Mass Transfer
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CHAPTER 1
DIFFUSION

1.1 INTRODUCTION

The mass transfer is also important subject for chemical engineer. It is like as heat and momentum transfer. Here is also two type of mass transfer that is molecular like as conduction in heat transfer and convective mass transfer. The driving force is required for any transfer; In mass transfer concentration difference is driving force. In this chapter we will discuss molecular mass transfer.

The flux is defined as anything is passing through per unit area per unit time. Molar flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given increment of time through a unit area normal to the vector. The flux of species defined with reference to fixed spatial coordinates, N_A is

$$N_A = C_A v_A \qquad\qquad \text{--------------------- (1.1)}$$

This could be written in terms of diffusion velocity of A, (i.e., $v_A - v$) and average velocity of mixture, v, as

$$N_A = C_A (v_A - v) + C_A v \qquad\qquad \text{--------------------- (1.2)}$$

By definition

$$v = v* = \frac{\sum_i C_i v_i}{C}$$

Therefore, equation (1.2) becomes

$$N_A = C_A (v_A - v) + \frac{C_A}{C} \sum_i C_i v_i$$

$$= C_A (v_A - v) + y_A \sum_i C_i v_i$$

For binary systems containing two components A and B,

$$N_A = C_A (v_A - v) + y_A (C_A v_A + C_B v_B)$$

$$= C_A (v_A - v) + y_A (N_A + N_B)$$

$$N_A = C_A (v_A - v) + y_A N \qquad\qquad \text{--------------------- (1.3)}$$

The first term on the right hand side of this equation is diffusional molar flux of A, and the second term is flux due to bulk motion.

1.2 FICK'S LAW:

An empirical relation for the diffusional molar flux, first postulated by Fick and, accordingly, often referred to as Fick's first law, defines the diffusion of component A in an isothermal, isobaric system. For diffusion in only the Z direction, the Fick's rate equation is

$$J_A = -D_{AB} \frac{dC_A}{dZ}$$

where D_{AB} is diffusivity or diffusion coefficient for component A diffusing through component B, and dC_A / dZ is the concentration gradient in the Z-direction.

A more general flux relation which is not restricted to isothermal, isobasic system could be written as

$$J_A = -CD_{AB} \frac{dy_A}{dZ} \qquad \text{-------------------- (1.4)}$$

using this expression, Equation (1.3) could be written as

$$N_A = -CD_{AB} \frac{dy_A}{dZ} + y_A N \qquad \text{-------------------- (1.5)}$$

1.3 RELATION AMONG MOLAR FLUXES:

For a binary system containing A and B, from Equation (1.5),

$$N_A = J_A + y_A N$$

Or
$$J_A = N_A + y_A N \qquad \text{-------------------- (1.6)}$$

Similarly,

$$J_B = N_B + y_B N \qquad \text{-------------------- (1.7)}$$

Addition of Equation (1.6) & (1.7) gives,

$$J_A + J_B = N_A + N_B - (y_A + y_B)N \qquad \text{-------------------- (1.8)}$$

By definition, $N = N_A + N_B$ and $y_A + y_B = 1$.
Therefore, equation (1.8) becomes,

$$J_A + J_B = 0$$
$$J_A = -J_B$$

$$CD_{AB} \frac{dy_A}{dz} = -CD_{BA} \frac{dy_B}{dZ} \qquad \text{-------------------- (1.9)}$$

From $y_A + y_B = 1$

$$dy_A = -dy_B$$

Therefore, Equation (1.9) becomes,

$$D_{AB} = D_{BA} \qquad \text{----------------------------- (1.10)}$$

This leads to the conclusion that diffusivity of A in B is equal to diffusivity of B in A.

1.4 DIFFUSIVITY

Fick's law proportionality, D_{AB}, is known as mass diffusivity (simply as diffusivity) or as the diffusion coefficient. D_{AB} has the dimension of L^2 / t, identical to the fundamental dimensions of the other transport properties: Kinematic viscosity, $v = (\mu/\rho)$ in momentum transfer, and thermal diffusivity, $\alpha (= k / \rho C_\rho)$ in heat transfer.

