

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

difficult to know the value of a distance in the turbulent region through which diffusion occurs, it is considered that the entire resistance to mass transfer lies in a laminar sublayer of thickness z (effective laminar film thickness). The resistance offered by the effective laminar film thickness is approximately the same as the combined resistance offered by three regions in turbulent motion. The flux equations for such situations are of the type :

$$\text{Flux} = (\text{Mass transfer coefficient}) \times (\text{Concentration difference})$$

As the concentration can be expressed in number of ways, we have a variety of types of mass transfer coefficients.

Mass transfer coefficient is thus defined as *the rate of mass transfer per unit area per unit concentration difference*.

The flux equation obtained for the steady state equimolar counter diffusion components A and B diffusing at the same molar rates in opposite directions for turbulent motion becomes

$$N_A = \frac{D_{AB}}{RTz_G} (p_{A1} - p_{A2}) \quad \dots (7.70)$$

The term $\frac{D_{AB}}{RTz_G}$ is constant for a given situation and it can be termed as the mass transfer film coefficient for the gas and may be denoted by the symbol k'_G . With this, Equation (7.70) becomes

$$N_A = k'_G (p_{A1} - p_{A2}) \quad \dots (7.71)$$

The flux equation obtained for the steady state diffusion of A through non-diffusing (stationary) B for turbulent motion may be written as :

$$N_A = \frac{D_{AB} P}{RTz_G p_{B,M}} (p_{A1} - p_{A2}) \quad \dots (7.72)$$

$$N_A = k_G (p_{A1} - p_{A2}) \quad \dots (7.73)$$

where,

$$k_G = \frac{D_{AB} P}{RTz_G p_{B,M}}$$

Similar equations can be written for the liquid phase.

The flux equation for the equimolar counter diffusion for the liquid phase is

$$N_A = \frac{D_{AB}}{z_L} (C_{A1} - C_{A2}) = k'_L (C_{A1} - C_{A2}) \quad \dots (7.74)$$

where z_L is the effective laminar film thickness and k'_L is the mass transfer film coefficient for the liquid or the liquid film mass transfer coefficient/individual mass transfer coefficient for the liquid phase.

Mass transfer film coefficient may be defined as *the rate of mass transfer from the bulk of one phase to an interface of unit area for a unit driving force*.

The flux equations for transfer of A through non-transferring B (i.e., diffusion of A through non-diffusing B) in terms of the driving force expressed in terms of concentration and molefraction are :

$$N_A = k_y (y_{A1} - y_{A2}), N_A = k_c (C_{A1} - C_{A2}) \quad \text{for gases ... (7.75)}$$

$$N_A = k_x (x_{A1} - x_{A2}), N_A = k_L (C_{A1} - C_{A2}) \quad \text{for liquids ... (7.76)}$$

Similar equations for equimolecular counter diffusion are :

$$N_A = k'_y (y_{A1} - y_{A2}), N_A = k'_c (C_{A1} - C_{A2}) \quad \text{for gases ... (7.77)}$$

$$N_A = k'_x (x_{A1} - x_{A2}), N_A = k'_L (C_{A1} - C_{A2}) \quad \text{for liquids ... (7.78)}$$

In two film concepts, z is the effective thickness of the film.

Relation between film coefficients :

$$\text{Gases : } k'_c \frac{P}{RT} = k'_c C = k_c \frac{p_{B,M}}{RT} = k'_G P = k'_y = k_v y_{B,M} = k_G p_{B,M} = k_G y_{B,M} \cdot P$$

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

$$\text{Liquids : } k'_L C = k'_L \rho / M = k'_c C = k'_x x_{B,M} = k_L x_{B,M} C$$

Overall Mass Transfer Coefficient :

The overall mass transfer coefficients are measured on the basis of the gas phase or the liquid phase driving force.

The flux equation in terms of the overall mass transfer coefficient and the overall driving force for diffusion of A through non-diffusion B is given by

$$N_A = K_G (p_A - p_A^*) \quad \text{... (7.79)}$$

K_G is the overall gas phase mass transfer coefficient in $\text{kmol}/(\text{m}^2 \cdot \text{s})$ and $(p_A - p_A^*)$ is the overall driving force for the gas phase in terms of partial pressure.

p_A^* is the partial pressure of solute A over the solution having a composition of the bulk liquid of C_A . (Partial pressure of A in the gas phase that would be in equilibrium with C_A , the concentration of A in the bulk liquid phase.)

