MOLECULAR DIFFUSION IN FLUIDS

Molecular diffusion:- Molecular diffusion is concerned with the movement of individual molecules through a substance by virtue of their thermal energy. The phenomenon of molecular diffusion ultimately leads to a completely uniform concentration of substances throughout a solution which may initially have been nonuniform. The substances moving from a place of higher concentration to one of low concentration.

Concentration, velocity and flux

In a multicomponent mixture, the concentration of particular species can be expressed in many ways. A mass concentration of each species, as well as for the mixture, can be defined. For species A, the mass concentration ρ_A is defined as the mass of A per unit volume of the mixture. The total mass concentration, or density ρ, is the total mass of the mixture contained in a unit volume.

$$\rho_A = \frac{\text{mass of A}}{\text{volume of mixture}}$$

$$\rho = \sum_{i=1}^{n} \rho_i \quad , \quad \rho = \rho_A + \rho_B + \cdots \rho_n$$

Mass fraction is the mass concentration of species A devided by the total mass density

$$\omega_A = \frac{\rho_A}{\rho} = \frac{\rho_A}{\sum_{i=1}^{n} \rho_i}$$

$$\rho_A = \omega_A \sum_{i=1}^{n} \rho_i \quad , \quad \sum \omega_i = 1$$

$$\text{Mass fraction of A} = \frac{\text{mass of A}}{\text{Total mass of mixture}}$$

$$= \frac{\rho_A \times \text{volume of mixture}}{\rho \times \text{volume of mixture}} = \frac{\rho_A}{\rho}$$

$$= \frac{\rho_A}{\sum_{i=1}^{n} \rho_i}$$

Similarly molar concentration of species A is the moles of species A per unit volume of the mixture

$$C_A = \frac{\text{moles of A}}{\text{Volume of mixture}}$$

The total molar concentration C, is the total moles of mixture contained in a unit volume.

$$C = \sum_{i=1}^{n} C_i$$

$$C = C_A + C_B + \cdots C_n$$

$$C = \frac{\text{moles of A}}{\text{Volume of mixture}} + \frac{\text{moles of B}}{\text{Volume of mixture}} + \cdots$$

$$C = \frac{(\text{moles of A} + \text{moles of B} + \cdots)}{\text{Volume of mixture}}$$

Mole fraction is the molar concentration of species A devided by the total molar concentration

$$x_A = \frac{C_A}{C} = \frac{C_A}{\sum_{i=1}^{n} C_i}$$

$$x_i = \frac{C_i}{\sum_{j=1}^{n} C_j}$$

For gaseous mixtures obeys the ideal gas law

$$C = \frac{P}{RT}, \quad P = \text{Total pressure}$$

$$T = \text{Absolute temperature}$$

$$\because \quad PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$$c = \frac{P}{RT}$$

For any component i

$$C_i = \frac{\bar{P}_i}{RT}$$, $\bar{P}_i$ = partial pressure of species i in mixture.

And,

$$\sum_{i=1}^{n} C_i = \sum_{i=1}^{n} \frac{\bar{P}_i}{RT}$$

$$c = \frac{P}{RT}$$ as, $\bar{P}_A + \bar{P}_B + \cdots \bar{P}_n = P$

for liquids and solids

$$x_A = \frac{C_A}{C}$$

and for gases

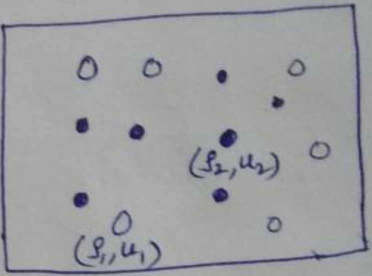
$$y_A = \frac{C_A}{C}$$

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} x_i = 1$$

Mass average velocity

The mass average velocity for a multicomponent mixture is defined in the terms of the mass densities.

$$u = \frac{\sum_{i=1}^{n} \rho_i u_i}{\sum_{i=1}^{n} \rho_i}$$



$$u = \sum_{i=1}^{n} \left(\frac{\rho_i}{\rho}\right) u_i = \sum_{i=1}^{n} \omega_i u_i$$

The molar average velocity for a multicomponent mixture is defined in terms of the molar concentration of all components by

$$U = \frac{\sum_{i=1}^{n} c_i u_i}{\sum_{i=1}^{n} c_i} = \sum_{i=1}^{n} \left(\frac{c_i}{c}\right) u_i$$

$$U = x_i u_i$$

Mass/Molar flux :- Mass/molar flux is the quantity per unit time and per unit area normal to the direction of the flow.

The mass flux of species i wrt coordinate that are fixed in the space is defined by

$$n_i = \rho_i u_i$$

$$\because \dot{m}_i = \rho_i u_i A_i \qquad \therefore n_i = \rho_i u_i = \frac{\dot{m}_i}{A_i}$$

The total flux will be the sum of fluxes i.e.

$$n = \sum_{i=1}^{n} n_i = \sum_{i=1}^{n} \rho_i u_i = \rho_A u_A + \rho_B u_B$$

$$n = \rho u$$

u = mixture average velocity

Similarly for molar flux of species i

$$N_i = C_i u_i$$

and, $$N = \sum_{i=1}^{n} N_i = \sum_{i=1}^{n} C_i u_i = CU$$

where,

C = Total molar concentration

U = Molar average velocity

The mass diffusion flux of species i wrt the mass average velocity is given by

$$j_i = \rho_i(u_i - u)$$

$$\sum_{i=1}^{n} j_i = 0$$

$$\because \quad j_i = \rho_i(u_i - u)$$

$$\sum_{i=1}^{n} j_i = \sum_{i=1}^{n} \rho_i(u_i - u) = \sum_{i=1}^{n} \rho_i u_i - u\sum_{i=1}^{n} \rho_i$$

$$\sum_{i=1}^{n} j_i = \rho u - \rho u = 0$$

The molar diffusion flux of species i wrt the molar average velocity is given by

$$J_i = C_i(u_i - U)$$

$$\text{and} \quad \sum_{i=1}^{n} J_i = 0$$

$$\sum_{i=1}^{n} J_i = \sum_{i=1}^{n} C_i(u_i - U) = \sum_{i=1}^{n} C_i u_i - U\sum_{i=1}^{n} C_i$$

$$\sum_{i=1}^{n} J_i = CU - CU = 0$$

Relation between mass flux n_i and mass diffusion flux j_i

$$j_i = \rho_i (u_i - u)$$

$$j_i = \rho_i u_i - \rho_i u = n_i - \rho_i u$$

$$n_i = j_i + \rho_i u$$

$$n_i = j_i + \omega_i \rho u = j_i + \omega_i (\rho u)$$

$$n_i = j_i + \omega_i n$$

The molar flux N_i is related to molar diffusion flux J_i as

$$J_i = C_i (u_i - U)$$

$$J_i = C_i u_i - C_i U$$

$$J_i = C_i u_i - (x_i C) U$$

$$J_i = N_i - x_i (CU)$$

$$J_i = N_i - x_i N$$

$$N_i = J_i + x_i N$$

Molar flux N_i is described by two vector quantities

J_i : The ~~f~~ molar diffusion flux resulting from the concentration gradient. This term is reffered to as concentration gradient contribution.

$x_i N = C_i \mathbf{U}$: The molar flux resulting as component i is carried in the bulk flow of the fluid. This flux term is designated the bulk motion contribution.

Fick's first law of diffusion

The Fick's law states that the molar diffusion flux of component A (J_A) is proportional to the concentration gradient of the species A. If A diffuses in a binary mixture of A and B, then molar diffusion flux in z-direction

$$J_{Az} \propto \frac{dC_A}{dz}$$

$$J_{AZ} = -D_{AB} \frac{dC_A}{dZ}$$

where, D_{AB} is the proportionality constant called diffusivity or diffusion coefficient.

The diffusion flux J_{Az} is a positive quantity by convention. Since, diffusion occurs spontaneously in the direction of decreasing concentration $\left(\frac{dC_A}{dz} < 0\right)$, the negative sign is incorporated in equation to make it consistant with sign.

The S.I unit of diffusivity is m^2/s.

General form of Fick's first law

$$J_1 = -c\,\mathcal{D}_{12}\,\nabla x_1$$

$$J_A = -c\,\mathcal{D}_{AB}\left(\frac{\partial x_A}{\partial x} + \frac{\partial x_A}{\partial y} + \frac{\partial x_A}{\partial z}\right)$$

Diffusion coefficients for binary ideal gas systems:-

The diffusion coefficient is a property of the system dependent upon temperature, pressure and nature of the components.

The Wilke-Lee modification of the Hirschfelder-Bird-Spotz method is recommended for mixtures of nonpolar gases or of a polar with nonpolar gas

$$\mathcal{D}_{AB} = \frac{10^{-4}\left(1{\cdot}084 - 0{\cdot}249\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}\right) T^{3/2}\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}}{P_t\,(r_{AB})^2\, f\left(\frac{KT}{\varepsilon_{AB}}\right)}$$

where,

$\mathcal{D}_{AB}$ = Diffusivity, m^2/s

T = Temperature, K

M_A, M_B = Molecular weight of A and B, respectively, Kg/Kmol

P_t = Absolute pressure, N/m^2

r_{AB} = Molecular separation at collision, nm
$= \frac{r_A + r_B}{2}$

ε_{AB} = Energy of molecular attraction $= \sqrt{\varepsilon_A \varepsilon_B}$

K = Boltzmann's constant

$f\left(\frac{KT}{\varepsilon_{AB}}\right)$ = Collision function (Treybal PP-32)

r and ε can be estimated empirically as

$$r = 1{\cdot}18\, v^{1/3}$$

$$\frac{\varepsilon}{K} = 1{\cdot}21\, T_b$$

where, v = molal volume of liquid at normal boiling point, $m^3/Kmol$

T_b = normal boiling point, K

Diffusivity of liquids :-

For dilute solutions of non-electrolytes, the empirical correlation of Wilke and Chang is recommended

$$\mathcal{D}_{AB}^{0} = \frac{117.3 \times 10^{-18} (\varphi M_B)^{0.5} T}{\mu v_A^{0.6}}$$

where,

$\mathcal{D}_{AB}^{0}$ = diffusivity of A in very dilute solution, m^2/s

M_B = Molecular weight of solvent kg/Kmol

T = Temperature, K

μ = Solution viscosity, kg/m.s

v_A = Solute molal volume at normal boiling point, m^3/Kmol

φ = Association factor for solvent. (2.26 for H_2O as solvent)

The diffusivity of concentrated solutions depends on viscosity as well as changes in the degree of nonideality of the solution.

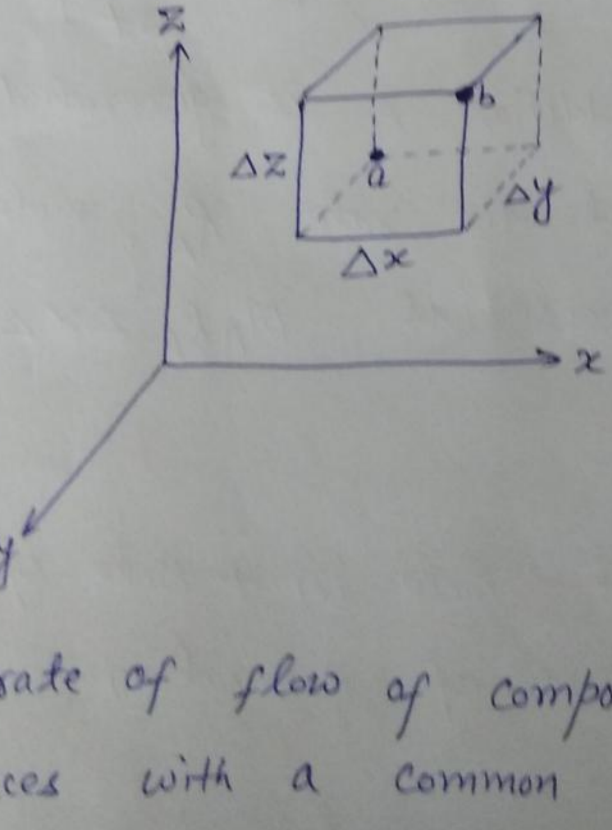
$$\mathcal{D}_A \mu = \left(\mathcal{D}^{0}_{BA}\,\mu_A\right)^{x_A} \left(\mathcal{D}^{0}_{AB}\,\mu_B\right)^{x_B} \left(1 + \frac{d\log\gamma_A}{d\log x_A}\right)$$

γ_A is calculated from VLE data

$$\gamma_A = \frac{\bar{P}_A}{x_A P_A} = \frac{y_A P_t}{x_A P_A}$$

Derivative $d(\log\gamma_A)/d(\log x_A)$ can be obtained graphically as the slope of a graph of $\log\gamma_A$ vs $\log x_A$.

Equation of continuity and Fick's second law:-



$a = a(x, y, z)$
$b = b(x+\Delta x, y+\Delta y, z+\Delta z)$

The mass rate of flow of component A into the three faces with a common corner at a is

$$M_A\left[(N_{A,x})_{/x}\,\Delta y\Delta z + N_{A,y/y}\,\Delta x\Delta z + N_{A,z/z}\,\Delta x\Delta y\right]$$

where $N_{A,x}$ signifies the x- direction flux and $N_{A,x}|_x$ its value at location x.

