N_A &= C_A u_A \\ &= C_A (U + u_A - U) \\ &= C_A U + C_A (u_A - U) \\ N_A &= C_A U + J_A \end{aligned} \quad \dots (7.29)$$

$$N_A = x_A (CU) + J_A$$

$$\sum N_i = \sum C_i u_i = CU$$

$$N_A = x_A (\sum N_i) + J_A \quad \dots (7.30)$$

Fick's law of diffusion :

A relation between the flux of the diffusing substance and the concentration gradient responsible for molecular diffusion-mass transfer was first proposed by FICK in 1855 and is therefore referred to as Fick's first law of diffusion.

The flux of a diffusing component A (diffusion flux of A) in z direction in a binary mixture of A and B is proportional to the concentration gradient.

Therefore, the Fick's law of diffusion for species/component A in a binary mixture of A and B for steady state diffusion in z direction can be expressed as

$$J_A = -D_{AB} \cdot \frac{dC_A}{dz} \quad \dots (7.31)$$

where J_A is the molar flux of A in the z direction relative to the molar average velocity [moles per unit area per unit time, $\text{kmol}/(\text{m}^2 \cdot \text{s})$].

C_A is the molar concentration of A [moles of A per unit volume, kmol/m^3]

$\frac{dC_A}{dz}$ is the concentration gradient in the z-direction.

D_{AB} is a proportionality constant, known as the molecular diffusivity or diffusion coefficient for component A diffusing through B, m^2/s and z is the distance in the direction of diffusion, m.

The negative sign in Equation (7.31) indicates/implies that diffusion occurs in the direction of decrease in concentration. Thus, the term dC_A/dz is -ve and the flux becomes +ve.

Diffusivity is defined as the ratio of the flux to the corresponding concentration gradient. The dimensions of the diffusivity are L^2/θ and its unit in the SI system is m^2/s . The diffusivity of any component is a measure of its diffusive mobility and is a function of temperature, pressure, nature, and composition.

Diffusivity increases with decrease in pressure and increases with increase in temperature.

For a binary system in z direction, dropping the subscript z , we have

$$J_A = C_A(u_A - U) \quad \dots (7.32)$$

Equating Equations (7.31) and (7.32), we get

$$J_A = C_A(u_A - U) = -D_{AB} \frac{dC_A}{dz}$$

$$C_A u_A = -D_{AB} \frac{dC_A}{dz} + C_A U \quad \dots (7.33)$$

According to Equation (7.12), U is given by

$$U = \frac{1}{C} (C_A u_A + C_B u_B)$$

$$C_A U = \frac{C_A}{C} (C_A u_A + C_B u_B)$$

$$C_A U = x_A (C_A u_A + C_B u_B)$$

Substituting $C_A U$ in Equation (7.33), we get

$$C_A u_A = -D_{AB} \frac{dC_A}{dz} + x_A (C_A u_A + C_B u_B)$$

Using Equation (7.23), the above expression becomes

$$N_A = -D_{AB} \frac{dC_A}{dz} + x_A (N_A + N_B)$$

$$N_A = J_A + x_A (N_A + N_B) \quad \dots (7.34)$$

Here, J_A is the concentration gradient contribution, the diffusion flux and $x_A (N_A + N_B)$ is the bulk motion contribution, the flux due to bulk flow.

Molecular Diffusion in Gases :

For a diffusion in the z direction and for N_A and N_B both constant (steady state), we will derive equations for the flux.

For an ideal gas, we have

$$\frac{C_A}{C} = \frac{p_A}{P} = y_A \quad \dots (7.35)$$

where p_A is the partial pressure of component A.

and P is the total pressure.

1. Steady state equimolar counter diffusion : For the steady state diffusion of two ideal gases A and B with an equal number of moles the gases diffusing counter current to each other (in opposite directions to each other), the flux equation for A is given by

$$N_A = \frac{D_{AB}}{RTz} (p_{A1} - p_{A2}) \quad \dots (7.36)$$

where N_A is the molar flux of A in $\text{kmol}/(\text{m}^2 \cdot \text{s})$, D_{AB} is the diffusivity of A in B in m^2/s , z ($z_2 - z_1$) is the distance through which diffusion occurs in m and p_{A1} and p_{A2} are the partial pressures of the component A (in Pa) at the beginning and end of the diffusion path respectively.