The flux can also be written as :

$$N_A = K_y (y_A - y_A^*) \quad \text{... (7.80)}$$

Similarly,

$$N_A = K_L (C_A^* - C_A) \quad \text{... (7.81)}$$

where K_L is the overall liquid phase mass transfer coefficient and is based on the concentration difference driving force for the liquid phase. C_A^* is the concentration of solute A in the liquid phase that would be in equilibrium with p_A , partial pressure of A in the bulk gas phase.

Mass transfer (film) coefficients in terms of the driving force in each phase are given by

$$N_A = k_G (p_A - p_{Ai}) = k_L (C_{Ai} - C_A) \quad \text{... (7.82)}$$

The overall driving force for the gas phase is

$$p_A - p_A^* = (p_A - p_{Ai}) + (p_{Ai} - p_A^*) \quad \text{... (7.83)}$$

For a state of equilibrium according to the Henry's law, we have :

$$p_A^* = H C_A, \quad p_{Ai} = H C_{Ai} \quad \text{and} \quad p_A = H C_A^*$$

With this, Equation (7.83) becomes

$$p_A - p_A^* = (p_A - p_{Ai}) + H (C_{Ai} - C_A) \quad \dots (7.83 A)$$

From Equations (7.81), (7.82) and (7.83), we have

$$p_A - p_A^* = \frac{N_A}{K_G}, \quad p_A - p_{Ai} = \frac{N_A}{k_G}, \quad C_{Ai} - C_A = \frac{N_A}{k_L}$$

Substituting for $(p_A - p_A^*)$, etc., Equation (7.83 A) becomes

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \quad \dots (7.84)$$

Here $\frac{1}{K_G}$ is the total resistance, the resistance in both the phases, based on the overall gas phase driving force. It is equal to the sum of the gas film resistance ($1/k_G$) and the liquid film resistance ($\frac{H}{k_L}$).

The overall driving force for the liquid phase :

$$C_A^* - C_A = (C_A^* - C_{Ai}) + (C_{Ai} - C_A)$$

Adopting the same procedure as for the gas phase, we get

$$C_A^* - C_A = \frac{p_A - p_{Ai}}{H} + (C_{Ai} - C_A)$$

and

$$\frac{1}{K_L} = \frac{1}{H k_G} + \frac{1}{k_L} \quad \dots (7.85)$$

C_{Ai} is the concentration of A at an interface between the phases.

Controlling Film Concept :

We have :

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \quad \dots (7.86)$$

If H is very small, $H \approx 0$ (a case with a highly soluble gas), the liquid film resistance $\frac{H}{k_L}$ is negligible compared to $\frac{1}{k_G}$ and the total resistance equals the gas film resistance (i.e., a gas film offers entire resistance to transfer). Such a transfer process is called gas film (gas phase) controlling as the resistance to transfer lies entirely in the gas film.

$$\therefore \frac{1}{K_G} = \frac{1}{k_G}$$

or

$$K_G \approx k_G$$

The overall mass transfer coefficients in such cases are based on the gas film coefficients only. A typical example of this kind is absorption of ammonia in water.

We have :

$$\frac{1}{K_L} = \frac{1}{H k_G} + \frac{1}{k_L} \quad \dots (7.87)$$

If H is very large, $H \gg 1$ (a case with a insoluble gas, i.e., a gas having low solubility), the gas film resistance $\frac{1}{H k_G}$ is negligible and the total resistance equals the liquid film resistance $\frac{1}{k_L}$ and the transfer process in such cases is considered to be liquid film controlling. A typical example of this kind is absorption of CO_2 in water.

$$\frac{1}{K_L} \approx \frac{1}{k_L}$$

$$K_L \approx k_L$$

\therefore The overall mass transfer coefficients in such cases are based on the liquid film coefficients only.