Similarly the mass rate of flow out of the three faces with a common corner at b is

$$M_A\left[N_{A,x}|_{x+\Delta x} \Delta y \Delta z + N_{A,y}|_{y+\Delta y} \Delta x \Delta z + N_{A,z}|_{z+\Delta z} \Delta x \Delta y \right]$$

The total component A in the element is $\Delta x \Delta y \Delta z \rho_A$ and its rate of accumulation is therefore $\Delta x \Delta y \Delta z \dfrac{\partial \rho_A}{\partial t}$

If, in addition A is generated by chemical reaction at the rate R_A, mole/(volume-time), its production rate is $M_A R_A \Delta x \Delta y \Delta z$, mass/time

In general:-

Rate out - Rate in + Rate of accumulation = Rate of generation

then,

$$M_A \left\{ \left[N_{A,x}|_{x+\Delta x} - N_{A,x}|_x \right] \Delta y \Delta z + \right.$$

$$\left[N_{A,y}\big|_{y+\Delta y} - N_{A,y}\big|_{y}\right]\Delta x\,\Delta z + \left[N_{A,z}\big|_{z+\Delta z} - N_{A,z}\big|_{z}\right]\Delta x\,\Delta y \Big\}$$

$$+ \Delta x\,\Delta y\,\Delta z\,\frac{\partial \rho}{\partial t} = M_A R_A\,\Delta x\,\Delta y\,\Delta z$$

dividing by $\Delta x \Delta y \Delta z$ and taking the limit as the three distances become zero gives

$$M_A\left(\frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z}\right) + \frac{\partial \rho_A}{\partial t} = M_A R_A \quad \text{—(1)}$$

Similarly for component B

$$M_B\left(\frac{\partial N_{B,x}}{\partial x} + \frac{\partial N_{B,y}}{\partial y} + \frac{\partial N_{B,z}}{\partial z}\right) + \frac{\partial \rho_B}{\partial t} = M_B R_B \quad \text{—(2)}$$

Total material balance is obtained by adding equation (1) and (2)

$$\frac{\partial\left(M_A N_A + M_B N_B\right)_x}{\partial x} + \frac{\partial\left(M_A N_A + M_B N_B\right)_y}{\partial y} + \frac{\partial\left(M_A N_A + M_B N_B\right)_z}{\partial z}$$

$$+ \frac{\partial\left(\rho_A + \rho_B\right)}{\partial t} = M_A R_A + M_B R_B$$

$$\text{—(3)}$$

$$\frac{\partial(M_A N_A + M_B N_B)_x}{\partial x} + \frac{\partial(M_A N_A + M_B N_B)_y}{\partial y} + \frac{\partial(M_A N_A + M_B N_B)_z}{\partial z}$$

$$+ \frac{\partial \rho}{\partial t} = 0 \quad \text{— (4)}$$

Where, $\rho = \rho_A + \rho_B$, solution density. Also, mass rate of generation of A and B must equal zero.

$$\because \quad N_{A,x} = C_A u_{A,x}$$

$$M_A N_{A,x} = \rho_A u_{A,x}$$

Now, $\quad M_A N_{A,x} + M_B N_{B,x} = \rho_A u_{A,x} + \rho_B u_{B,x}$

$$= \rho u_x$$

where, u_x is the mass average velocity.

$$\frac{\partial(M_A N_A + M_B N_B)_x}{\partial x} = \frac{\partial}{\partial x}(\rho u_x)$$

$$= \rho \frac{\partial u_x}{\partial x} + u_x \frac{\partial \rho}{\partial x}$$

Therefore equation (4) becomes

$$\rho \frac{\partial u_x}{\partial x} + u_x \frac{\partial \rho}{\partial x} + \rho \frac{\partial u_y}{\partial y} + u_y \frac{\partial \rho}{\partial y} + \rho \frac{\partial u_z}{\partial z} + u_z \frac{\partial \rho}{\partial z}$$

$$+ \frac{\partial \rho}{\partial t} = 0$$

$$\rho\left(\frac{\partial u_x}{\partial x}+\frac{\partial u_y}{\partial y}+\frac{\partial u_z}{\partial z}\right)+u_x\frac{\partial \rho}{\partial x}+u_y\frac{\partial \rho}{\partial y}+u_z\frac{\partial \rho}{\partial z}+\frac{\partial \rho}{\partial t}=0 \qquad -(5)$$

Equation (5) is known as the continuity equation.

If solution density is constant, then

$$\frac{\partial u_x}{\partial x}+\frac{\partial u_y}{\partial y}+\frac{\partial u_z}{\partial z}=0$$

$$\nabla\cdot\bar{u}=0$$

Again from equation (1)

$$M_A\left(\frac{\partial N_{A,x}}{\partial x}+\frac{\partial N_{A,y}}{\partial y}+\frac{\partial N_{A,z}}{\partial z}\right)+\frac{\partial \rho_A}{\partial t}=M_A R_A$$

$$\because\ N_{A,x}=C_A u_{A,x}=C_A U_x+J_{A,x}$$

$$M_A N_{A,x}=\rho_A u_x+M_A J_{A,x}$$ (in terms of masses)

$$M_A\frac{\partial N_{A,x}}{\partial x}=\frac{\partial}{\partial x}\left(\rho_A u_x\right)+\frac{\partial}{\partial x}\left(M_A J_{A,x}\right)$$

$$=\rho_A\frac{\partial u_x}{\partial x}+u_x\frac{\partial \rho_A}{\partial x}+M_A\frac{\partial J_{A,x}}{\partial x}$$

$$M_A \frac{\partial N_{A,x}}{\partial x} = \rho_A \frac{\partial u_x}{\partial x} + u_x \frac{\partial \rho_A}{\partial x} - M_A D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

$$\rho_A \frac{\partial u_x}{\partial x} + u_x \frac{\partial \rho_A}{\partial x} - M_A D_{AB} \frac{\partial^2 C_A}{\partial x^2} + \rho_A \frac{\partial u_y}{\partial y} + u_y \frac{\partial \rho_A}{\partial y} - M_A D_{AB} \frac{\partial^2 C_A}{\partial y^2} + \rho_A \frac{\partial u_z}{\partial z} + u_z \frac{\partial \rho_A}{\partial z} - M_A D_{AB} \frac{\partial^2 C_A}{\partial z^2} + \frac{\partial \rho_A}{\partial t} = M_A R_A$$

$$\rho_A \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) + u_x \frac{\partial \rho_A}{\partial x} + u_y \frac{\partial \rho_A}{\partial y} + u_z \frac{\partial \rho_A}{\partial z} - M_A D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + \frac{\partial \rho_A}{\partial t} = M_A R_A \quad \text{— (6)}$$

Equation (6) is known as continuity equation for component A.

For a solution of constant density, the first term of equation (6) will be zero, then,

$$u_x \frac{\partial \rho_A}{\partial x} + u_y \frac{\partial \rho_A}{\partial y} + u_z \frac{\partial \rho_A}{\partial z} - M_A D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + \frac{\partial \rho_A}{\partial t} = M_A R_A$$

Divide both side by M_A, we get,

$$u_x \frac{\partial C_A}{\partial x} + u_y \frac{\partial C_A}{\partial y} + u_z \frac{\partial C_A}{\partial z} - D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right) + \frac{\partial C_A}{\partial t} = R_A$$

In the special case where the velocity equals zero and there is no chemical reaction, it reduces to Fick's second law

$$\frac{\partial C_A}{\partial t} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right)$$

$$\frac{\partial C_A}{\partial t} = D_{AB}\nabla^2 C_A$$

This is frequently applicable to diffusion in solids and to limited situations in fluids.

Multicomponent diffusivity

Though multicomponent diffusion is a more complex process, a simple analysis can be done following the Maxwell- Stefan approach.

First this approach will be applied for binary mixture and then it extended to the case of a multicomponent mixture.

In this method a non-uniform binary mixture of A and B in which A is diffusing at steady state. The difference in partial pressure of A $(\Delta \bar{P}_A)$ over a small distance Δz is proportional to

(a) the molar concentration of A and B $(C_A \& C_B)$

(b) the length of diffusing path (Δz)

(c) the difference in velocities of A and B $(u_A - u_B)$

$$-\Delta \bar{P}_A \propto C_A C_B \Delta z (u_A - u_B)$$

$$-\Delta \bar{P}_A = K C_A C_B \Delta z (u_A - u_B)$$

where, K = proportionality constant

when $\Delta z \rightarrow 0$

$$-\frac{d\bar{P}_A}{dz} = K C_A C_B (u_A - u_B)$$

$$= K C_B C_A u_A - K C_A C_B u_B$$

$$= K C_B N_A - K C_A N_B \quad \text{——} \; (1)$$

For a binary system

$$C_A + C_B = C \quad , \text{ and } \quad C_A = \frac{P_A}{RT}$$

then,

$$-RT \frac{dC_A}{dZ} = K(C - C_A) N_A - K C_A N_B$$

$$-RT \frac{dC_A}{dZ} = KCN_A - KC_A(N_A + N_B)$$

$$N_A = \frac{C_A}{C}(N_A + N_B) - \frac{RT}{KC}\frac{dC_A}{dZ} \qquad \text{— (2)}$$

The general formula for binary mixture

$$N_A = \frac{C_A}{C}(N_A + N_B) - \mathcal{D}_{AB}\frac{dC_A}{dZ} \qquad \text{— (3)}$$

Comparison of equations (2) and (3) gives

$$\mathcal{D}_{AB} = \frac{RT}{KC}$$ = diffusivity of A in a mixture of A and B.

Now we consider a multicomponent mixture containing n components. For component i, we can generalize equation (1) by summing up the contributions of all possible binaries containing this component. There are $(n-1)$ such binaries.

Therefore,

$$-RT\frac{dc_i}{dz} = \sum_{\substack{j=1\\ j\neq i}}^{n} K_{ij}\left(c_j N_i - c_i N_j\right)$$

$$-\frac{dy_i}{dz} = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{K_{ij}}{RT}\left(y_j N_i - y_i N_j\right)$$

$$-\frac{dy_i}{dz} = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{1}{c\mathcal{D}_{ij}}\left(y_j N_i - y_i N_j\right) \quad -(4)$$

where, $\mathcal{D}_{ij} = \frac{RT}{cK_{ij}}$ = diffusivity of the component i in a binary mixture of i and j

The general equation for diffusion of component i in a multicomponent mixture of i and j

$$N_i = y_i \sum_{j=1}^{n} N_j - c\mathcal{D}_{im}\frac{dy_i}{dz} \quad — ⑤$$

comparison of equations ④ and ⑤ gives

$$\frac{N_i - y_i \sum_{j=1}^{n} N_j}{c\mathcal{D}_{im}} = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{1}{c\mathcal{D}_{ij}} \left(y_j N_i - y_i N_j \right)$$

$$\mathcal{D}_{im} = \frac{N_i - y_i \sum_{j=1}^{n} N_j}{\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{1}{\mathcal{D}_{ij}} \left(y_j N_i - y_i N_j \right)}$$

For the special case, when all components except i are non-diffusing, then,

$$\mathcal{D}_{im} = \frac{N_i - y_i N_i}{\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{1}{\mathcal{D}_{ij}} y_j N_i}$$

$$\mathcal{D}_{im} = \frac{(1 - y_i)}{\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{y_j}{\mathcal{D}_{ij}}} = \frac{1}{\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{y_j'}{\mathcal{D}_{ij}}}$$

where, y_j' is the mole fraction of the component j in the mixture on i-free basis.

Steady state molecular diffusion in fluids at rest and in laminar flow :-

$$\because \quad N_A = (N_A + N_B)\frac{C_A}{c} + J_A$$

$$N_A = (N_A + N_B)\frac{C_A}{c} - \mathcal{D}_{AB}\frac{dC_A}{dZ}$$

$$N_A C = (N_A + N_B) C_A - C\mathcal{D}_{AB}\frac{dC_A}{dZ}$$

$$N_A C - (N_A + N_B) C_A = - C\mathcal{D}_{AB}\frac{dC_A}{dZ}$$

$$\int_{C_{A1}}^{C_{A2}} \frac{-dC_A}{N_A C - (N_A + N_B) C_A} = \frac{1}{C\mathcal{D}_{AB}} \int_{Z_1}^{Z_2} dZ$$

Let

$$N_A C - (N_A + N_B) C_A = P$$

$$-(N_A + N_B)\, dC_A = dP$$

$$-dC_A = \frac{dP}{(N_A + N_B)}$$

then,

$$\int_{C_{A1}}^{C_{A2}} \frac{dP}{(N_A + N_B) P} = \frac{1}{C\mathcal{D}_{AB}}(Z_2 - Z_1)$$

$$\frac{1}{(N_A+N_B)} \ln P \Big|_{C_{A1}}^{C_{A2}} = \frac{1}{C\mathcal{D}_{AB}} z \qquad (z = z_2 - z_1)$$

$$\frac{1}{(N_A+N_B)} \left[\ln N_A C - (N_A+N_B) C_A\right]\Big|_{C_{A1}}^{C_{A2}} = \frac{z}{C\mathcal{D}_{AB}}$$

$$\frac{1}{(N_A+N_B)} \ln\left(\frac{N_A C - (N_A+N_B) C_{A2}}{N_A C - (N_A+N_B) C_{A1}}\right) = \frac{z}{C\mathcal{D}_{AB}}$$

$$N_A = \frac{N_A}{N_A+N_B} \frac{C\mathcal{D}_{AB}}{z} \ln\left(\frac{N_A C - (N_A+N_B) C_{A2}}{N_A C - (N_A+N_B) C_{A1}}\right)$$

$$N_A = \frac{N_A}{N_A+N_B} \frac{C\mathcal{D}_{AB}}{z} \ln\left(\frac{\frac{N_A}{N_A+N_B} - \frac{C_{A2}}{C}}{\frac{N_A}{N_A+N_B} - \frac{C_{A1}}{C}}\right) \quad -(1)$$

Equation (1) is a general equation for steady state molecular diffusion, which can be used for gases and liquids for various cases.