We have :

$$N_A = J_A + x_A (N_A + N_B), \quad \text{and } \frac{C_A}{C} = \frac{p_A}{P} \text{ for ideal gas}$$

$$N_A = -D_{AB} \frac{dC_A}{dz} + \frac{C_A}{C} (N_A + N_B) \quad \dots (7.36 A)$$

From the ideal gas law, for the component A, we can write :

$$p_A = C_A RT$$

$$\therefore C_A = \frac{p_A}{RT}$$

$$dC_A = \frac{dp_A}{RT}$$

$$C = \frac{P}{RT} \quad \dots \text{for gas as a whole}$$

Substituting for C_A , C and dC_A in Equation (7.36 A), we get

$$N_A = -\frac{D_{AB}}{RT} \frac{dp_A}{dz} + \frac{p_A}{P} (N_A + N_B) \quad \dots (7.37)$$

For equimolar counter diffusion,

$N_A = -N_B = \text{constant}$. Therefore, Equation (7.37) reduces to

$$N_A = -\frac{D_{AB}}{RT} \frac{dp_A}{dz} \quad \dots (7.38)$$

If D_{AB} is constant, then the above equation can be integrated. Therefore,

$$N_A \int_{z_1}^{z_2} dz = -\frac{D_{AB}}{RT} \int_{p_{A1}}^{p_{A2}} dp_A$$

$$N_A (z_2 - z_1) = -\frac{D_{AB}}{RT} (p_{A2} - p_{A1})$$

Let $z_2 - z_1 = z$. Rearranging the above equation, we get

$$N_A = \frac{D_{AB}}{RTz} (p_{A1} - p_{A2}) \quad \dots (7.39)$$

Here, the concentration difference is expressed in terms of partial pressure difference. It can also be expressed in terms of mole fraction or molar concentration.

2. Steady state diffusion of A through nondiffusing/stagnant B :

Gas absorption and humidification are typical operation of this kind.

For the steady state diffusion of an ideal gas A through a stagnant gas B, the molar flux of A is given by

$$N_A = \frac{D_{AB} P}{RTz \cdot p_{B,M}} (p_{A1} - p_{A2}) \quad \dots (7.40)$$

where $p_{B,M}$ is the log mean partial pressure of the gas B.

We have :

$$N_A = -D_{AB} \frac{dC_A}{dz} + \frac{C_A}{C} (N_A + N_B)$$

$$N_A = \frac{-D_{AB}}{RT} \frac{dp_A}{dz} + \frac{p_A}{P} (N_A + N_B)$$

For the steady state diffusion of A through a nondiffusing B, we have

$$N_A = \text{constant and } N_B = 0$$

With this, the above equation reduces to

$$N_A = \frac{-D_{AB}}{RT} \frac{dp_A}{dz} + \frac{p_A}{P} \cdot N_A$$

Rearranging, we get

$$N_A \left(\frac{P - p_A}{P} \right) = \frac{-D_{AB}}{RT} \frac{dp_A}{dz}$$

If D_{AB} is constant, then the above equation can be integrated. Therefore,

$$N_A \int_{z_1}^{z_2} dz = \frac{-D_{AB} \cdot P}{RT} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{P - p_A}$$

$$N_A = \frac{D_{AB} P}{RTz} \ln \left[\frac{P - p_{A2}}{P - p_{A1}} \right] \quad \dots (7.41)$$

According to the Dalton's law of partial pressure, we have

$$p_{A1} + p_{B1} = P$$

and

$$p_{A2} + p_{B2} = P$$

\therefore

$$p_{B1} = P - p_{A1}$$

$$p_{B2} = P - p_{A2}$$

\therefore

$$p_{B2} - p_{B1} = p_{A1} - p_{A2}$$

\therefore

$$N_A = \frac{D_{AB} P}{RTz} \ln \left(\frac{p_{B2}}{p_{B1}} \right)$$

$$N_A = \frac{D_{AB} P}{RTz} \frac{(p_{B2} - p_{B1})}{(p_{B2} - p_{B1})} \ln (p_{B2}/p_{B1}) \quad \dots (7.41 A)$$

$p_{B,M}$ is the log mean partial pressure of component B and is given by

$$p_{B,M} = \frac{p_{B2} - p_{B1}}{\ln (p_{B2}/p_{B1})}$$

Replacing $(p_{B2} - p_{B1})$ by $(p_{A1} - p_{A2})$ since $(p_{B2} - p_{B1}) = (p_{A1} - p_{A2})$ in the numerator of Equation (7.41 A) and substituting $p_{B,M}$ for $(p_{B2} - p_{B1})/\ln(p_{B2}/p_{B1})$, we get

$$N_A = \frac{D_{AB} P}{RTz \cdot p_{B,M}} (p_{A1} - p_{A2}) \quad \dots (7.42)$$

In this case, the flux is proportional to the concentration difference expressed in terms of partial pressure of A and inversely proportional to the distance z and the concentration of the stagnant gas $(p_{B,M})$. Increase in z and $p_{B,M}$, increases resistance to diffusion and thus, flux decreases.