For absorption of a moderately soluble gas obeying Henry's law either K_G or K_L can be used for mass transfer calculations. The absorption of sulphur dioxide in water is an example of this type.

Interphase Mass Transfer :

In most important industrial applications of mass transfer, the material is transferred across a phase boundary (an interface). For example, in distillation, the vapour and liquid are brought into contact in a fractionating column and the more volatile component is transferred from the liquid to vapour, while the less volatile component is transferred from the vapour to liquid. In gas absorption, the solute gas is transferred from the gas to the liquid. In both of these examples, one phase is liquid and the other is gas.

Phase : It is a homogeneous and physically distinct part of a system which is bounded by a surface and, therefore, can be separated from the other parts of the system, e.g., water is one phase, but ice is another phase. Phases may be liquid, solid or gaseous.

Interphase mass transfer : It is the process of mass transfer from the bulk of one phase to the interphase surface, and then from the interphase to the bulk of another phase.

In the absorption of ammonia by water from an ammonia-air mixture, the solute ammonia may diffuse through the gas phase and then pass through the interface between the phases, and finally diffuse through the adjacent immiscible water phase (liquid phase).

In each phase, mass transfer occurs owing to the concentration gradient existing in that phase and a state of equilibrium is assumed to exist at the interface between the two fluid phases.

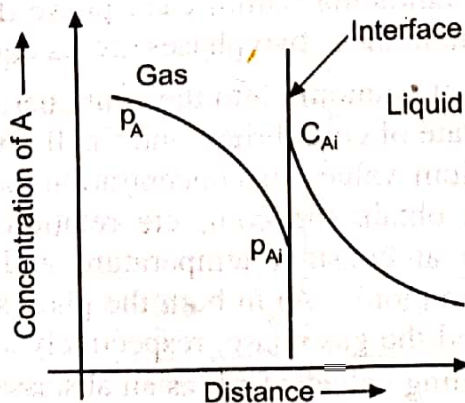


Fig. 7.2

In absorption of a solute gas A in a liquid solvent from a gas mixture, as shown in Fig. 7.2, mass transfer occurs in the gas phase from p_A to p_{Ai} (at the interface) and in the liquid phase from C_{Ai} (at the interface) to C_A . Equilibrium exists at the interface (between the phases) and due to this there is no resistance to mass transfer at the interface and p_{Ai} and C_{Ai} are related through the equilibrium relationship :

$$p_{Ai} = H C_{Ai}$$

... (7.88)

where H is the Henry's law constant for the system under consideration.

Equilibrium :

In mass transfer operations usually there are two phases which are brought in contact for the transfer of constituent material(s) from one phase to another or in both the phases. If two phases come to a state of equilibrium, then the net transfer of material ceases. The equilibrium relationship between the phases involved is of basic importance in all the mass transfer calculations. The equilibrium relationships can be expressed by an equation or can be shown graphically.

For gas absorption operation, the relationship between the equilibrium concentrations of solute in a gas phase and a liquid phase at constant temperature and pressure is the desired equilibrium relationship between the two phases. Now we will obtain the equilibrium relationship for absorption of ammonia in water from an ammonia-air mixture. Consider that a definite amount of liquid water along with a gaseous mixture of ammonia and air is placed in a closed container which is maintained at constant temperature and pressure. As the ammonia is very soluble in water, some of the ammonia molecules will transfer from the gas phase to the liquid phase, crossing the interface separating the two phases. Some of the ammonia molecules return back into the gas, at a rate proportional to the ammonia concentration in the liquid. As more and more ammonia enters the liquid, its concentration in that phase increases and due to this the rate at which ammonia returns back to the gas phase increases. This will continue and ultimately a stage will reach at which the rate with which ammonia enters the liquid phase becomes exactly equal to the rate with which it leaves the liquid phase and also at the same time ammonia concentration throughout each phase becomes uniform through the mechanism of diffusion, at this stage, a dynamic equilibrium is now said to exist between the phases. In a state of equilibrium, the net transfer of ammonia ceases even though the ammonia molecules continue to transfer to and fro from one phase to another. The concentrations of ammonia within each phase do not change with time. Then these concentrations of ammonia in these two phases are its equilibrium concentrations.