Molecular diffusion in gases:-

When ideal-gas can be applied equation (1) can be written in a form more convenient for use with gases. Thus

$$\frac{c_A}{c} = \frac{\bar{p}_A}{P_t} = y_A$$

where, $\bar{p}_A$ = partial pressure of component A

P_t = total pressure

y_A = mole fraction

Further $c = \frac{n}{V} = \frac{P_t}{RT}$

Equation (1) becomes,

$$N_A = \frac{N_A}{N_A+N_B} \frac{\mathcal{D}_{AB} P_t}{RTZ} \ln\left[\frac{\frac{N_A}{N_A+N_B} - y_{A_2}}{\frac{N_A}{N_A+N_B} - y_{A_1}}\right] \quad -(2)$$

or

$$N_A = \frac{N_A}{N_A+N_B} \frac{\mathcal{D}_{AB} P_t}{RTZ} \ln\left[\frac{\frac{N_A P_t}{N_A+N_B} - \bar{p}_{A2}}{\frac{N_A P_t}{N_A+N_B} - \bar{p}_{A_1}}\right] \quad -(3)$$

In order to use above equations (2) or (3), the relation between N_A and N_B must be known. For example CH_4 is being cracked on a catalyst,

$$CH_4 \longrightarrow C + 2H_2$$

under circumstances such that CH_4 (A) diffuses to the cracking surface and H_2 (B) diffuses back, then

$$-\frac{N_A}{1} = \frac{N_B}{2}$$

$$N_B = -2N_A$$

and $$\frac{N_A}{N_A+N_B} = \frac{N_A}{N_A-2N_A} = -1$$

In the case of purely separational operations (i.e. operations without any chemical reaction), there are two situations which frequently arise.

Steady state diffusion of A through nondiffusing B :-

For steady state diffusion of A through non-diffusing B, N_A = constant, $N_B = 0$

Then, $$\frac{N_A}{N_A+N_B} = 1$$

From equation (8)

$$N_A = \frac{D_{AB}P_t}{RTZ} \ln \frac{P_t - \bar{p}_{A2}}{P_t - \bar{p}_{A1}}$$

$$\because \bar{p}_{A1} + \bar{p}_{B1} = \bar{p}_{A2} + \bar{p}_{B2} = P_t$$

$$N_A = \frac{D_{AB}P_t}{RTZ} \ln\left(\frac{\bar{p}_{B2}}{\bar{p}_{B1}}\right)$$

if we let,

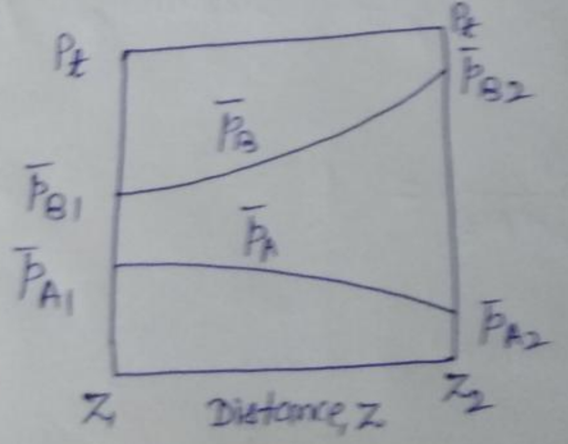
$$\bar{p}_{B,m} = \frac{\bar{p}_{B2} - \bar{p}_{B1}}{\ln\left(\frac{\bar{p}_{B2}}{\bar{p}_{B1}}\right)}$$

Then, $$\ln\left(\frac{\bar{p}_{B2}}{\bar{p}_{B1}}\right) = \frac{\bar{p}_{B2}-\bar{p}_{B1}}{\bar{p}_{B,M}} = \frac{\bar{p}_{A1}-\bar{p}_{A2}}{\bar{p}_{B,M}}$$

Therefore,

$$N_A = \frac{\mathcal{D}_{AB} P_t}{RTZ\,\bar{p}_{B,M}}\left(\bar{p}_{A1}-\bar{p}_{A2}\right)$$

The graphical representation of above equation is given below:-



substance A diffuses by virtue of its concentration gradient $-d\bar{p}_A/dz$. substance B is also diffusing relative to the average molar velocity at a flux J_B, which depends upon $-d\bar{p}_B/dz$, but like a fish which swims at the same velocity as the water flows down-stream, $N_B=0$ relative to a fixed place in space.

Steady state equimolar counterdiffusion :-

For this case, $N_A = -N_B = \text{Constant}$

Here, $N_A + N_B = 0$, equation (2) or ⑧ cannot be used.

From general equation

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

For gases, the above equation becomes,

$$N_A = (N_A + N_B)\frac{\bar{P}_A}{P_t} - \frac{\mathcal{D}_{AB}}{RT}\frac{d\bar{P}_A}{dz}$$

For equimolar counterdiffusion, $N_A + N_B = 0$

Therefore,

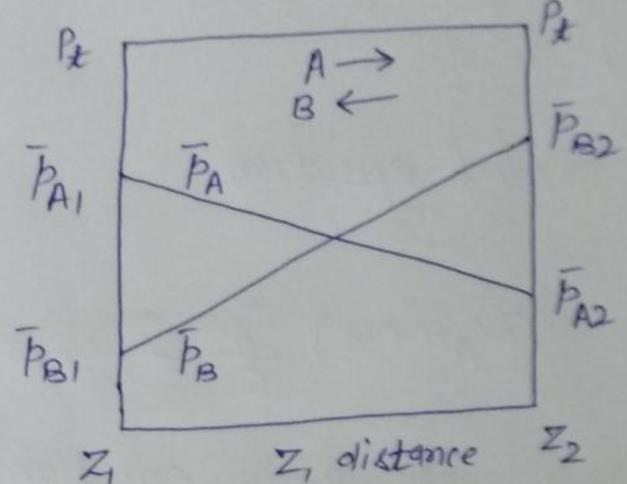
$$N_A = -\frac{\mathcal{D}_{AB}}{RT}\frac{d\bar{P}_A}{dz}$$

$$N_A\int_{z_1}^{z_2} dz = -\frac{\mathcal{D}_{AB}}{RT}\int_{\bar{P}_{A_1}}^{\bar{P}_{A_2}} d\bar{P}_A$$

$$N_A(z_2 - z_1) = -\frac{\mathcal{D}_{AB}}{RT}\left(\bar{P}_{A_2} - \bar{P}_{A_1}\right)$$

$$N_A = \frac{\mathscr{D}_{AB}}{RTZ}\left(\bar{p}_{A_1} - \bar{p}_{A_2}\right)$$

The graphical representation of above equation is given below :-



Moleculer diffusion in liquids :-

For the moleculer diffusion in liquids, the c is replaced by average c which is equal to $\left(\frac{\rho}{M}\right)_{av}$. The equation(1) will be,

$$N_A = \frac{N_A}{N_A+N_B}\frac{\mathscr{D}_{AB}}{Z}\left(\frac{\rho}{M}\right)_{av} \ln \frac{N_A/(N_A+N_B) - x_{A2}}{N_A/(N_A+N_B) - x_{A1}} \quad -(4)$$

where, ρ & M are the solution density and molecular weight, respectively.

Steady state diffusion of A through nondiffusing B :-

$$N_A = \text{constant}, \quad N_B = 0$$

Therefore $\frac{N_A}{N_A + N_B} = 1$

From equation (4)

$$N_A = \frac{\mathcal{D}_{AB}}{Z}\left(\frac{\rho}{M}\right)_{av} \ln\left(\frac{1 - x_{A_2}}{1 - x_{A_1}}\right)$$

$$\because \quad x_{A_1} + x_{B_1} = x_{A_2} + x_{B_2} = 1$$

Let, $x_{B,M} = \frac{x_{B2} - x_{B1}}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)}$

$$\ln\left(\frac{x_{B2}}{x_{B_1}}\right) = \frac{x_{B2} - x_{B1}}{x_{B,M}}$$

$$N_A = \frac{\mathcal{D}_{AB}}{Z}\left(\frac{\rho}{M}\right)_{av.} \ln\left(\frac{x_{B2}}{x_{B1}}\right)$$

$$N_A = \frac{\mathcal{D}_{AB}}{Z\, x_{B,M}}\left(\frac{\rho}{M}\right)_{av} (x_{B2} - x_{B1})$$

$$N_A = \frac{\mathcal{D}_{AB}}{Z\, x_{B,M}}\left(\frac{\rho}{M}\right)_{av} (x_{A_1} - x_{A_2})$$

Steady state equimolal counterdiffusion :-

$$N_A = -N_B = \text{constant}$$

$$(N_A + N_B) = 0$$

$$N_A = \frac{D_{AB}}{z}(C_{A_1} - C_{A_2}) = \frac{D_{AB}}{z}\left(\frac{\rho}{M}\right)_{av}(x_{A_1} - x_{A_2})$$

Diffusion in solids :-

In operations such as leaching, drying, adsorption, and membrane operations involve contact of fluids with solids. In these cases some of the diffusion occurs in the solid phase and may proceed according to any of several mechanisms.

Steady state diffusion in solids :-

The structure of solid and its interaction with the diffusing substance determine how diffusion occurs and the rate of mass transport. The solid may be polymeric, crystalline, or porous. Consider two proportions of a gas at different pressures separated by a polymeric membrane.

The gas disolves in the solid at the faces exposed to the gas to an extent usually directly proportional to the pressure. The dissolved gas then diffuses from the high - to the low pressure side in a manner described by Fick's first law.

When the concentration gradient remains unchanged with passage of time, so that the rate of diffusion is constant and if diffusivity of component A is constant and independent of concentration and there is no bulk flow. The rate of diffusion of substance A per unit cross section of solid is given as:-

$$N_A = -\mathcal{D}_A \frac{dC_A}{dz}$$

where $\mathcal{D}_A$ = Diffusivity of A through solid.

$$N_A = \frac{\mathcal{D}_A (C_{A1} - C_{A2})}{z}$$

(for a flat slab of thickness z)

For other solid shapes, the rate is given by

$$w = N_A S_{av} = \frac{\mathcal{D}_A S_{av} (C_{A_1} - C_{A_2})}{z}$$

where S_{av} = average cross section for diffusion.

For radial diffusion through a solid cylinder of inner and outer radii a_1 and a_2, respectively, and of length l,

$$S_{av} = \frac{2\pi l\,(a_2 - a_1)}{\ln\left(\frac{a_2}{a_1}\right)}$$

and $z = a_2 - a_1$

For radial diffusion through a spherical shell of inner and outer radii a_1 and a_2

$$S_{av} = 4\pi a_1 a_2$$

$$z = a_2 - a_1$$

Diffusion through crystalline solids:-

Diffusion through nonporous crystalline solids depends markedly on the crystal lattice structure and the diffusing entity. The mechanism of diffusion in crystalline solids include

(a) Direct exchange of lattice position by two atoms or ions.

(b) Migration of small solutes through inter-lattice spaces called interstitial sites.

(c) Migration to a vacant site in the lattice.

(d) Migration along lattice imperfections or grain boundaries.

Diffusion in porous Solids:-

When solids are porous, it is possible to predict the diffusivity of gaseous and liquid solute species in the pores. In this case any of the following mass transfer mechanisms or combinations thereof may take place.

(a) ordinary molecular diffusion through pores, which present tortuous paths and hinder the movement of large molecules when their diameter is more than 10% of the pore diameter.

(b) Knudsen diffusion, which involves collision of diffusing gaseous molecules with the pore walls when the pore diameter and gas pressure are such that the molecular mean free path is large compared to the pore diameter.

(c) Surface diffusion involving the jumping of molecules, adsorbed on the pore walls, from one adsorption site to another based on surface concentration driving force.

(d) Hydrodynamic flow through or into the pores driven by a total pressure gradient.

Steady state binary molecular diffusion in porous solids:-

When treating diffusion of solutes in porous materials where diffusion is considered to occur only in the fluid inside the pores, it is common to refer to an effective diffusivity, $\mathcal{D}_{AB,eff}$, which is based on (1) the total cross sectional area of the porous solid rather than the cross-sectional area of the poreand (2) on a straight path, rather than the actual pore path, which is usually quite tortuous.

In a binary system, if pore diffusion occurs only by the ordinary molecular diffusion, Fick's law can be used with an effective diffusivity that can be expressed in terms of the ordinary diffusion coefficient, $\mathcal{D}_{AB}$, as

$$\mathcal{D}_{AB,eff} = \frac{\varepsilon \mathcal{D}_{AB}}{\tau} \quad \text{—— (1)}$$

where, ε is the fractional porosity (typically 0.5) of a solid and τ is the pore-path tortuosity (typically 2 to 4). The tortuosity is defined as the ratio of the pore actual length to the length if the pore were straight in the direction of diffusion.

For binary mixtures diffusing inside porous solids, the applicability of equation (1) depends upon the value of a dimensionless ratio called the Knudsen number, Kn, defined as

$$Kn = \frac{\lambda}{d}$$

where d is the pore diameter and λ is the mean free path of the diffusing molecules. Equation (1) applies when Kn is less than ~0.05 for all the diffusing species.

For liquids, the mean free path is commonly a few angstroms, so the Knudsen number is almost always very small and diffusion inside the pores is usually only by ordinary molecular diffusion. Knudsen diffusion is not known for liquids, but important reductions in diffusion rates occur when the molecular size of the diffusing solute becomes significant relative to the pore size of the solid. In that case, the effective diffusivity is given by

$$\mathcal{D}_{AB,\,eff} = \frac{\epsilon \mathcal{D}_{AB}}{\tau} K_r \qquad \text{— (2)}$$

where, K_r is a restrictive factor that accounts for interfering collisions of the diffusing solute with the pore wall, and is given by

$$K_r = \left[1 - \frac{d_m}{d}\right]^4, \qquad \frac{d_m}{d} \leq 1 \qquad \text{— (3)}$$

where, d_m = molecular diameter

d = pore diameter

From equation (3), when $\left(\frac{d_m}{d}\right) = 0.01$, $K_r = 0.96$, but when $\left(\frac{d_m}{d}\right) = 0.3$, $K_r = 0.24$. When $d_m > d$, $K_r = 0$, and the solute cannot diffuse through the pore.