Molecular Diffusion in Liquids :

1. Steady-state equimolar counter diffusion :

We have : $N_A = -N_B = \text{constant}$

The flux equation for steady state equimolar counter diffusion for component A is given by

$$N_A = \frac{D_{AB}}{z} (C_{A1} - C_{A2}) = \frac{D_{AB}}{z} \left(\frac{\rho}{M} \right)_{\text{avg.}} (x_{A1} - x_{A2}) \quad \dots (7.43)$$

where $x_{A1} - x_{A2}$ is the concentration difference of component A in terms of mole fraction.

$$(\rho/M)_{\text{avg.}} = C_{\text{avg.}} = [\rho_1/M_1 + \rho_2/M_2]/2 \quad \dots (7.44)$$

$C_{\text{avg.}}$ is the total average concentration of A and B in kmol/m^3 , ρ_1 and ρ_2 are the average densities of the solution in kg/m^3 at locations 1 and 2 respectively, and M_1 and M_2 are the average molecular weights of the solution at locations 1 and 2, respectively in kg/kmol .

2. Steady state diffusion of A through nondiffusing B :

Here, we have : $N_A = \text{constant}, N_B = 0$

The flux for component A is given by

$$N_A = \frac{D_{AB}}{z \cdot x_{B,M}} (\rho/M)_{\text{avg.}} (x_{A1} - x_{A2}) \quad \dots (7.45)$$

where

$$x_{B,M} = \text{logarithmic mean mole fraction of B} \\ = (x_{B2} - x_{B1})/\ln(x_{B2}/x_{B1})$$

Diffusion in Solids :

The operations like leaching, drying, etc. involve contact of fluids with solids and involve diffusion in the solid phase.

Fick's law for the steady state diffusion can be written as

$$N_A = -D_A \frac{dC_A}{dz} \quad \dots (7.46)$$

where N_A is the rate of diffusion of A per unit cross-section of solid. D_A is the diffusivity of A through the solid, $-dC_A/dz$ is the concentration gradient in the direction of diffusion.

1. Diffusion through a flat slab of thickness z :

Considering D_A constant, integration of Equation (7.46) yields

$$N_A = \frac{D_A [C_{A1} - C_{A2}]}{z} \quad \dots (7.47)$$

$z = z_2 - z_1 = \text{thickness of the slab}$

C_{A1} and C_{A2} are the concentrations of A at the opposite sides of the slab.

For other solid shapes, the rate of diffusion is given by

$$W = N_A A_{\text{avg.}} = \frac{D A_{\text{avg.}} (C_{A1} - C_{A2})}{z} \quad \dots (7.48)$$

$A_{\text{avg.}}$ is the average cross-section available for diffusion.

For the radial diffusion through a solid cylinder of inner and outer radii r_1 and r_2 and length L :

$$A_{\text{avg.}} = \frac{2\pi (r_2 - r_1) L}{\ln (r_2/r_1)}, \text{ and } z = r_2 - r_1$$

For the radial diffusion through a spherical shell of inner and outer radii r_1 and r_2 ,

$$A_{\text{avg.}} = 4\pi r_1 r_2 \text{ and } z = r_2 - r_1$$

Steady State Equimolar Counter Diffusion :

The diffusion of two components in opposite directions to each other in a stationary mixture is of importance in distillation of a binary system. If the two components are at the same temperature and the same total pressure, then no net movement of the mixture will take place and it will be simply the replacement of the molecules of one component by the molecules of other component. In a language of diffusion, two components diffuse at the same molar flow rate in the opposite directions to each other. This overall transfer process is called as **equimolar counter diffusion**.

Consider a case of two gases A and B at constant total pressure P in two chambers.

Let us consider that two large chambers containing gases A and B are connected by a tube in such a way that molecular diffusion at steady state is occurring. The total pressure P is uniform (constant) throughout.

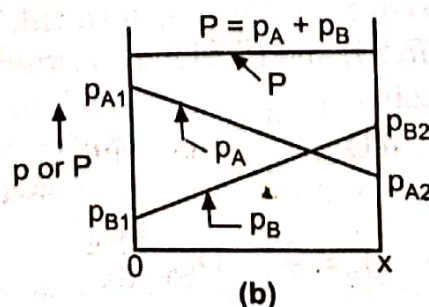
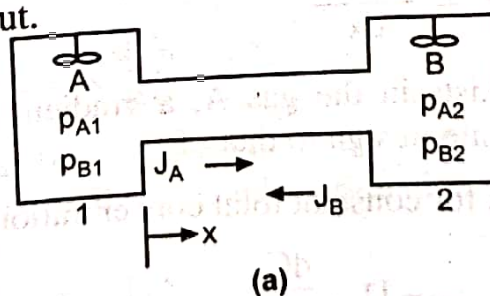


Fig. 7.1 : Equimolar counter diffusion of gases A and B;
(a) system, (b) concentration profile

Stirring provided in each chamber keeps the concentration in each chamber uniform. The partial pressure $p_{A1} > p_{A2}$ and $p_{B2} > p_{B1}$. The molecules of A diffuse to the right, while the molecules of B diffuse to the left.