Diffusivity is normally reported in cm² / sec; the SI unit being m² / sec.

Diffusivity depends on pressure, temperature, and composition of the system.

In table, some values of D_{AB} are given for a few gas, liquid, and solid systems.

Diffusivities of gases at low density are almost composition independent, increase with the temperature and vary inversely with pressure. Liquid and solid diffusivities are strongly concentration dependent and increase with temperature.

General range of values of diffusivity:

Gases: 5×10^{-6} ------------- 1×10^{-5} m² / sec.
Liquids: 10^{-6} ------------- 10^{-9} m² / sec.
Solids: 5×10^{-14} ------------- 1×10^{-10} m² / sec.

In the absence of experimental data, semi theoretical expressions have been developed which give approximation, sometimes as valid as experimental values, due to the difficulties encountered in experimental measurements.

1.4.1 DIFFUSIVITY IN GASES:

Pressure dependence of diffusivity is given by

$$D_{AB} \propto \frac{1}{P} \qquad\qquad \text{-------------------- (1.11)}$$

And temperature dependency is according to

$$D_{AB} \propto T^{3/2} \qquad\qquad \text{-------------------- (1.12)}$$

Diffusivity of a component in a mixture of components can be calculated using the diffusivities for the various binary pairs involved in the mixture. The relation given by Wilkes is

$$D_{1-mixture} = \cfrac{1}{\cfrac{y_2'}{D_{1-2}} + \cfrac{y_3'}{D_{1-3}} + \text{...........} + \cfrac{y_n'}{D_{1-n}}} \qquad\qquad \text{-------------------- (1.13)}$$

Where $D_{1\text{-mixture}}$ is the diffusivity for component 1 in the gas mixture; $D_{1\text{-n}}$ is the diffusivity for the binary pair, component 1 diffusing through component n; and y'_n is the mole fraction of component n in the gas mixture evaluated on a component 1 free basis, that is

$$y'_2 = \frac{y_2}{y_2 + y_3 + \ldots\ldots + y_n}$$
------------------- (1.14)

1.4.2 DIFFUSIVITY IN LIQUIDS:

Diffusivity in liquid is exemplified by the experimental values. Most of these values are nearer to 10^{-5} cm^2 / sec, and about ten thousand times shower than those in dilute gases. This characteristic of liquid diffusion often limits the overall rate of processes accruing in liquids (such as reaction between two components in liquids).

In chemistry, diffusivity limits the rate of acid-base reactions; in the chemical industry, diffusion is responsible for the rates of liquid-liquid extraction. Diffusion in liquids is important because it is slow.

Certain molecules diffuse as molecules, while others which are designated as electrolytes ionize in solutions and diffuse as ions. For example, sodium chloride (NaCl), diffuses in water as ions Na$^+$ and Cl$^-$. Though each ion has a different mobility, the electrical neutrality of the solution indicates the ions must diffuse at the same rate; accordingly, it is possible to speak of a diffusion coefficient for molecular electrolytes such as NaCl. However, if several ions are present, the diffusion rates of the individual captions and anions must be considered, and molecular diffusion coefficients have no meaning.

Diffusivity varies inversely with viscosity when the ratio of solute to solvent ratio exceeds five. In extremely high viscosity materials, diffusion becomes independent of viscosity.

1.4.3 DIFFUSIVITY IN SOLIDS:

Typical values for diffusivity in solids are shown in table. One outstanding characteristic of these values is their small size, usually thousands of time less than those in a liquid, which are in turn 10,000 times less than those in a gas.

Diffusion plays a major role in catalysis and is important to the chemical engineer. For metallurgists, diffusion of atoms within the solids is of more importance.

1.5 STEADY STATE DIFFUSION

In this section, steady-state molecular mass transfer through simple systems in which the concentration and molar flux are functions of a single space coordinate will be considered.