In gases, the mean free path can be estimated from the following equation :-

$$\lambda = \frac{KT}{\sqrt{2}\,\pi \sigma_{AB}^2 P}$$

where k is the Boltzmann constant and σ_{AB} is the collision diameter of the diffusing species.

Knudsen diffusion in porous solids :-

When the Knudsen number is large ($Kn > 5$), the molecular mean free path is much larger than the diameter of the channel in which the diffusing molecules reside. When this happens, the molecules bounce from wall to wall rather than colliding with other molecules. Since molecular collision are unimportant under these conditions, each gas diffuses independently. This mode of transport is known as Knudsen diffusion. From the kinetic theory of gases, in a straight cylindrical pore of diameter d and length l, the Knudsen diffusivity, $\mathcal{D}_{K,i}$, is given by

$$\mathcal{D}_{K,i} = \frac{d}{3}\left(\frac{8RT}{\pi M_i}\right)^{1/2} \quad \text{———} \quad (4)$$

and the Knudsen flux is given by

$$N_i = \frac{\mathcal{D}_{K,i}\left(\bar{p}_{i1} - \bar{p}_{i2}\right)}{RTl} \quad \text{——} \quad (5)$$

Since normally d is not constant and the true

l is unknown, l in equation (5) is ordinarily replaced by z, the membrane thickness, and $\mathcal{D}_{K,i}$ by $\mathcal{D}_{K,i,eff}$, the effective Knudsen diffusivity, which is determined by experiment. $\mathcal{D}_{K,i,eff}$ is independent of pressure and varies as $\left(\frac{T}{M}\right)^{1/2}$. For binary gas mixtures,

$$\frac{N_B}{N_A} = -\left(\frac{M_A}{M_B}\right)^{1/2} \quad \text{———} \quad (6)$$

or, for a multicomponent system

$$\sum_{j=1}^{n} N_j \sqrt{M_j} = 0 \quad \text{———} \quad (7)$$

This is known as Graham's law of effusion for Knudsen diffusion of a multicomponent system at constant total pressure.

For Knudsen diffusion in porous solids of porosity ϵ and tortuosity τ,

$$\mathcal{D}_{K,i,eff} = \frac{\epsilon \mathcal{D}_{K,i}}{\tau}$$

and

$$N_i = \frac{\mathcal{D}_{K,i,eff}\left(\bar{P}_{i1} - \bar{P}_{i2}\right)}{RTl}$$

$\because l = z$, $$N_i = \frac{\mathcal{D}_{K,i,eff}\left(\bar{P}_{i1} - \bar{P}_{i2}\right)}{RTz}$$

In the range of Kn from roughly 0.05 to 5, a transition range, both molecular and Knudsen diffusion have influence, and the flux for binary mixtures is given by

$$N_A = \frac{N_A}{N_A + N_B} \frac{\mathcal{D}_{AB,eff} P_t}{RTZ} \ln \left[\frac{\frac{N_A}{N_A+N_B}\left(1+\frac{\mathcal{D}_{AB,eff}}{D_{K,A,eff}}\right) - y_{A2}}{\frac{N_A}{N_A+N_B}\left(1+\frac{\mathcal{D}_{AB,eff}}{D_{K,A,eff}}\right) - y_{A1}} \right]$$

The above equation is known as the "dusty gas" equation because a porous medium consisting of a random grouping of spheres in space was used as a model for its derivation.

When, $\mathcal{D}_{K,A,eff} >> \mathcal{D}_{AB,eff}$, the above equation reverts to molecular diffusion equation. When $\mathcal{D}_{AB,eff} >> \mathcal{D}_{K,A,eff}$, the above equation reverts to Knudsen diffusion equation.

$$N_A = \frac{N_A}{N_A + N_B} \frac{\mathcal{D}_{AB,eff} P_t}{RTZ} \ln \frac{N_A/(N_A+N_B) - y_{A2}}{N_A/(N_A+N_B) - y_{A1}}$$

for $\mathcal{D}_{K,A,eff} >> \mathcal{D}_{AB,eff}$

and

$$N_A = \frac{\mathcal{D}_{K,A,eff}\left(\bar{p}_{A1} - \bar{p}_{A2}\right)}{RTZ}$$

for $\mathcal{D}_{AB,eff} >> \mathcal{D}_{K,A,eff}$

For open-ended pores, equation (6) applies throughout the transition range for solids whose pore diameters are of the order of 10 um or less.

Hydrodynamic flow of gases in porous solids :-

If there is a difference in total pressure across a porous solid, a hydrodynamic flow of gas through the solid will occur. consider a solid consisting of uniform straight capillary tubes of diameter d and length l reaching from the high- to the low- pressure side. In most practical applications, the flow inside the capillaries will be laminar. For a single gas, this can be described by Poiseuille's law for compressible fluids obeying the ideal gas law :-

$$N_A = \frac{d^2 P_{av}}{32 \mu l RT} \left(P_1 - P_2 \right) \qquad (8)$$

where, $P_{av} = (P_1 + P_2)/2$. This assumes that the entire pressure difference is the result of friction in the pores and ignores entrance and exit losses and Kinetic-energy effects, which is satisfactory for present purposes.

Derivation of equation (8) :-

$$\because \quad N_A = C_A u_A$$

From Poiseuille's law

$$(P_1 - P_2) = \frac{32 \mu u_A l}{d^2}$$

$$\therefore \quad u_A = \frac{d^2 (P_1 - P_2)}{32 \mu l}$$

For ideal gas

$$C_A = \frac{P_A}{RT}$$

Here, C_A is evaluated at average pressure $(P_1 + P_2)/2$

$$\therefore \quad C_A = \frac{P_{avg}}{RT}$$

$$\therefore \quad N_A = \frac{P_{avg}}{RT} \cdot \frac{d^2 (P_1 - P_2)}{32 \mu l}$$

$$\therefore \quad N_A = \frac{d^2 P_{av}}{32 \mu R T l} (P_1 - P_2)$$

Since the pores are neither straight nor of constant diameter, just as with diffusive flow it is best to base N_A on the gross external cross-sectional area of solid and write equation (8) as

$$N_A = \frac{B_0 P_{av}}{\mu l RT}(P_1 - P_2) \qquad (9)$$

Where, B_0 is an empirical factor characterizing the porous solid called the viscous flow parameter.

$B_0 = \frac{d^2}{32}$ for straight circular capillaries of diameter d.

$$(B_0)_{\text{porous medium}} = \frac{\varepsilon}{\varphi}(B_0)_{\text{single mean diameter pore}}$$

$$(B_0)_{\text{porous medium}} = \frac{\varepsilon^3}{(1-\varepsilon)^2} \frac{1}{k\left(\frac{S}{V_s}\right)^2}$$

Where, $k = 2\varphi^2$ is called the Kozeny function, and value of k is approximately 5. It is better to consider the Kozeny function as being a separate experimental fiddle factor, rather than a function of tortuosity. S is total surface area per unit volume, and V_s is the solid fraction of the media.

Equation (9) can be written as:-

$$N_A = \frac{k}{RTZ} P_{av} (P_1 - P_2)$$

where $k = \frac{B_0}{\mu RT}$.

If conditions of pore diameter and pressure occur for which Knudsen flow prevails ($Kn > 5$) the flow will be described by Knudsen's law, equation (4) and (5).

$$\mathcal{D}_{K,A} = \frac{d}{3} \left(\frac{8RT}{\pi M_A} \right)^{1/2}$$

and
$$N_A = \frac{\mathcal{D}_{K,A} (\bar{P}_{A1} - \bar{P}_{A2})}{RTZ}$$

When the gas is a mixture, the hydrodynamic flux given by equation (8) or (9) is the flux of the mixture, that is the mixture moves as a whole under the total pressure gradient. All species move at the same speed (i.e., no separation is achieved), and the individual flux of each component is the product of its mole fraction times the total flux. In that case, the viscosity in equations (8) and (9) is the viscosity of the mixture. If the gas is a mixture with different concentrations and different total pressure on either side of the porous solid, the flow may be a combination of hydrodynamic, Knudsen, and diffusive.

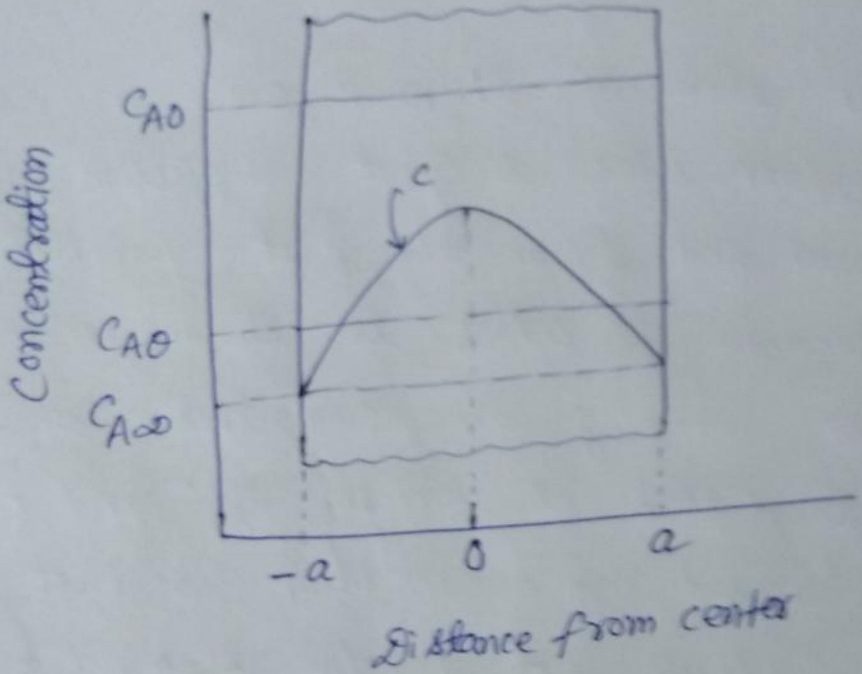
Unsteady-state diffusion :-

Since solids are not so readily transported through equipment as fluids, the application of batch and semibatch processes and consequently unsteady-state diffusional conditions arise much more frequently than with fluids. Even in continuous operations, e.g., a continuous drier, the history of each solid piece as it passes through equipment is representative of the unsteady state. These cases are therefore of considerable importance. When there is no bulk flow, and in the absence of chemical reaction, Fick's second law can be used to solve problems of unsteady-state diffusion by integration with appropriate boundary conditions. It is useful to note that Fick's second law is of the same form as Fourier's equation for heat conduction, with molecular rather than thermal diffusivity and concentration rather than temperature. consequently the lengthy catalog of solutions to the problem of heat transfer can be made applicable to diffusion by appropriate substitutions.

For some simple cases, Newman has summarized the results most conveniently.

1. Diffusion from a slab with sealed edges:-

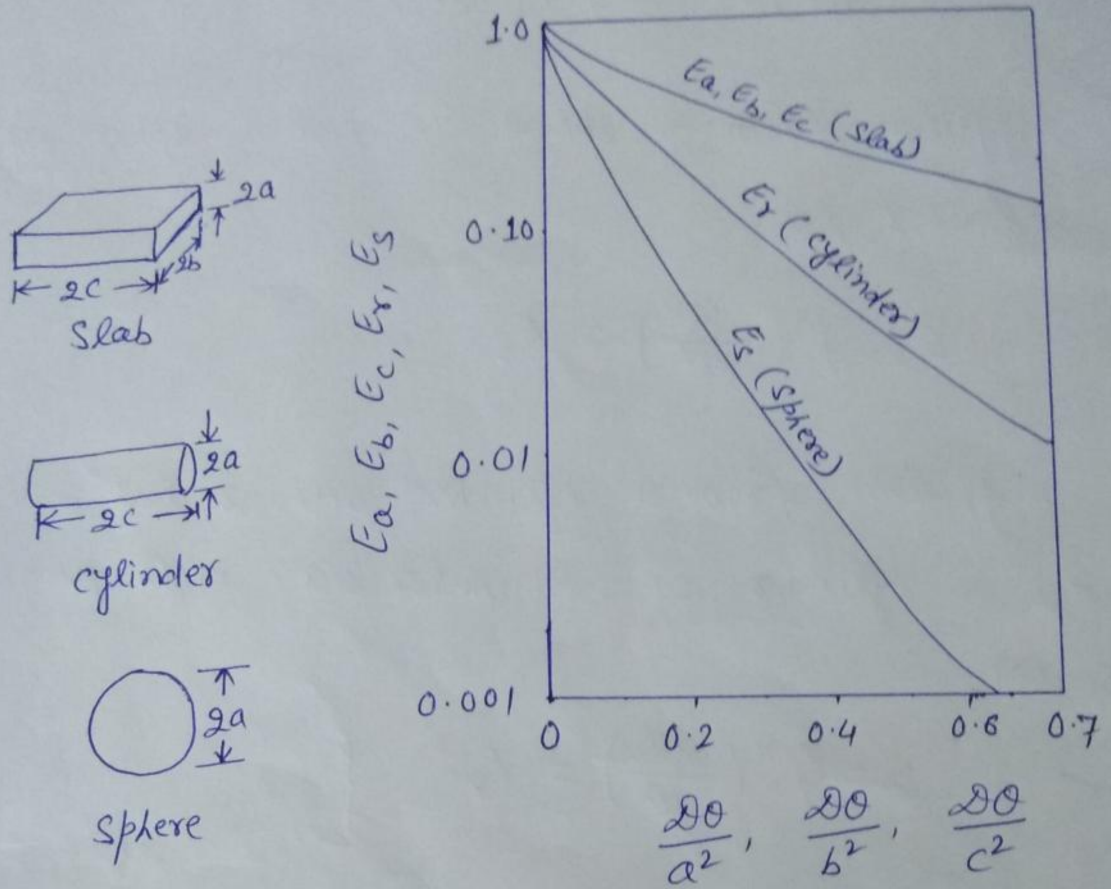
Consider a slab of thickness 2a, with sealed edges on four sides, so that diffusion can take place toward and from the flat parallel faces, a cross section of which is shown in below figure. Suppose initially the concentration of solute throughout the slab is uniform, C_{A0} and the slab is immersed in a medium so that the solute will diffuse out of the slab. Let the concentration at the surface be $C_{A\infty}$, invariant with passage of time. If diffusion were allowed to continue indefinitely, the concentration would fall to the uniform value $C_{A\infty}$, and $C_{A0} - C_{A\infty}$ is a measure of the amount of solute removed. On the other hand if diffusion was stopped at time θ, the distribution of solute would be given by the curve marked C, which by internal diffusion would level off to the uniform concentration $C_{A\theta}$, where $C_{A,\theta}$ is the average concentration at time θ. The quantity $C_{A\theta} - C_{A\infty}$ is a measure of the amount of solute still unremoved. The fraction unremoved E is given by integration of $\frac{\partial C_A}{\partial \theta} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right)$.



$$E = \frac{C_{A,\theta} - C_{A\infty}}{C_{A0} - C_{A\infty}} = f\left(\frac{D\theta}{a^2}\right)$$

$$= \frac{8}{\pi^2}\left(e^{-D\theta\pi^2/4a^2} + \frac{1}{9}e^{-9D\theta\pi^2/4a^2} + \frac{1}{25}e^{-25D\theta\pi^2/4a^2} + \cdots\right) = E_a$$

The function is shown graphically in below figure.