If we further inject additional ammonia into the container, equilibrium will be disturbed, the system will try to attain a state of equilibrium and finally we get a new set of equilibrium concentrations. These equilibrium values of concentrations are higher than those previously obtained. In this way we can obtain the complete relationship between the equilibrium concentrations in both phases at constant temperature and pressure. If we express the equilibrium concentrations of ammonia (A) in both the phases in terms of its mole fractions x_A and y_A in the liquid phase and the gas phase, respectively and plot the values of y_A (as an ordinate) against the corresponding values of x_A (as an abscissa), we obtain a curve as shown in Fig. 7.3. Such a curve is called an equilibrium distribution curve. This curve changes only

by changing the conditions imposed on the system such as temperature and pressure. One should note here that at equilibrium, the concentrations of ammonia in the two phases are not equal but it is the chemical potential of ammonia which is the same in both the phases and it is this equality of chemical potentials and not of concentrations, because of which the net transfer of the solute ammonia ceases.

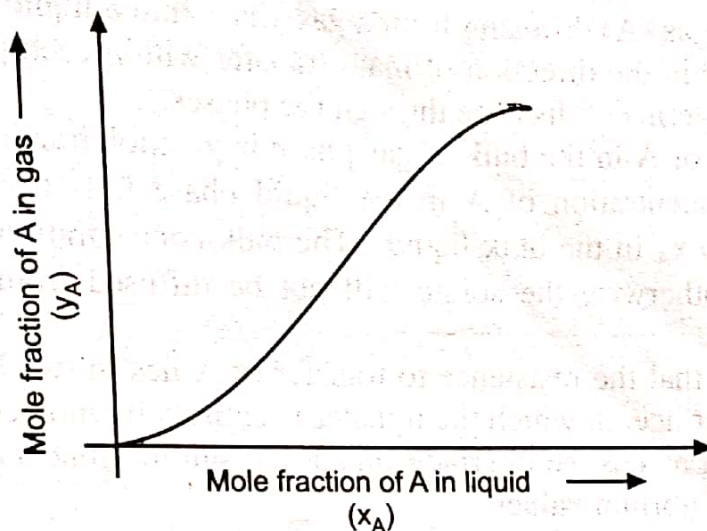


Fig. 7.3 : Equilibrium-distribution curve at constant temperature

Mechanism of Mass Transfer :

The mechanism of mass transfer across a phase boundary (an interface) can be explained by the various theories such as :

- (i) Whitman's two-film theory
- (ii) Higbie's penetration theory
- (iii) Danckwert's surface renewal theory
- (iv) Toor and Marchello's film penetration theory.

The Two-film Theory :

Salient features of Whitman's two film theory are :

- (i) Resistance to transfer in each phase is regarded as lying in a thin film close to the interface (i.e., in two fictitious films one on each side close to the interface).
- (ii) The transfer in these films is by a steady state process of molecular diffusion.
- (iii) The concentration gradient is assumed to be linear in these films and it is zero outside the films, i.e., zero in the bulk fluid.

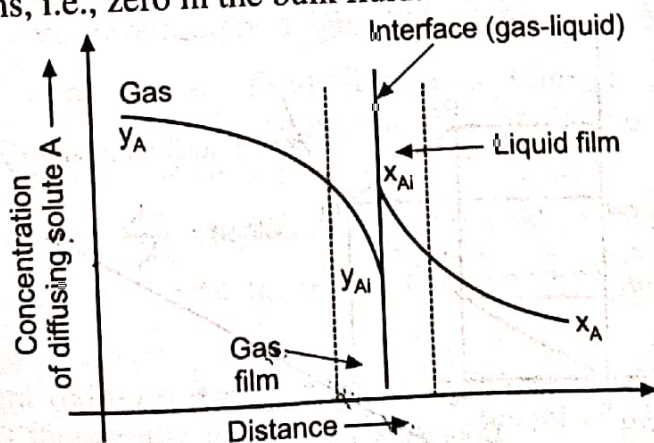


Fig. 7.4

- (iv) The theory assumes that the turbulence in the bulk fluid vanishes at the interface of the films.
- (v) The film capacity is negligible, i.e., the time taken for a concentration gradient to establish is small compared to the time of transfer.