In a binary system, containing A and B, this molar flux in the direction of z, as given by Eqn (1.5) is

$$N_{A-} - CD_{AB}\frac{dy_A}{dz} + y_A(N_A + N_B) \qquad \text{-------------------- (1.15)}$$

1.5.1 DIFFUSION THROUGH A STAGNANT GAS FILM

The diffusivity or diffusion coefficient for a gas can be measured, experimentally using Arnold diffusion cell. This cell is illustrated schematically in figure

The narrow tube of uniform cross section which is partially filled with pure liquid A, is maintained at a constant temperature and pressure. Gas B which flows across the open end of the tub, has a negligible solubility in liquid A, and is also chemically inert to A. (i.e. no reaction between A & B).
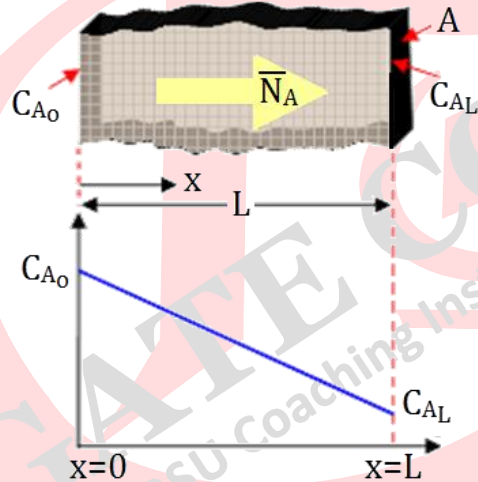
Figure 1.1

Component A vaporizes and diffuses into the gas phase; the rate of vaporization may be physically measured and may also be mathematically expressed in terms of the molar flux.

Consider the control volume S Δ z, where S is the cross sectional area of the tube. Mass balance on A over this control volume for a steady state operation yields.

[Moles of A leaving at z + Δz] – [Moles of A entering at z] = 0.

(i.e.) $$SN_A\big|_{Z+\Delta z} - SN_A\big|_Z = 0. \qquad \text{-------------------- (1.16)}$$

Dividing through by the volume, SΔZ, and evaluating in the limit as ΔZ approaches zero, we obtain the differential equation

$$\frac{dN_A}{dz} = 0 \qquad \text{-------------------- (1.17)}$$

This relation stipulates a constant molar flux of A throughout the gas phase from Z_1 to Z_2. A similar differential equation could also be written for component B as,

$$\frac{dN_B}{dZ} = 0, \qquad \text{-------------------- (1.18)}$$

and accordingly, the molar flux of B is also constant over the entire diffusion path from z_1 and z_2.

Considering only at plane z_1, and since the gas B is insoluble is liquid A, we realize that N_B, the net flux of B, is zero throughout the diffusion path; accordingly, B is a stagnant gas.
From equation (1.15)

$$N_A = -CD_{AB}\frac{dy_A}{dz} + y_A(N_A + N_B)$$

Since $N_B = 0$,

$$N_A = -CD_{AB}\frac{dy_A}{dz} + y_A N_A$$

Rearranging,

$$N_A = \frac{-CD_{AB}}{1-y_A}\frac{dy_A}{dz} \qquad \text{------------------ (1.19)}$$

This equation may be integrated between the two boundary conditions:

$$\text{at } z = z_1 \qquad Y_A = Y_{A1}$$

And

$$\text{at } z = z_2 \qquad Y_A = y_{A2}$$

Assuming the diffusivity is to be independent of concentration, and realizing that N_A is constant along the diffusion path, by integrating equation (1.19) we obtain

$$N_A\int_{Z_1}^{Z_2} dz = CD_{AB}\int_{y_{A1}}^{y_{A2}}\frac{-dy_A}{1-y_A}$$

$$N_A = \frac{CD_{AB}}{Z_2 - Z_1}\ln\left(\frac{1-y_{A2}}{1-y_{A1}}\right) \qquad \text{------------------ (1.20)}$$