(2) Diffusion from a rectangular bar with sealed ends:-

For a rectangular bar of thickness 2a and width 2b, with sealed ends,

$$E = f\left(\frac{D\theta}{a^2}\right) f\left(\frac{D\theta}{b^2}\right) = E_a E_b$$

(3) Diffusion for a rectangular parallelepiped :-

For a brick-shaped bar, of dimensions 2a, 2b, and 2c, with diffusion from all six faces,

$$E = f\left(\frac{D\theta}{a^2}\right) f\left(\frac{D\theta}{b^2}\right) f\left(\frac{D\theta}{c^2}\right) = E_a E_b E_c$$

(4) Diffusion from a sphere :- For a sphere of diameter 2a,

$$E = f'\left(\frac{D\theta}{a^2}\right) = E_s$$

(5) Diffusion from a cylinder with sealed ends:- For a cylinder of diameter 2a, with plane ends sealed.

$$E = f''\left(\frac{D\theta}{a^2}\right) = E_r$$

(6) Diffusion from a cylinder :- For a cylinder of diameter 2a and length 2c, with diffusion from both ends as well as from the cylindrical surface,

$$E = f\left(\frac{D\theta}{c^2}\right) f''\left(\frac{D\theta}{a^2}\right) = E_c E_r$$

For solid shapes where the diffusion takes place from one rather than two opposite faces, the functions are calculated as if the thickness were twice the true value. For example, if diffusion occurs through only one face of the flat slab of thickness 2a, edges sealed, the calculation is made with $D\theta/4a^2$.

Convective mass transfer :-

Mass transfer by convection involves the transport of material between a boundary surface and a moving fluid, or between two relatively immicible moving fluids. This mode of transfer depends both on the transport properties and on the dynamic characteristics of the flowing fluid. When a fluid flows past a solid surface under conditions such that turbulence generally prevails, there is a region close to the surface where the flow is predominantly laminar and fluid particles immediately adjacent to the solid boundary are at rest. Molecular diffusion is responsible for mass transfer through the stagnant and laminar flowing fluid layers. The controlling resistance to convective mass transfer is often the result of this 'film' of fluid. However, under most convective conditions (particularly for turbulent conditions), this film is extremely thin and its thickness is virtually impossible to measure or predict theoretically. Therefore, mass transfer rates cannot be calculated based on the concepts of molecular diffusion alone.

With increasing the distance from the surface, the character of flow gradually changes, becoming increasingly turbulent, until in the outermost region of the fluid, fully turbulent conditions prevail. In the turbulent region of the fluid, particles of fluid no longer flow in the orderly manner found in the laminar sublayer. Instead relatively large portions of the fluid, called eddies, move rapidly from one position to another with an appreciable component of their velocity in the direction perpendicular to the surface past which the fluid is flowing. These eddies contribute considerably to the mass-transfer process. Because the rapid eddy motion, mass transfer in the turbulent region is much more rapid than it would be under laminar flow conditions. This situation cannot be modeled in terms of Fick's law. Instead, it is explained in terms of a mass-transfer coefficient, an approximate engineering idea that simplifies the analysis of a very complex problem.

Mass transfer coefficients :-

The mechanism of flow process involving the movement of the eddies in the turbulent region is not throughly understood. on the other hand, the mechanism of molecular diffusion, at least for the gases, is fairly well known. The rate of mass transfer through the various regions from surface to the turbulent zone can be described in the same manner as that found useful for molecular diffusion. Thus, the $\frac{c D_{AB}}{z}$ of equation

$$N_A = \frac{N_A}{N_A+N_B} \frac{c D_{AB}}{z} \ln \frac{N_A/(N_A+N_B) - c_{A2}/c}{N_A/(N_A+N_B) - c_{A1}/c}$$

which is characteristic of molecular diffusion, is replaced by F, a mass transfer coefficient.

Then,

$$N_A = \frac{N_A}{N_A+N_B} F \ln \frac{N_A/(N_A+N_B) - c_{A2}/c}{N_A/(N_A+N_B) - c_{A1}/c} \quad -(1)$$

where, c_A/c is the mole-fraction concentration, x_A for liquids, y_A for gases. As in molecular diffusion, the ratio $N_A/(N_A+N_B)$ is ordinarily established by nondiffusional considerations.

Since the surface through which the transfer takes place may not be plane, so that the diffusion path in the fluid may be of variable cross-section, N_A is defined as the flux at the phase interface or boundary where substance A enters or leaves the phase for which F has been defined. When C_{A1} is at the begining of the transfer path and C_{A2} is at the end, N_A is positive. In any case, one of these concentration will be at the phase boundary. The manner of defining the concentration of A in the fluid will influence the value of F, and it must be clearly established when the mass-transfer coefficient is defined for a particular situation.

The F of equation (1) is a local mass transfer coefficient, defined for a particular location on the phase boundary surface. Since the value of F depends on the local nature of the fluid motion, which may vary along the surface, an average value F_{av} is sometimes used in equation (1) with constant C_{A1} and C_{A2}, which takes into account these variations in F. The effect of variation in C_{A1} and C_{A2} on the flux must be accounted for separately.

The two situations namely equimolar counter-diffusion and transfer of one substance through another which is not transferred, occur so frequently that special mass transfer coefficients are usually used for them. These are defined by equation of the form :-

Flux = (coefficient) (Concentration difference)

Since concentration may be defined in a number of ways and standards have not be established, we have a variety of coefficients for each situation :-

Transfer of A through non-diffusing B :-

For gases

$$N_A = \frac{\mathcal{D}_{AB} P_t}{RTz \bar{p}_{B,M}} (\bar{p}_{A1} - \bar{p}_{A2}) \quad — (2)$$

The flux can also be defined in the form of concentration difference as :-

$$N_A = k_G(\bar{p}_{A1} - \bar{p}_{A2}) = k_y(y_{A1} - y_{A2}) = k_c(C_{A1} - C_{A2}) \quad — (3)$$

Equation (2) can be written in various concentration difference form as

$$N_A = \frac{\mathcal{D}_{AB} P_t}{RTz \bar{p}_{B,M}} (\bar{p}_{A1} - \bar{p}_{A2}) = \frac{\mathcal{D}_{AB} P_t^2}{RTz \bar{p}_{B,M}} (y_{A1} - y_{A2}) =$$

$$\frac{\mathcal{D}_{AB} P_t}{z \bar{p}_{B,M}} (C_{A1} - C_{A2}) = \frac{F_G}{\bar{p}_{B,M}} (\bar{p}_{A1} - \bar{p}_{A2}) \quad — (4)$$

$$\left(\because F = \frac{\mathcal{D}_{AB} C}{z}\right)$$

From equations (3) and (4)

$$k_G = \frac{F_G}{\bar{p}_{B,M}} \quad , \quad k_y = \frac{\mathcal{D}_{AB} P_t^2}{RTZ\, \bar{p}_{B,M}} = \frac{F_G P_t}{\bar{p}_{B,M}}$$

$$k_c = \frac{\mathcal{D}_{AB} P_t}{Z\, \bar{p}_{B,M}} = \frac{\mathcal{D}_{AB} C RT}{Z\, \bar{p}_{B,M}} = \frac{F_G RT}{\bar{p}_{B,M}}$$

Therefore,

$$F_G = k_G \bar{p}_{B,M} = k_y \frac{\bar{p}_{B,M}}{P_t} = k_c \frac{\bar{p}_{B,M}}{RT} \quad -(5)$$

For liquids,

$$N_A = \frac{\mathcal{D}_{AB}}{Z\, x_{B,M}} \left(\frac{\rho}{M}\right)_{av} (x_{A1} - x_{A2}) \quad - \quad (6)$$

The flux can also be defined in the form of concentration difference as :-

$$N_A = k_x (x_{A1} - x_{A2}) = k_L (C_{A1} - C_{A2}) \quad - \quad (7)$$

Equation (6) can be written in various concentration difference form as

$$N_A = \frac{\mathcal{D}_{AB}}{Z\, x_{B,M}} \left(\frac{\rho}{M}\right)_{av} (x_{A1} - x_{A2}) = \frac{\mathcal{D}_{AB}}{Z x_{B,M}} (C_{A1} - C_{A2})$$

$$= \frac{F_L}{x_{B,M}} (x_{A1} - x_{A2}) \quad - (8)$$

From equations (7) and (8)

$$k_x = \frac{F_L}{x_{B,M}} \; , \; k_L = \frac{D_{AB}}{Z\, x_{B,M}} = \frac{D_{AB}\left(\frac{\rho}{M}\right)_{av}}{Z\, x_{B,M}\left(\frac{\rho}{M}\right)_{av}} = \frac{F_L}{x_{B,M}\left(\frac{\rho}{M}\right)_{av}}$$

Therefore,

$$F_L = k_x x_{B,M} = k_L x_{B,M}\left(\frac{\rho}{M}\right)_{av} = k_L x_{B,M} c \quad \text{—(9)}$$

$$\because c = \left(\frac{\rho}{M}\right)_{av}$$

Equimolar counterdiffusion :-

For gases,

$$N_A = \frac{D_{AB}}{RTZ}\left(\bar{p}_{A1} - \bar{p}_{A2}\right) \quad \text{—— (10)}$$

The flux can also be defined in the form of various concentration difference as :-

$$N_A = k'_G\left(\bar{p}_{A1} - \bar{p}_{A2}\right) = k'_y\left(y_{A1} - y_{A2}\right) = k'_c\left(c_{A1} - c_{A2}\right) \quad \text{— (11)}$$

Equation (10) can be written in various concentration difference form as

$$N_A = \frac{D_{AB}}{RTZ}\left(\bar{p}_{A1} - \bar{p}_{A2}\right) = \frac{D_{AB} P_t}{RTZ}\left(y_{A1} - y_{A2}\right) =$$

$$\frac{D_{AB}}{Z}\left(c_{A1} - c_{A2}\right) = F_G\left(y_{A1} - y_{A2}\right) \quad \text{— (12)}$$

From equations (11) and (12)

$$k'_G = \frac{\mathcal{D}_{AB}}{RTZ} = \frac{\mathcal{D}_{AB} P_t}{RTZ P_t} = \frac{\mathcal{D}_{AB} C}{Z P_t} = \frac{F_G}{P_t}$$

$$k'_y = F_G$$

$$k'_c = \frac{\mathcal{D}_{AB}}{Z} = \frac{\mathcal{D}_{AB}\, C}{Z\, C} = \frac{F_G}{C} = \frac{F_G RT}{P_t}$$

Therefore,

$$F_G = k'_G P_t = k'_y = k'_c \frac{P_t}{RT} \quad — (13)$$

For liquids :-

$$N_A = \frac{\mathcal{D}_{AB}}{Z}(C_{A1} - C_{A2}) = \frac{\mathcal{D}_{AB}}{Z}\left(\frac{\rho}{M}\right)_{av}(x_{A1} - x_{A2}) \quad — (14)$$

The flux can also be written in the form of concentration difference as

$$N_A = k'_x (x_{A1} - x_{A2}) = k'_L (C_{A1} - C_{A2}) \quad — (15)$$

From equations (14) and (15)

$$k'_L = \frac{\mathcal{D}_{AB}}{Z} = \frac{\mathcal{D}_{AB}\, C}{Z\, C} = \frac{F_L}{C} = \frac{F_L}{\left(\frac{\rho}{M}\right)_{av}}$$

and $k'_x = \frac{\mathcal{D}_{AB}}{Z}\left(\frac{\rho}{M}\right)_{av} = F_L$

Therefore, $F_L = k'_x = k'_L C = k'_L \left(\frac{\rho}{M}\right)_{av}$ — (16)

Relations between mass transfer coefficients :-

From equations (5), (9), (13), and (16) we get

$$F_G = k_G \bar{p}_{B,M} = k_y \frac{\bar{p}_{B,M}}{P_t} = k_c \frac{\bar{p}_{B,M}}{RT} = k'_G P_t = k'_y = k'_c \frac{P_t}{RT}$$

and

$$F_L = k_x x_{B,M} = k_L x_{B,M} \left(\frac{\rho}{M}\right)_{av} = k_L x_{B,M} C = k'_x = k'_L C = k'_L \left(\frac{\rho}{M}\right)_{av}$$

- When we deal with situations which do not involve either diffusion of only one substance or equimolar counterdiffusion, or if mass transfer rates are large, k-type coefficients can not be used. Before these can be used for other situations, they must be conveted into F's.