As the temperature and total pressure P is constant throughout, the net moles of A diffusing to the right must be equal to the net moles of B diffusing to the left. If this is not so, the total pressure would not remain constant throughout the system. This implies/indicates that

$$J_A = -J_B \quad \dots (7.49)$$

J_A is the molar flux of component A in the x-direction due to molecular diffusion in $\text{kmol}/(\text{m}^2.\text{s})$.

Fick's law for component B for constant molar concentration, C , becomes

$$J_B = -D_{BA} \frac{dC_B}{dx} \quad \dots (7.50)$$

Here the flux is in the x-direction.

According to the Dalton's law, the total pressure is the sum of the partial pressures of A and B.

$$\therefore P = p_A + p_B \quad \dots (7.51)$$

and we know that : $p_A \propto C_A \quad \dots (7.52)$

The total molar concentration for the gaseous mixture is given by

$$C = C_A + C_B \quad \dots (7.53)$$

Differentiating both the sides of Equation (7.53) with respect to x gives

$$0 = \frac{dC_A}{dx} + \frac{dC_B}{dx} \quad \dots (7.54)$$

or $\frac{dC_A}{dx} = -\frac{dC_B}{dx} \quad \dots (7.55)$

Therefore, if a gradient exists in the gas A, a gradient also exists in the gas B. The gradient of B is equal but opposite in sign to that of A.

Fick's law for component A for constant total concentration is

$$J_A = -D_{AB} \frac{dC_A}{dx} \quad \dots (7.56)$$

Combining Equations (7.49), (7.50) and (7.51),

$$\begin{aligned} J_A &= -D_{AB} \frac{dC_A}{dx} \\ &= -J_B = -\left[-D_{BA} \frac{dC_B}{dx}\right] \end{aligned} \quad \dots (7.57)$$

$$-D_{AB} \frac{dC_A}{dx} = D_{BA} \frac{dC_B}{dx} \quad \dots (7.58)$$

but
$$\frac{dC_A}{dx} = -\frac{dC_B}{dt} \quad \dots (7.59)$$

$$D_{AB} = D_{BA} \quad \dots (7.60)$$

\therefore This shows that for a binary mixture of A and B, the diffusivity coefficient D_{AB} for A diffusing in B is the same as D_{BA} , for B diffusing in A.

We have :
$$J_A = -D_{AB} \frac{dC_A}{dx} \quad \dots (7.61)$$

For ideal gases, the molar concentration of A is related to the partial pressure of A by

$$C_A = \frac{N_A}{V} = \frac{p_A}{RT} \quad \dots (7.62)$$

$$\therefore \frac{dC_A}{dx} = \frac{1}{RT} \frac{dp_A}{dx} \quad \dots (7.63)$$

$$\therefore J_A = -\frac{D_{AB}}{RT} \frac{dp_A}{dx} \quad \dots (7.64)$$

Integrating, we get

$$J_A = \frac{D_{AB}}{RT} \frac{(p_{A1} - p_{A2})}{(x_2 - x_1)} \quad \dots (7.65)$$

$$= \frac{D_{AB}}{RT} \frac{(p_{A1} - p_{A2})}{x}, \quad x = x_2 - x_1 \quad \dots (7.66)$$

For species B,

$$J_B = \frac{D_{BA}}{RT} \frac{(p_{B1} - p_{B2})}{x} \quad \dots (7.67)$$

Equations (7.66) and (7.67) are the equations for steady state equimolar counter diffusion.

We know that

$$\frac{dC_A}{dx} = -\frac{dC_B}{dx} \quad \dots (7.68)$$

The gradient of B is equal but opposite in sign to that of A. Since the gradient for B exists, there must be molar flux of B, as stated by Equation (7.50). Combining of Equations (7.50), (7.56) and (7.68) gives

$$J_A = -J_B \quad \dots (7.69)$$

This shows that the rates of diffusion are equal but in opposite directions. Equation (7.69) is always true in the binary mixtures inspite of any other mechanism for mass transfer may be occurring. The rates of transfer of the two species by molecular motion (diffusion) are always equal but in opposite directions. When molecular motion is the only mechanism, the overall transfer process is called as an *equimolar counter diffusion*.

Mass Transfer Coefficients :

In many mass transfer operations, the turbulent flow is desired to increase the rate of mass transfer per unit area. In such cases, the mass transfer rate is expressed in terms of mass transfer coefficients. In turbulent flow there are three regions of mass transfer but as it is very