The log mean average concentration of component B is defined as

$$y_{B,lm} = \frac{y_{B2} - y_{B1}}{\ln\left(y_{B2}\middle/y_{B1}\right)} \qquad \text{-------------------- (1.21)}$$

Since, $y_B = 1 - y_A$,

$$y_{B,lm} = \frac{(1-y_{A2}) - (1-y_{A1})}{\ln\left(y_{A2}/y_{A1}\right)} = \frac{y_{A1} - y_{A2}}{\ln\left(y_{A2}/y_{A1}\right)} \qquad \text{-------------------- (1.22)}$$

Substituting from Eqn (5) in Eqn (4),

$$N_A = \frac{CD_{AB}}{Z_2 - z_1} \frac{(y_{A1} - y_{A2})}{y_{B,lm}} \qquad \text{------------------ (1.23)}$$

For an ideal gas $\quad C = \dfrac{n}{V} = \dfrac{p}{RT}$, and for mixture of ideal gases $y_A = \dfrac{P_A}{P}$

Therefore, for an ideal gas mixture equation. (1.23) becomes

$$N_A = \frac{D_{AB}}{RT(z_2 - z_1)} \frac{(p_{A1} - p_{A2})}{p_{B,lm}} \qquad \text{------------------ (1.24)}$$

This is the equation of molar flux for steady state diffusion of one gas through a second stagnant gas.

Many mass-transfer operations involve the diffusion of one gas component through another non-diffusing component; absorption and humidification are typical operations defined by these equations.

Example 1.1 *Oxygen is diffusing in a mixture of oxygen-nitrogen at 1 std atm, 25 °C. Concentration of oxygen at planes 2 mm apart are 10 and 20 volume % respectively. Nitrogen is non-diffusing.*
   (a) Derive the appropriate expression to calculate the flux oxygen. Define units of each term clearly.
   *(b) Calculate the flux of oxygen. Diffusivity of oxygen in nitrogen = 1.89 * 10^{-5} m/ s.*

Solution:
Let us denote oxygen as A and nitrogen as B. Flux of A (i.e.) N_A is made up of two components, namely that resulting from the bulk motion of A (i.e.), Nx_A and that resulting from molecular diffusion J_A:

$$N_A = Nx_A + J_A \qquad \text{----------------------- (1)}$$

From Fick's law of diffusion,

$$J_A = -D_{AB} \frac{dC_A}{dz} \qquad \text{----------------------- (2)}$$

Substituting this equation (1)

$$N_A = Nx_A - D_{AB} \frac{dC_A}{dz} \qquad \text{----------------------- (3)}$$

Since N = N_A + N_B and x_A = C_A / C equation (3) becomes

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

Rearranging the terms and integrating between the planes between 1 and 2,

$$\int \frac{dz}{cD_{AB}} = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{N_A C - C_A\left(N_A + N_B\right)} \qquad \text{----------------------- (4)}$$

Since B is non diffusing N_B = 0. Also, the total concentration C remains constant. Therefore, equation (4) becomes

$$\frac{z}{CD_{AB}} = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{N_A C - N_A C_A} = \frac{1}{N_A}\ln\frac{C-C_{A2}}{C-C_{A1}}$$

Therefore, $\qquad\qquad\qquad N_A = \frac{CD_{AB}}{z}\ln\frac{C-C_{A2}}{C-C_{A1}} \qquad \text{--------------------- (5)}$

Replacing concentration in terms of pressures using Ideal gas law, equation (5) becomes

$$N_A = \frac{D_{AB}P_t}{RTz}\ln\frac{P_t - P_{A2}}{P_t - P_{A1}} \qquad \text{--------------------- (6)}$$

Where
D_{AB} = molecular diffusivity of A in B
P_T = total pressure of system
R = universal gas constant
T = temperature of system in absolute scale
z = distance between two planes across the direction of diffusion
P_{A1} = partial pressure of A at plane 1, and
P_{A2} = partial pressure of A at plane 2