- The k-type mass transfer coefficients are not constant for diffusion of A through stagnant B, but usually depend on the concentration driving force. For very dilute solutions, the bulk motion contribution is negligible and driving force becomes approximately linear. In mathematical terms, this follows from the fact that for very dilute solutions $y_{B,M} \cong x_{B,M} \cong 1$.

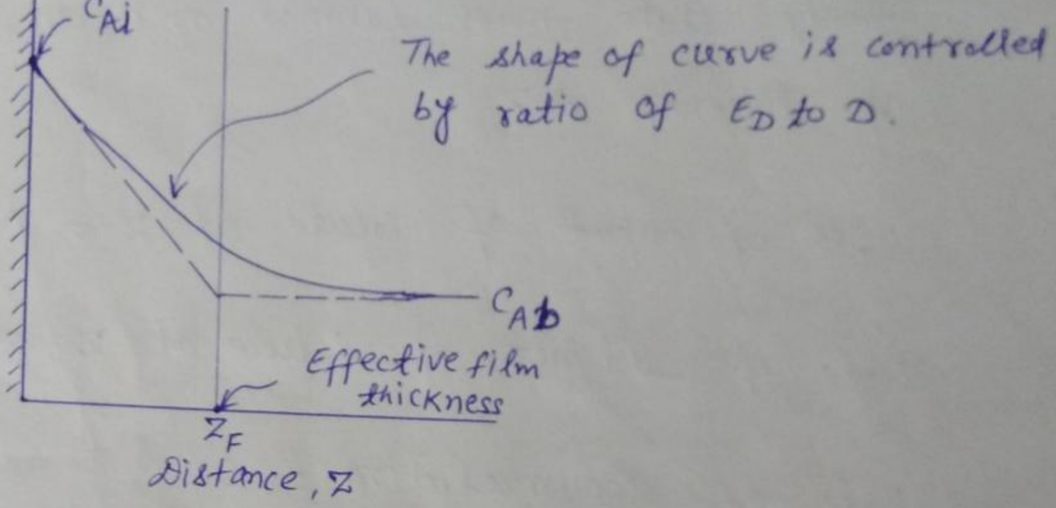
Therefore, for diffusion of A through stagnant B, k- type coefficients are recommended only for very dilute solutions, otherwise F- type coefficients should be used.

In a few limited situations mass transfer coefficients can be deduced from theoretical principles. In the great majority of cases, however, we depend upon direct measurement under known conditions, for use later in design.

Theories of mass transfer :-

Many theories are available to explain the behavier of mass transfer coefficient such as the film, penetration, surface renewal and others. The theories are based on both molecular and turbulent diffusion. The theories are explained in details in the following sections.

Film theory :- When a fluid flows turbulently past a solid surface, with mass transfer occuring from the surface to the fluid, the concentration - distance relation is as shown by the full curve of below figure, the shape of which is controlled by the continuously varying ratio of E_D to D (eddy diffusivity to molecular diffusivity).



The film theory is based on the following assumptions :-

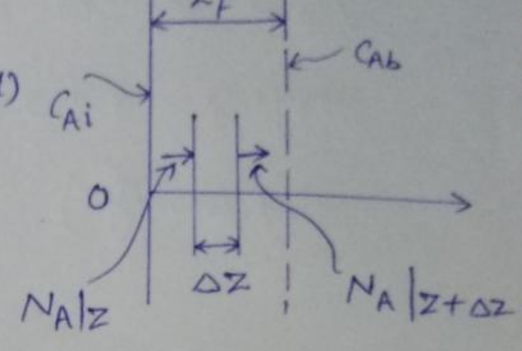
(a) Mass transfer occurs by molecular diffusion within an effective film of thickness z_F. Beyond this film, concentration is homogeneous and is C_{Ab}.

(b) Mass transfer through the film occurs at steady state.

(c) Flux is low and mass transfer occurs at low concentration.

Hence,

$$N_A = -\mathscr{D}_{AB}\frac{dC_A}{dZ} \quad -(1)$$



Steady state mass balance over an elementary volume of thickness ΔZ.

Rate of input of solute at $Z = N_A|_Z$

Rate of output of solute at $Z+\Delta Z = N_A|_{Z+\Delta Z}$

Rate of accumulation = 0

Therefore, at steady state

$$N_A|_Z - N_A|_{Z+\Delta Z} = 0$$

$$\lim_{\Delta Z \to 0} \frac{N_A|_Z - N_A|_{Z+\Delta Z}}{\Delta Z} = 0$$

$$\frac{dN_A}{dZ} = 0$$

Putting the value of N_A from equation (1), we get

$$\frac{d}{dZ}\left(-\mathscr{D}_{AB}\frac{dC_A}{dZ}\right) = 0$$

$$-\mathcal{D}_{AB}\frac{d^2C_A}{dz^2}=0$$

$$\frac{d^2C_A}{dz^2}=0 \quad \text{---} \quad (2)$$

Integrating equation (2) for the following boundary conditions, we get

$$C_A = C_{Ai} \quad \text{for} \quad z=0$$

$$C_A = C_{Ab} \quad \text{for} \quad z=z_F$$

$$C_A = C_{Ai}-(C_{Ai}-C_{Ab})\frac{z}{z_F}$$

Hence, according to film theory, concentration profile in stagnant film is linear.

Molar flux through film, N_A :-

$$N_A = -\mathcal{D}_{AB}\left.\frac{dC_A}{dz}\right|_{z=0}$$

$$N_A = \frac{\mathcal{D}_{AB}}{z_F}(C_{Ai}-C_{Ab}) \quad \text{---} \quad (3)$$

The flux N_A can also be written in form of mass transfer coefficient as,

$$N_A = k_L (C_{Ai} - C_{Ab}) \quad — (4)$$

comparison of equations (3) and (4) gives

$$k_L = \frac{\mathcal{D}_{AB}}{Z_F}$$

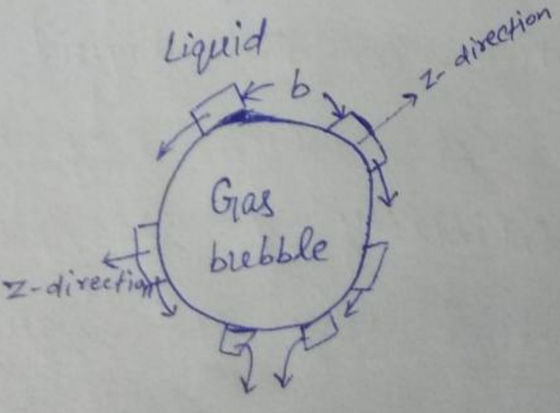
For the film theory, mass transfer coefficient is directly proportional to diffusion coefficient, under the same fluid flow conditions. For turbulent flow, the mass transfer coefficient has much smaller dependency compared to laminar flow. In the turbulent flow, the mass transfer coefficient is proportional to $\mathcal{D}_{AB}^{n}$, where n may be anything from nearly zero to 0.8 or 0.9, depending upon the operating conditions. Although the film theory offers some explanation of the mechanism of mass transfer in fluid media, it does not explain the estimation thickness of the film. Due to this disadvantage, application of the model is restricted to mass transfer in a diffusion cell.

Mass transfer at fluid surfaces :-

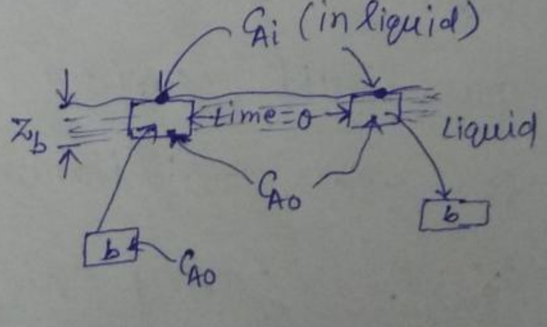
Because the velocity of a fluid surface, as in the contact of a gas and liquid, is not zero, a number of theories have been developed to replace the film theory.

Penetration theory :-

In many situations the time of exposure of a fluid to mass transfer is short, so that the concentration gradient of film theory, which is characteristic of steady state, would not have time to develop. As shown in the below figure(a) a bubble of gas rises through a liquid which absorbs the gas.



(a)



(b)

A particle of liquid b, initially at the top of the bubble, is in contact with the gas for the time θ required for the bubble to rise a distance equal to its diameter while liquid particle slips along the surface of the bubble. An extension to cases where the liquid may be in turbulent motion as shown in above figure (b). An eddy b rising from the turbulent depths of the liquid and remaining exposed for a time θ to the action of the gas. In this theory the time of exposure is taken as constant for all such eddies or particles of liquid.

Initially, the concentration of dissolved gas in the eddy is uniformly C_{A0}, and internally the eddy is considered to be stagnant. when the eddy is exposed to the gas at the surface, the concentration in the liquid at the gas-liquid surface is C_{Ai}, which may be taken as the equilibrium solibility of the gas in the liquid. During the time θ, the liquid particle is subject to unsteady-state diffusion or penetration of solute in the z-direction, and as an approximation equation $\frac{\partial C_A}{\partial \theta} = D_{AB}\frac{\partial^2 C_A}{\partial z^2}$ may be applied.

For short exposure times, and with slow diffusion in the liquid, the molecules of dissolving solute are never able to reach the depth z_b corresponding to the thickness of eddy, so that from solute point of view, z_b is essentially infinite.

$$\frac{\partial C_A}{\partial \theta} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial z^2} \quad \text{—— (5)}$$

The conditions of above equation are :-

$$C_A = \begin{cases} C_{A0} & \text{at } \theta = 0 \quad \text{for all } z \quad -(6) \\ C_{Ai} & \text{at } z = 0 \quad \text{for } \theta > 0 \quad -(7) \\ C_{A0} & \text{at } z = \infty \quad \text{for all } \theta \quad -(8) \end{cases}$$

Solving above equation provides the average flux over the time of exposure

$$N_{A,av} = 2(C_{A,i} - C_{A0}) \sqrt{\frac{\mathcal{D}_{AB}}{\pi \theta}} \quad \text{—— (9)}$$

which gives,

$$K_{L,av} = 2 \sqrt{\frac{\mathcal{D}_{AB}}{\pi \theta}} \quad - (10)$$

with $K_{L,av}$ proportional to $\mathcal{D}_{AB}^{0.5}$ for different solutes under the same circumstances.

Surface-renewal theories :-

Danckwerts pointed out that the Higbie theory with its constant time of exposure of the eddies of the fluid at the surface is a special case of what may be a more realistic picture, where the eddies are exposed for varying lengths of time. Since the rate of solute penetration depends upon exposure time, the average rate for a unit surface area must be determined by summing up the individual values. If s is the fractional rate of replacement of elements, Danckwerts found

$$N_{A,av} = (C_{Ai} - C_{A0})\sqrt{D_{AB}\, s} \qquad — (11)$$

and therefore,

$$K_{L,av} = \sqrt{D_{AB}\, s} \qquad — (12)$$

Combination film-surface-renewal theory :-

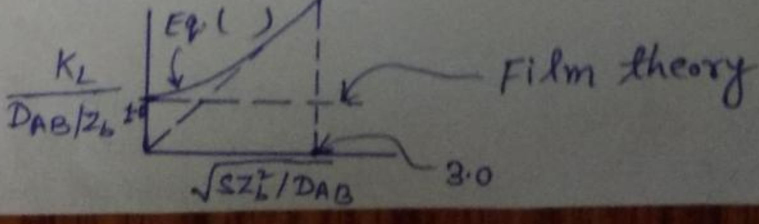
The film theory $(K_L \propto D_{AB})$ assumes a time of exposure of the surface elements sufficiently long for the concentration profile within the film to be characteristic of steady state, whereas the penetration and surface-renewal theories

($K_L \propto \mathcal{D}_{AB}^{0.5}$) assume the surface elements to be essentially infinitely deep, the diffusing solute never reaching the region of constant concentration below. The observed dependence, $K_L \propto D_{AB}^{n}$, with n dependent upon circumstances, might be explained by allowing for a finite depth of the surface elements or eddies.

Accordingly, the third boundary condition, equation (8) is replaced by $C_A = C_{A0}$ for $z = z_b$, where z_b is finite.

$$K_{L,av} = \sqrt{\mathcal{D}_{AB} S}\ \coth\sqrt{\frac{S z_b^2}{\mathcal{D}_{AB}}} \quad \text{—— (13)}$$

This is shown in below figure. For rapid penetration ($\mathcal{D}_{AB}$ large), the rate of surface small (S small), or for thin surface elements, the mass transfer coefficient takes on the character described by the film theory, whereas for slow penetration or rapid renewal, it follows equation $K_{L,av} = \sqrt{\mathcal{D}_{AB} S}$. consequently $K_L \propto D_{AB}^{n}$, where n may have any value between the limits 0.5 and 1, which could account for many observations.