Consider a solute gas (A) diffusing from a gas phase into a liquid phase. There must be a concentration gradient in the direction of mass transfer within each phase. This is shown in Fig. 7.4 graphically in terms of distance through the phases.

The concentration of A in the bulk of gas phase is y_A molefraction, and it falls to y_{Ai} at the interface. The concentration of A in the liquid phase falls from x_{Ai} at the interface between the phases to x_A in the bulk liquid. The bulk concentrations y_A and x_A are not in equilibrium because otherwise the solute will not be diffused from the gas to the liquid phase.

Whitman assumed that the resistance to transfer of A lies in two hypothetical films, one on each side of the interface, in which the transfer is entirely by molecular diffusion. There is no resistance to transfer across the interface and as a result the concentrations y_{Ai} and x_{Ai} are the equilibrium values.

For steady state mass transfer, the rate of transfer of A to the interface must be equal to the rate at which A is transferred from the interface to the bulk of liquid phase so that there is no accumulation or depletion of A at the interface.

Therefore, we can write the mass transfer flux of A or rate of transfer of A in terms of mass transfer coefficients and concentration changes occurring in the phases involved.

$$\begin{aligned} N_A &= k_y (y_A - y_{Ai}) \\ &= k_x (x_{Ai} - x_A) \end{aligned} \quad \dots (7.89)$$

The differences in y's and x's are the driving forces for mass transfer.

Rearranging Equation (7.89), we get

$$\frac{k_x}{k_y} = \frac{y_A - y_{Ai}}{x_{Ai} - x_A} \quad \dots (7.90)$$

$$\frac{y_A - y_{Ai}}{x_A - x_{Ai}} = -\frac{k_x}{k_y} \quad \dots (7.91)$$

Fig. 7.5 shows typical values of the concentrations of the bulk phases (P) and at the interface (Q).

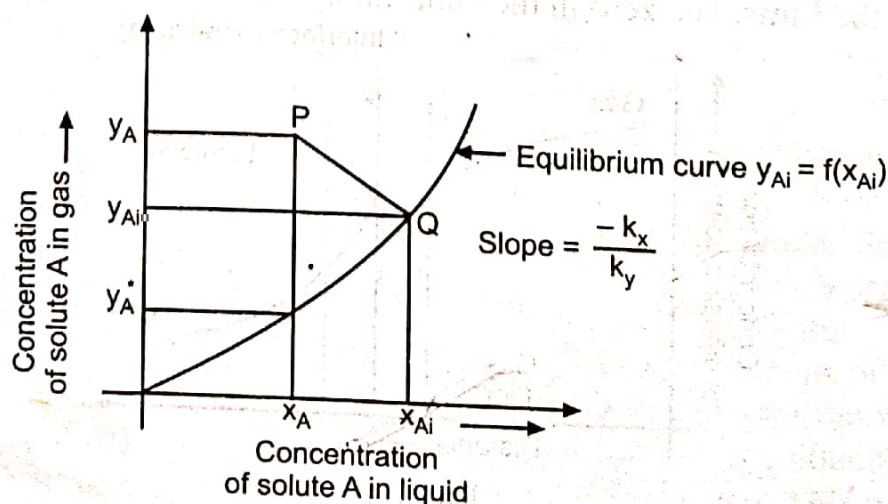


Fig. 7.5

In experimental determinations of the rate of transfer of the solute A, it is possible to measure only the bulk concentrations of the solute A and to measure the interface concentrations is ordinarily impossible. The equilibrium-distribution curve shown in Fig. 7.5 is unique at fixed T and P, so y_A^* in equilibrium with x_A is a good measure of x_A . Therefore, the entire two phase mass transfer effects can be measured in terms of overall mass transfer coefficient, K_y , i.e., the rate of mass transfer can also be set equal to the overall coefficient K_y times the driving force $(y_A - y_A^*)$, where y_A^* is the composition of the solute A in the gas phase which is in equilibrium with x_A .