Given:
*D_{AB} = 1.89 * 10 $^{-5}$ m²/sec*
*P_t = 1 atm = 1.01325 * 10 ^{5} N/m ^{2}*
T = 25 ℃ = 273 + 25 = 298 K
z = 2 mm = 0.002 m
*P_{A1} = 0.2 * 1 = 0.2 atm (From Ideal gas law and additive pressure rule)*
*P_{A2} = 0.1 * 1 = 0.1 atm*
Substituting these in equation (6)

$$N_A = \frac{\left(1.89*10^{-5}\right)\left(1.01325*10^5\right)}{\left(8314\right)\left(298\right)\left(0.002\right)}\ln\left(\frac{1-0.1}{1-0.2}\right)$$
$$N_A = 4.55\times10^{-5}\ kmol/m^2.s$$

1.5.2 EQUI-MOLAR COUNTER DIFFUSION:

A physical situation which is encountered in the distillation of two constituents whose molar latent heats of vaporization are essentially equal, stipulates that the flux of one gaseous component is equal to but acting in the opposite direction from the other gaseous component; that is, $N_A = -N_B$.

The molar flux N_A, for a binary system at constant temperature and pressure is described by

$$N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A + N_B)$$

or

$$N_A = -D_{AB} \frac{dC_A}{dz} + y_A (N_A + N_B) \qquad \text{-------------------- (1.25)}$$

With the substitution of $N_B = -N_A$, Equation (1.25) becomes,

$$N_A = -D_{AB} \frac{dC_A}{dz} \qquad \text{----------------- (1.26)}$$

For steady state diffusion Equation (1.26) may be integrated, using the boundary conditions:

at $z = z_1$ $C_A = C_{A1}$
and $z = z_2$ $C_A = C_{A2}$
Giving,
From which

$$N_A = \frac{D_{AB}}{z_2 - z_1} (C_{A1} - C_{A2}) \qquad \text{-------------------- (1.27)}$$

For ideal gases, $C_A = \frac{n_A}{V} = \frac{p_A}{RT}$. Therefore, Equation (1.27) becomes

$$N_A = \frac{D_{AB}}{RT(z_2 - z_1)} (P_{A1} - P_{A2}) \qquad \text{-------------------- (1.28)}$$

This is the equation of molar flux for steady-state equi-molar counter diffusion.
Concentration profile in this equi-molar counter diffusion may be obtained from,

$\frac{d}{dz} (N_A) = 0$ (Since N_A is constant over the diffusion path).

And from equation.(1.27)

$$N_A = -D_{AB} \frac{dC_A}{dz} .$$

Therefore

$$\frac{d}{dz} \left(-D_{AB} \frac{dC_A}{dz} \right) = 0.$$

or
$$\frac{d^2 C_A}{dz^2} = 0.$$
-------------------- (1.29)

This equation may be solved using the boundary conditions to give

$$\frac{C_A - C_{A1}}{C_{A1} - C_{A2}} = \frac{z - z_1}{z_1 - z_2}$$
------------------ (1.30)

Equation, (1.30) indicates a linear concentration profile for equi-molar counter diffusion.

Example 1.2 *Methane diffuses at steady state through a tube containing helium. At point 1 the partial pressure of methane is p_{A1} = 55 kPa and at point 2, 0.03 m apart P_{A2} = 15 kPa. The total pressure is 101.32 kPa, and the temperature is 298 K. At this pressure and temperature, the value of diffusivity is 6.75 * 10⁻⁵ m²/sec.*
(i) Calculate the flux of CH₄ at steady state for equi-molar counter diffusion.
(ii) Calculate the partial pressure at a point 0.02 m apart from point 1.