Surface-stretch theory :-

Lightfoot and his coworkers have extended the penetration - surface-renewal concepts to situations where the interfacial surface through which mass transfer occurs changes periodically with time. For these cases the theory leads to

$$K_{L,av} = \frac{(A/A_r)\sqrt{D_{AB}/\pi\theta_r}}{\sqrt{\int_0^{\theta/\theta_r} \left(\frac{A}{A_r}\right)^2 d\theta}} \quad —(14)$$

where A = time-dependent interface surface

A_r = reference value of A, defined for each situation

θ_r = constant, with dimensions of time, defined for each situation; e.g., for drop formation θ_r might be drop-formation time.

Theory	Advantages	Disadvantages
The film theory	Simple, good base for extension	Film thickness z_b is unknown
The penetration theory	Simplest including flow	Contact time $\theta\ (d_b/u_{max})$ usually unknown
The surface-renewal theory	Similar math to penetration theory, but better physical picture	Surface-renewal rate (S) is unknown

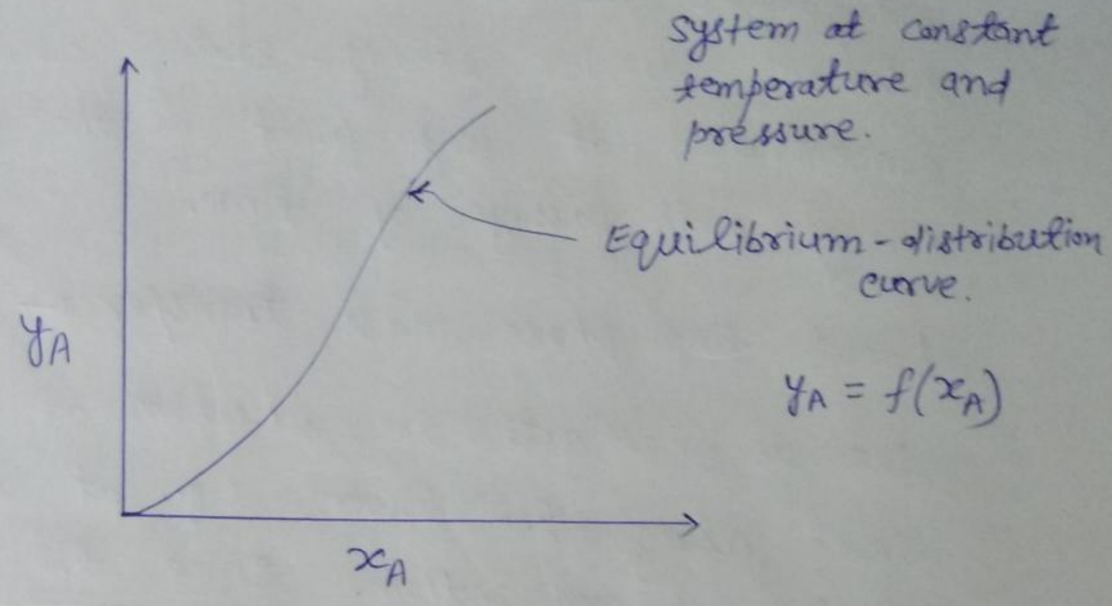
Interphase mass transfer :-

In most of the mass transfer operations, two insoluble phases are brought into contact in order to permit transfer of constituent substances between them. The concentration gradients of the two phase-system are indicative of the departure from equilibrium which exists between the phases. At equilibrium, diffusional phenomena seize. It is therefore, necessary to consider both diffusional phenomena and the equilibria in order to describe the various situations fully.

Equilibria :-

Consider a fixed amount of liquid water is placed in a closed container together with a gaseous mixture of ammonia and air at constant temperature and pressure. Since ammonia is very soluble in water, some ammonia molecules will instantly transfer from the gas into the liquid, crossing the interfacial surface separating the two phases. A portion of the ammonia molecules escapes back into the gas, at a rate proportional to their concentration in the liquid. As more ammonia enters into the liquid, with consequent increase in concentration within the liquid, the rate a which ammonia returns to the gas increases, until eventually the rate at which it enters the liquid exactly equals that at which it leaves. Meanwhile, thorough the mechanism of diffusion, the concentrations throughout each phase become uniform. A dynamic equilibrium now exists, and while ammonia molecules continue to transfer back and forth from one phase to other, the net transfer falls to zero. The concentration within each phase no longer change.

If addition ammonia is further injected into the container, a new set of equilibrium concentrations will be established, with higher concentrations in each phase than were at first obtained. In this manner we can eventually obtain the complete reletionship between the equilibrium concentrations in both phases. If ammonia is denoted as substance A, the equilibrium concentrations in the gas and liquid, y_A and x_A mole fractions, respectively, give rise to an equilibrium-distribution curve of the type shown in below figure. This curve results irrespective of the amounts of water and air that we start with and is influenced only by the conditions such as temperature and pressure.

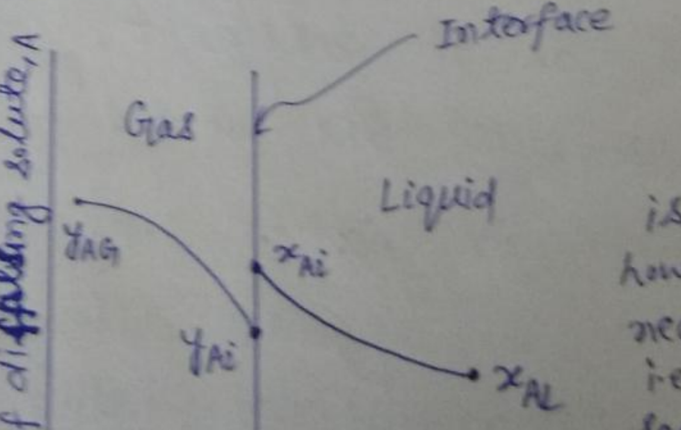


Diffusion between phases :-

As it was observed that departure from equilibrium provides the driving force for diffusion, we can now study the rate of diffusion in terms of the driving forces. consider the absorption of the solute gas (e.g. ammonia, substance A) from a mixture such as air and ammonia, by the liquid water as the absorbent, in one of the simplest of apparatus, the wetted-wall tower, in which ammonia-air mixture may enter at the bottom and flow upward while the water flows the downward around the inside of the pipe. The gas mixture changes its composition from a high - to a low solute concentration as it flows upward, while the water dissolves the ammonia and leaves as the bottom as an aqueous ammonia solution. Under steady-state conditions, the concentration at any point in the apparatus do not change with passage of time.

Local two-phase mass transfer :-

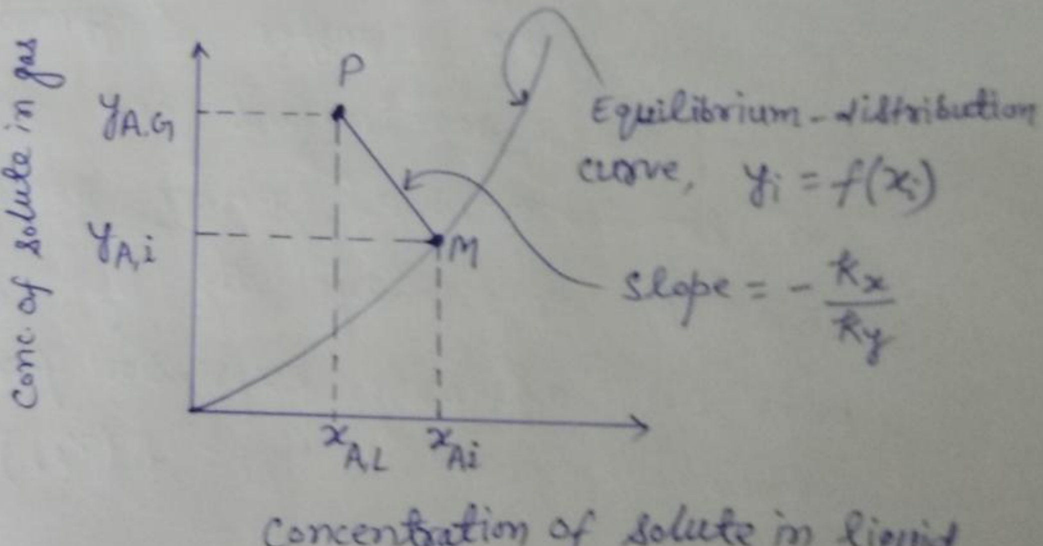
Let us investigate the situation at a particular level along the tower, e.g., at a point midway between top and bottom. Since the solute is diffusing from the gas phase into the liquid, there must be a concentration gradient in the direction of mass transfer within each phase. This can be shown graphically in terms of the distance through the phases, as shown in below fig. use, where a section through the two phases in contact is shown It will be assumed that no chemical reaction occurs.



x_{Ai} and y_{Ai} is at equilibrium however it is not necessary that $x_{Ai} = y_{Ai}$ i.e concentration of solute in both phases may not be equal at interface. chemical potential of A in both phases is equal at equilibrium.

The concentration of A in the main body of gas is $y_{A,G}$ mole fraction and it falls to $y_{A,i}$ at the interface. In the liquid, the concentration falls from $x_{A,i}$ at the interface to $x_{A,L}$ in the bulk liquid. The bulk concentration $y_{A,G}$ and $x_{A,L}$ are clearly not equilibrium values, since otherwise diffusion of the solute would not occur.

The various concentrations can be shown graphically, as in below figure, whose coordinates are those of the equilibrium-distribution curve.



Point P represents the two bulk phase concentrations and point M those at the interface. For steady state mass transfer, the rate at which A reaches the interface from gas must equal that at which it diffuses to the bulk liquid, so that the no accumulation or depletion of A at the interface occurs.

when k_x and k_y are the locally applicable coefficients, then

$$N_A = k_y \left(y_{A,G} - y_{A,i} \right) = k_x \left(x_{A,i} - x_{A,L} \right) \quad \text{— (1)}$$

and the differences in the y's and x's are considered the driving force for the mass transfer.

From above equation, we get

$$\frac{y_{A,G} - y_{A,i}}{x_{A,L} - x_{A,i}} = -\frac{k_x}{k_y} \quad \text{—— (2)}$$

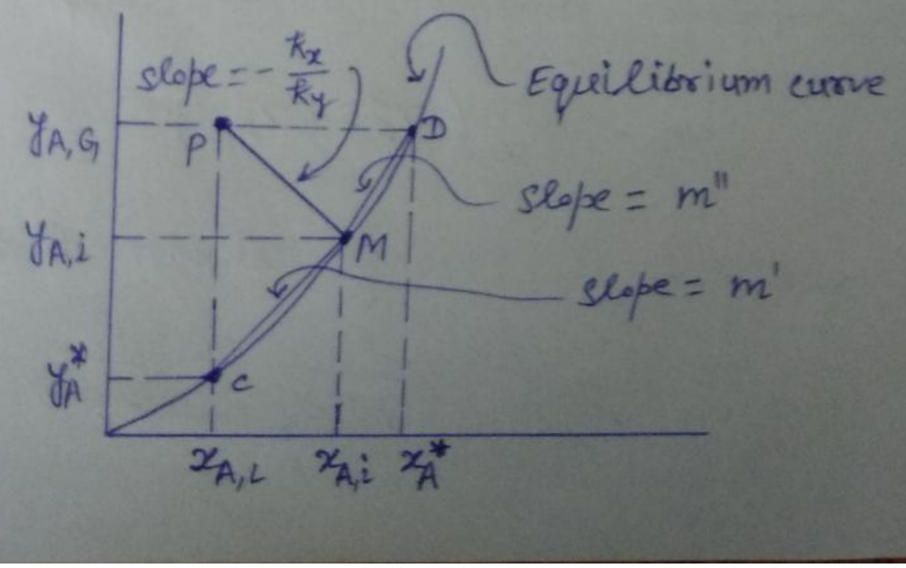
If the mass-transfer coefficients are known, the interfacial concentrations and hence the flux N_A can be determined, either graphically by plotting line PM or analytically by solving equation (2) with an algebraic expression for the equilibrium-distribution curve, $y_{Ai} = f(x_{A,i})$.

Local overall mass-transfer coefficients :-

It is usually possible to determine the solute concentrations in the bulk of the fluids by sampling and analyzing. However, sampling of the fluids at the interface, is ordinarily impossible, since the greatest part of the concentration differences such as $y_{A,G} - y_{A,i}$, takes place over extremely small distances. Sampling and analyzing provide $y_{A,G}$ and $x_{A,L}$ but not y_{Ai} and $x_{A,i}$. Under these circumstances, only an overall effect, in terms of the bulk concentrations can be determined.

Consider the situation shown in below figure since the equilibrium-distribution curve for the system is unique at fixed temperature and pressure, then y_A^*, in equilibrium with $x_{A,L}$, is a good measure of $x_{A,L}$ as $x_{A,L}$ itself, and moreover it is on same basis as $y_{A,G}$. The entire two-phase mass-transfer effect can then be measured in terms of an overall mass-transfer coefficient K_y

$$N_A = K_y \left(y_{A,G} - y_A^* \right) \quad — \quad (3)$$



From the geometry of the figure,

$$y_{A,G} - y_A^* = (y_{A,G} - y_{A,i}) + (y_{A,i} - y_A^*)$$

$$y_{A,G} - y_A^* = (y_{A,G} - y_{A,i}) + m'(x_{A,i} - x_{A,L}) \quad \text{— (4)}$$

where, m' is the slope of chord CM. substituting for concentration differences the equivalents (flux/coefficient) as given by equations (1) and ⑧

$$\frac{N_A}{K_y} = \frac{N_A}{k_y} + \frac{m' N_A}{k_x} \quad \text{— (5)}$$

$$\text{or} \quad \frac{1}{K_y} = \frac{1}{k_y} + \frac{m'}{k_x} \quad \text{— (6)}$$

This shows that the relationship between the individual-phase transfer coefficient and the overall coefficient takes the form of addition of resistances (hence "two-resistance" theory). In similar fashion, x_A^* is a measure of $y_{A,G}$ and can be used to define another overall coefficient K_x

$$N_A = K_x(x_A^* - x_{A,L}) \quad \text{— (7)}$$

and it is readily shown that

$$\frac{1}{K_x} = \frac{1}{m'' k_y} + \frac{1}{k_x} \quad \text{— (8)}$$

where, m'' is the slope of the chord MD in the above figure.