$$N_A = K_y (y_A - y_A^*) \quad \dots (7.92)$$

$$\frac{1}{K_y} = \frac{y_A - y_A^*}{N_A} = \frac{(y_A - y_{Ai}) + (y_{Ai} - y_A^*)}{N_A}$$

$$\frac{1}{K_y} = \frac{y_A - y_{Ai}}{N_A} + \frac{y_{Ai} - y_A^*}{N_A}$$

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{y_{Ai} - y_A^*}{k_x (x_{Ai} - x_A)}$$

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{m}{k_x} \quad \dots (7.93)$$

where, $m = \text{slope} = (y_{Ai} - y_A^*) / (x_{Ai} - x_A)$

$1/K_y$ is the overall resistance to mass transfer and $1/k_y$ and m/k_x are the resistances in the liquid and gas films. The resistances in two phases are added to get an overall resistance and hence it is also called as two resistance theory.

On the similar line, x_A^* is a measure of y_A and it can be easily shown that

$$\frac{1}{K_x} = \frac{1}{m k_y} + \frac{1}{k_x} \quad \dots (7.94)$$

The Penetration Theory :

The penetration theory was proposed by Higbie. The main features of this theory are :

1. As the time of exposure of fluid for mass transfer generally being short, development/establishment of the concentration gradient of the film theory (the characteristic of a steady state) is not possible.
2. The transfer is largely because of fresh material brought to the interface by the eddies.
3. A process of unsteady state transfer occurs for a fixed period at the freshly exposed surface.
4. Each fluid element (eddy) resides for the same length of time period at the surface. According to this theory, the mass transfer coefficient is proportional to the square root of the diffusivity.

Surface Renewal Theory :

According to this theory (proposed by Danckwerts) :

1. The eddies of the fluid at the surface are exposed to varying lengths of time.
2. On the basis of exposure-time histories, an age distribution for the surface elements is calculated.
3. The mass transfer coefficient is proportional to the square root of the diffusivity regardless of the nature of the surface renewal rate.

Counter current and Cocurrent Mass Transfer :

Mass transfer processes that involve two fluid streams are frequently carried out continuously by passing the fluid streams either in a counter current or a cocurrent fashion in a column or device. The average driving force for a given situation will be larger in the countercurrent operation than in the cocurrent operation and because of which a smaller size equipment is needed for a given set of flow conditions for the countercurrent operation and thus, the counter current flow is more common.

Examples of counter current mass transfer processes are :

- (i) **Distillation in packed column :** In this case, a vapour stream (thermally created) is moving up against the downward flow of a liquid reflux. At steady state, a state of dynamic equilibrium is set up. The more volatile component under the action of a concentration gradient is transferred from the liquid phase to the interface and then from the interface into the vapour phase. The less volatile component is transferred in the opposite direction and passes through the vapour into the liquid. Here equimolar counter diffusion takes place since the molar latent heats of vaporisation of two components are essentially the same.
- (ii) **Absorption in packed column :** In this case, a solute gas together with a carrier gas moves up against the downward flow of a liquid (solvent). The solute gas diffuses through the gas phase to the interface where it dissolves and is then transferred into the bulk of the liquid.
- (iii) **Liquid-liquid extraction in packed/spray column :** In this case, both the streams are liquid. The lighter liquid rises through the denser one. The solute diffuses from the raffinate phase to the interface and away from the interface into the extract phase.

Examples of Cocurrent Flow :

The cocurrent flow of gas and liquid streams usually in the downward direction through a packed column is used for – catalytic chemical reaction between components of fluids, diffusional operation when a gas to be dissolved in a liquid is a pure substance and for diffusional operation accompanying a chemical reaction, e.g., in the absorption of hydrogen sulfide in a sodium hydroxide solution. The cocurrent flow produces a separation effect equivalent to that obtained with only one theoretical stage so used for such cases only. With cocurrent flow there is no flooding and there is no upper limit for permissible phase flow rates. The cocurrent flow is rarely used in the absence of a chemical reaction.

Analogies among Heat, Mass and Momentum Transfer :

Depending upon the fluid flow conditions, the mechanism of transfer process can be classified as molecular transport (characteristic of stream line flow) and combined molecular and eddy transfer (characteristic of total flow regime). There are similarities in governing