Solution:
For steady state equi-molar counter diffusion, molar flux is given by

$$N_A = \frac{D_{AB}}{R T z}\left(p_{A1} - p_{A2}\right)$$
----------------------- *(1)*

Therefore;

$$N_A = \frac{6.75 * 10^{-5}}{8.314 * 298 * 0.03}\left(55 - 15\right)\frac{kmol}{m^2 \cdot sec}$$

$$N_A = 3.633 * 10^{-5}\frac{kmol}{m^2\, sec}$$

And from (1), partial pressure at 0.02 m from point 1 is:

$$3.633 * 10^{-5} = \frac{6.75 * 10^{-5}}{8.314 * 298 * 0.02}\left(55 - p_A\right)$$ *, thus p_A = 28.33 kPa*

Example 1.3 *For Equimolar counter diffusion from a sphere to a surrounding stationary infinite medium, the mass flux N_{Ai} of the diffusing component A at the interface is given by*

$N_{Ai} = \frac{D_A}{R T}\left(C_{Ai} - C_{Ab}\right)$ *where D_A is the diffusivity, R the radius of sphere and C_{Ai} and C_{Ab} the molar*

concentrations of A at the interface and at a point far away from the sphere. Show that the Sherwood number, based on the diameter of the sphere is equal to 2.

Solution:
The mass flux N_{Ai} is given by

$$N_{Ai} = \frac{D_A}{R}\left(C_{Ai} - C_{Ab}\right) \qquad \text{----------------------- } (1)$$

The mass flux N_{Ai} of the diffusing component A at the interface is also given by

$$N_{Ai} = k_c\left(C_{Ai} - C_{Ab}\right) \qquad \text{----------------------- } (2)$$

From the equations (1) and (2), we get

$$k_c = \frac{D_A}{R}$$

$$\Rightarrow \qquad \frac{k_c R}{D_A} = 1$$

$$\Rightarrow \qquad \frac{k_c d}{D_A} = 2 \quad \left(\text{since } R = \frac{d}{2}, \text{ d = diameter of sphere}\right)$$

$$\Rightarrow \qquad N_{Sh} = \frac{k_c d}{D_A} = 2$$

1.5.3 DIFFUSION INTO AN INFINITE STANDARD MEDIUM:

Here we will discuss problems involving diffusion from a spherical particle into an infinite body of stagnant gas. The purpose in doing this is to demonstrate how to set up differential equations that describe the diffusion in these processes. The solutions, obtained are only of academic interest because a large body of gas in which there are no convection currents is unlikely to be found in practice. However, the solutions developed here for these problems actually represent a special case of the more common situation involving both molecular diffusion and convective mass transfer.

- **EVAPORATION OF A SPHERICAL DROPLET:**

Let us consider the evaporation of spherical droplet such as a raindrop or sublimation of naphthalene ball. The vapor formed at the surface of the droplet is assumed to diffuse by molecular motions into the large body of stagnant gas that surrounds the droplet.
Consider a raindrop, as shown in below figure. At any moment, when the radius of the drop is r_0, the flux of water vapor at any distance r from the center is given by
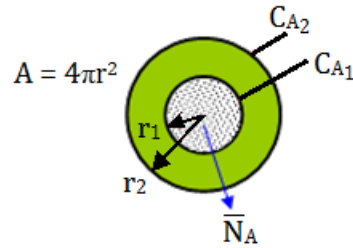
Figure 1.2

$$N_A = -CD_{AB}\frac{dy_A}{dr} + y_A\left(N_A + N_B\right)$$

Here $N_B = 0$ (since air is assumed to be stagnant)

Therefore,
$$N_A = -CD_{AB}\frac{dy_A}{dr} + y_A N_A$$

On Rearrangement,
$$N_A = \frac{-CD_{AB}}{1-y_A}\frac{dy_A}{dr}$$
-------------------- (1.31)

The flux N_A is not constant, because of the spherical geometry; decreases as the distance from the center of sphere increases. But the molar flow rates at r and r + δr are the same. This could be written as,

$$AN_A\bigg|_r = AN_A\bigg|_{r+\delta r}$$
-------------------- (1.32)