Equations (6) and (8) lead to the following relationships between the mass-transfer resistances :-

$$\frac{\text{Resistance in gas phase}}{\text{Total resistance, both phases}} = \frac{1/k_y}{1/K_y} \quad \text{— (9)}$$

and

$$\frac{\text{Resistance in liquid phase}}{\text{Total resistance, both phases}} = \frac{1/k_x}{1/K_x} \quad \text{— (10)}$$

Assuming that the numerical values of k_x and k_y are roughly the same, the importance of the slope of the equilibrium-curve chords can readily be demonstrated. If m' is small (equilibrium-distribution curve very flat), so that at equilibrium only a small concentration of A in the gas will provide a very large concentration in the liquid (solute A is very soluble in the liquid), the term m'/k_x of equation (6) becomes minor, the major resistance is represented by $\frac{1}{k_y}$, and it is said that the rate of mass transfer is gas-phase-controlled.

In the extreme, this becomes

$$\frac{1}{K_y} \approx \frac{1}{k_y} \qquad \text{--- (11)}$$

or.

$$y_{A,G} - y_A^* \approx y_{A,G} - y_{A,i} \qquad \text{--- (12)}$$

under such cirmustances, even fairly large percentage changes in k_x will not significantly affect K_y, and efforts to increase the rate of mass transfer would best be directed toward decreasing the gas phase resistance.

Conversely, when m'' is very large (solute A relatively insoluble in the liquid), with k_x and k_y nearly equal, the first term on the right of equation (8) becomes minor and the major resistance to mass transfer resides within the liquid, which is then said to liquid-phase controlled mass transfer. Ultimately, this becomes

$$\frac{1}{K_x} \approx \frac{1}{k_x} \qquad \text{--- (13)}$$

$$x_A^* - x_{A,L} \approx x_{A,i} - x_{A,L} \qquad \text{--- (14)}$$

In such cases efforts to increase mass transfer rate would best be directed toward decreasing the liquid-phase resistance.

For cases where k_x and k_y are not nearly equal, it will be the relative size of the ratio k_x/k_y and of m' (or m'') which will determine the location of the controlling mass-transfer resistance.

It is sometimes useful to note that the effect of temperature is much larger for liquid mass transfer coefficient than for those for gases, consequently a large effect of temperature on the overall coefficient, when it is determined experimentally, it is usually a fairly clear indication that the controlling mass-transfer resistance is in the liquid phase.

Local coefficients - General case :-

When we deal with situations which do not involve either diffusion of only one substance or equimolar counter diffusion, or if mass-transfer rates are large, the F-type coefficients should be used. In a situation like that, the mass-transfer flux is.

$$N_A = \frac{N_A}{\Sigma N} F_G \ln \frac{N_A/\Sigma N - y_{A,i}}{N_A/\Sigma N - y_{A,G}} = \frac{N_A}{\Sigma N} F_L \ln \frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - x_{A,i}} \qquad (15)$$

where F_G and F_L are the gas- and liquid-phase coefficients for substance A, respectively and $\Sigma N = N_A + N_B + N_C + \cdots$

From equation (15),

$$\frac{N_A/\Sigma N - y_{Ai}}{N_A/\Sigma N - y_{A,G}} = \left(\frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - x_{A,i}}\right)^{F_L/F_G} \quad \text{— (16)}$$

$$\left(\because a \ln p = b \ln q \quad \ln p^a = \ln q^b \quad p^a = q^b \quad \text{or } p = q^{b/a} \right)$$

We can also define the overall coefficients F_{OG} and F_{OL} as

$$N_A = \frac{N_A}{\Sigma N} F_{OG} \ln \frac{N_A/\Sigma N - y_A^*}{N_A/\Sigma N - y_{A,G}} = \frac{N_A}{\Sigma N} F_{OL} \ln \frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - x_A^*} \quad \text{— (17)}$$

It can be shown that the overall and individual phase F's are related :-

$$\exp\left[\frac{N_A}{(N_A/\Sigma N) F_{OG}}\right] = \exp\left[\frac{N_A}{(N_A/\Sigma N) F_G}\right] + m' \frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - y_{A,G}} \cdots \left\{1 - \exp\left[-\frac{N_A}{(N_A/\Sigma N) F_L}\right]\right\} \quad \text{— (18)}$$

and,

$$\exp\left[-\frac{N_A}{(N_A/\Sigma N)F_{OL}}\right] = \frac{1}{m''}\left(\frac{N_A/\Sigma N - y_{A,G}}{N_A/\Sigma N - x_{A,L}}\right)\left\{1 - \exp\left[\frac{N_A}{(N_A/\Sigma N)F_G}\right]\right\} + \exp\left[-\frac{N_A}{(N_A/\Sigma N)F_L}\right] \quad -(19)$$

For the two important special cases:-

(1) Diffusion of one component ($\Sigma N = N_A$, $N_A/\Sigma N = 1$)

$$e^{N_A/F_{OG}} = e^{N_A/F_G} + m'\frac{1-x_{A,L}}{1-y_{A,G}}\left(1-e^{-N_A/F_L}\right) \quad -(20)$$

$$e^{-N_A/F_{OL}} = \frac{1}{m''}\frac{1-y_{A,G}}{1-x_{A,L}}\left(1-e^{N_A/F_G}\right) + e^{-N_A/F_L} \quad -(21)$$

Equations (20) and (21) can also be written as:-

$$\frac{1}{F_{OG}} = \frac{1}{F_G}\frac{(1-y_A)_{iM}}{(1-y_A)_{*M}} + \frac{m'(1-x_A)_{im}}{F_L(1-y_A)_{*M}}$$

$$\frac{1}{F_{OL}} = \frac{1}{m''F_G}\frac{(1-y_A)_{iM}}{(1-x_A)_{*M}} + \frac{1}{F_L}\frac{(1-x_A)_{iM}}{(1-x_A)_{*M}}$$

where $(1-y_A)_{iM}$ = logarithmic mean of $(1-y_{A,G})$ and $(1-y_{A,i})$
$(1-y_A)_{*M}$ = logarithmic mean of $(1-y_{A,G})$ and $(1-y_A^*)$
$(1-x_A)_{iM}$ = logarithmic mean of $(1-x_{A,L})$ and $(1-x_{A,i})$
$(1-x_A)_{*M}$ = logarithmic mean of $(1-x_{A,L})$ and $(1-x_A^*)$

(2) Equimolar counter diffusion :-

$\Sigma N = 0 \; (F_G = k'_y \, , \, F_L = k'_x)$

$$\frac{1}{F_{OL}} = \frac{1}{m'' F_G} + \frac{1}{F_L} \quad \text{— (22)}$$

and $$\frac{1}{F_{OG}} = \frac{1}{F_G} + \frac{m'}{F_L} \quad \text{— (23)}$$

Generalized relations between K-type of mass transfer coefficients :-

If the generalized phase are termed E (equivalant to gas phase) with concentration expressed as i and R (equivalant to liquid phase) with concentration j,

$$\frac{1}{K_E} = \frac{1}{k_E} + \frac{m'}{k_R}$$

$$\frac{1}{K_R} = \frac{1}{m'' k_E} + \frac{1}{k_R}$$

$$m' = \frac{i_{A,i} - i_{A^*}}{j_{A,i} - j_{A,R}} \, , \quad m'' = \frac{i_{A,E} - i_{A,i}}{j_A^* - j_{A,i}}$$

$$i_{A^*} = f(j_{A,R}) \qquad i_{A,E} = f(j_{A^*})$$

where, f is the equilibrium distribution function.

Remember that the relationships derived between the individual coefficients and the overall coefficients are valid only for a straight equilibrium distribution line. under such situations, the use of overall coefficients will eliminate the need to calculate the concentrations at the interface. If the distribution line is not straight, the overall mass transfer coefficients will change with concentrations of the two phases, and the local coefficients should be used instead.

Analogies among molecular transport Phenomena:-

In the flow of a fluid past a phase boundary, there will be a velocity gradient within the fluid which results in a transfer of momentum through it. In some cases, there is also a transfer of heat by virtue of a temperature gradient. The processes of momentum, heat, and mass transfer under these conditions are intimately related, and it is useful at this point to consider the analogies among them.

Consider the velocity profile for the case of a fluid flowing past a stationary flat plate. Since the velocity at the solid surface is zero, there must necessarily be a sub-layer adjacent to the surface where the flow is predominantly laminar. within this region, the shear stress τ required to maintain the velocity gradient is given by

$$\tau = -\mu \frac{du}{dz} \quad \text{———} \quad (1)$$

where u is the fluid velocity parallel to the surface and z is measured as increasing toward the surface. This can be written as

$$\tau = -\frac{\mu}{\rho} \frac{d(\rho u)}{dz} = -\nu \frac{d(\rho u)}{dz} \quad \text{———} \quad (2)$$

Where ν is the kinematic viscosity, μ/ρ, also known as the momentum diffusivity.

The kinematic viscosity has the same dimensions as the mass diffusivity, length^2/time, while the quantity ρu can be interpreted as a volumetric momentum concentration. The shear stress τ may also be interpreted as as viscous momentum flux toward the solid surface. Equation (2) is, therefore, a rate equation analogous to Fick's first law

$$J_A = -\mathcal{D}_{AB} \frac{dC_A}{dz} \quad \text{———} \quad (3)$$

The Schmidt number is defined as the dimensionless ratio of the momentum and mass diffusivities :-

$$S_c = \frac{\mu}{\rho \mathcal{D}_{AB}} \quad \text{———} \quad (4)$$

when a temperature gradient exists between the fluid and the plate, the rate of heat transfer in the laminar region is

$$q = -K \frac{dT}{dZ} \quad \text{———} \quad (5)$$

where K is the thermal conductivity of the fluid. This can also be written as

$$q = -\frac{K}{\rho C_p} \frac{d(\rho C_p T)}{dZ} = -\alpha \frac{d(\rho C_p T)}{dZ} \quad \text{—} \quad ⑥$$

where C_p is the specific heat at constant pressure. The quantity $\rho C_p T$ may be interpreted as volumetric thermal energy concentration, and $\alpha = K/\rho C_p$ is the thermal diffusivity, which like the momentum and mass diffusivities, has dimensions of length^2/time. Equation (6) is therefore a rate equation analogous to the corresponding equations for momentum and mass transfer.

The Prandtl number is defined as the dimensionless ratio of the momentum and thermal diffusivities :-

$$Pr = \frac{\nu}{\alpha} = \frac{C_p \mu}{K} \quad — \quad (7)$$

A third dimensionless group, the Lewis number, is formed by dividing the thermal by the mass diffusivity :-

$$Le = \frac{\alpha}{\mathscr{D}_{AB}} = \frac{Sc}{Pr} \quad — \quad (8)$$

The Lewis number plays an important role in problems of simultaneous heat and mass transfer, such as humidification operations.

Dimensionless groups of heat and mass transfer-

Most practically useful mass-transfer situations involve turbulent flow, and for these it is generally not possible to compute mass-transfer coefficients from theoretical considerations. Instead, we must rely principally on experimental data. There are many more experimental data available for heat transfer than for mass-transfer. Therefore to convert equations or correlations of data on heat transfer to correlations on mass transfer, the dimensionless groups of heat transfer are replaced by the corresponding groups of mass transfer.

The limitations for converting/replacing the groups are :-

1. The flow-conditions and geometry must be the same.
2. Most heat transfer data are based on situations involving no mass transfer. Use of the analogy would then produce mass-transfer coefficients corresponding to no net mass transfer, in turn corresponding most closely to k'_G, k'_c, or $k'_y (= F)$. Sherwood numbers are commonly written in terms of any of the coefficients, but when derived by replacement of Nusselt numbers for use where the net mass transfer is not zero, they should be taken as

$$Sh = \frac{Fl}{c\mathcal{D}_{AB}}.$$

Mass transfer	Heat transfer
Reynolds number $Re = \frac{\rho u l}{\mu}$	Reynolds number $Re = \frac{\rho u l}{\mu}$
Schmidt number $Sc = \frac{\mu}{\rho \mathcal{D}_{AB}}$	Prandtl number $Pr = \frac{C_p \mu}{K}$
Sherwood number $Sh = \frac{Fl}{c\mathcal{D}_{AB}}, \frac{k_G \bar{P}_{B,M} RTl}{P_t \mathcal{D}_{AB}},$ $\frac{k_c \bar{P}_{B,M} l}{P_t \mathcal{D}_{AB}}, \frac{k_c' l}{\mathcal{D}_{AB}},$ $\frac{k_y' RTl}{P_t \mathcal{D}_{AB}}$, etc.	Nusselt number $Nu = \frac{hl}{K}$
Peclet number $Pe_D = ReSc = \frac{lu}{\mathcal{D}_{AB}}$	Peclet number $Pe_H = RePr = \frac{C_p l u \rho}{K}$
Stanton number $St_D = \frac{Sh}{ReSc} = \frac{Sh}{Pe_D} = \frac{F}{cu},$ $\frac{F}{G}, \frac{k_G \bar{P}_{B,M} M_{av}}{\rho u}$, etc.	Stanton number $St_H = \frac{Nu}{RePr} = \frac{Nu}{Pe_H} =$ $\frac{h}{\rho C_p u}$
Chilton-colburn j-factor $j_D = St_D Sc^{2/3}$	Chilton-colburn j-factor $j_H = St_H Pr^{2/2}$