Where A = surface area of sphere at r or r + δr.
Substituting for A = 4 π r² in equation (1.32),

$$4\pi r^2 N_A\bigg|_{r+\delta r} - 4\pi r^2 N_A\bigg|_r = 0$$

Or
$$\lim_{\delta r \to 0}\frac{r^2 N_A\bigg|_{r+\delta r} - r^2 N_A\bigg|_r}{\delta r} = 0$$

So
$$\frac{d}{dr}\left(r^2 N_A\right) = 0$$
-------------------- (1.33)

Integrating,
$$r^2 N_A = \text{constant}$$
-------------------- (1.34)

From equation (1.34), $r^2 N_A = r_0^2 N_{A_0}$

Substituting for N_A from equation (1.31),

$$\frac{-r^2 CD_{AB}}{1-y_A} \frac{dy_A}{dr} = r_0^2 N_{A_0}$$

$$r_0^2 N_{A_0} \int \frac{dr}{r^2} = -CD_{AB} \int \frac{dy_A}{1-y_A} \qquad \text{------------------- (1.35)}$$

Boundary condition:

At $r = r_0$, $y_A = y_{AS}$

and   At $r = \infty$ $y_A = y_{A\infty}$

Therefore, equation (1.35) becomes,

$$r_0^2 N_{A_0} \left(-\frac{1}{r} \right)_{r_0}^{\infty} = \left[CD_{AB} \ln\left(1-y_A\right) \right]_{y_{AS}}^{y_{A\infty}}$$

Simplifying,

$$N_{A_0} = \frac{CD_{AB}}{r_0} \ln\left(\frac{1-y_{A\infty}}{1-y_{AS}} \right) \qquad \text{------------------- (1.36)}$$

Time required for complete evaporation of the droplet may be evaluated from making mass balance.

$$\frac{\text{Moles of water diffusing}}{\text{unit time}} = \frac{\text{moles of water leaving the droplet}}{\text{unit time}}$$

$$4\pi r_0^2 N_{A0} = -\frac{d}{dt}\left(\frac{4}{3} \pi r_0^3 \frac{\rho_L}{M_A} \right) = -4\pi r_0^2 \frac{\rho_L}{M_A} \frac{dr_0}{dt} \qquad \text{------------------- (1.37)}$$

Substituting for N_{A0} from equation (1.36) in equation (1.37),

$$\frac{CD_{AB}}{r_0} \ln\left(\frac{1-y_A}{1-y_{AS}} \right) = \frac{-\rho_L}{M_A} \frac{dr_0}{dt} \qquad \text{------------------- (1.38)}$$

Initial condition:

When $t = 0$ $r_0 = r_1$

Integrating equation (1.38) with these initial condition,

$$\int_0^t dt = \frac{-\rho_L}{M_A} \frac{1}{CD_{AB}} \frac{1}{\ln\left(\dfrac{1-y_{A\infty}}{1-y_{AS}} \right)} \int_{r_1}^0 r_0 \, dr_0$$

$$t = \frac{\rho_L}{M_A} \frac{1}{2CD_{AB}} \frac{r_1^2}{\ln\left(\frac{1-y_{A\infty}}{1-y_{AS}}\right)} \qquad \text{---------------------- (1.39)}$$

Equation (1.39) gives the total time t required for complete evaporation of spherical droplet of initial radius r_1.

Example 1.4 *A sphere of naphthalene having a radius of 2mm is suspended in a large volume of shell air at 318 K and 1 atm. The surface pressure of the naphthalene can be assumed to be at 318K is 0.555 mm Hg. The D_{AB} of naphthalene in air at 318 K is 6.92 * 10 $^{-6}$m ^{2}/sec. Calculate the rate of evaporation of naphthalene from the surface.*

Solution:
Steady state mass balance over an element of radius r and r + δr leads to

$$SN_A\Big|_r - SN_A\Big|_{r+\delta r} = 0 \qquad \text{---------------------- (1)}$$

Where S is the surface are (= 4 πr^2)
Dividing (1) by Sδr, and taking the limit as δr approaches zero, gives:

$$\frac{d\left(r^2 N_A\right)}{dr} = 0$$

Integrating $r^2 N_A$ = constant (or) 4 $\pi r^2 N_A$ = constant
We can assume that there is a film of naphthalene – vapor / air film around naphthalene through which molecular diffusion occurs.
Diffusion of naphthalene vapor across this film could be written as,

$$N_A = -CD_{AB}\frac{dy_A}{dr} + y_A\left(N_A + N_B\right)$$

N_B = 0 (since air is assumed to be stagnant in the film)

$$N_A = -CD_{AB}\frac{dy_A}{dr} + y_A N_A$$

$$N_A = -CD_{AB}\frac{d}{dr}\left(\frac{y_A}{1-y_A}\right)$$

$$N_A = CD_{AB}\frac{d\left[\ln\left(1-y_A\right)\right]}{dr}$$

W_A = Rate of evaporation = 4 $\pi r^2 N_A\big/_R$ = constant.

$$W_A = \frac{4\pi r^2 CD_{AB}\, d\big(\ln(1-y_A)\big)}{dr}$$

$$W_A \int \frac{dr}{r^2} = 4\pi D_{AB} \int C\, d\ln(1-y_A)$$

Boundary condition:

At r = R $y_A = \dfrac{0.555}{760} = 7.303 * 10^{-4}$

                   *ln (1 − y$_A$) = −7.3 * 10^{-4}*

At r = ∞   *y$_A$ = 0   ln (1−y$_A$) = 0*

Therefore $W_A \int\limits_{R}^{\infty} \frac{dr}{r^2} = 4\pi D_{AB}\, C \int\limits_{-7.3*10^{-4}}^{0} d\Big[\ln(1-y_A)\Big]$

$$W_A \left[\frac{-1}{r}\right]_{R}^{\infty} = 4\pi D_{AB}\, C\left[\ln(1-y_A)\right]_{-7.3*10^{-4}}^{0}$$

$$W_A\left[0+\frac{1}{R}\right] = 4\pi D_{AB}\, C\left[0+7.3*10^{-4}\right]$$

   *W$_A$ = 4 πR D$_{AB}$ C * 7.3 * 10^{-4}*

$$C = \frac{P}{\text{Gas constant} * T} = \frac{1.01325 * 10^5}{8314 * 318}$$

       = 0.0383 k mol/m^3

Initial rate of evaporation:
Therefore,   *W$_A$ = 4 * 3.142 * 2 * 10^{-3} * 6.92 * 10^{-6} * 0.0383 * 7.3 * 10^{-4}*
                   *= 4.863 * 10^{-12} k mol/sec*
                   *W$_A$= 1.751 * 10^{-5} mol/hr.*

1.5.4 DIFFUSION IN LIQUIDS:

Equation derived for diffusion in gases equally applies to diffusion in liquids with some modifications. Mole fraction in liquid phases is normally written as 'x' (in gases as y). The concentration term 'C' is replaced by average molar density, $\left(\dfrac{\rho}{M}\right)_{av}$.

(a) For steady – state diffusion of A through non diffusing B:
N$_A$ = constant, N$_B$ = 0

$$N_A = \frac{D_{AB}}{z\, x_{BM}}\left(\frac{\rho}{M}\right)_{av}\left(x_{A1} - x_{A2}\right)$$ ------------------- (1.40)

Where, $Z = Z_2 - Z_1$, the length of diffusion path; and

$$X_{BM} = \frac{X_{B2} - X_{B1}}{\ln\left(X_{B2}/X_{B1}\right)}$$ ------------------- (1.41)

b) For steady – state equi-molar counter diffusion:
$N_A = - N_B$ = constant

$$N_A = \frac{D_{AB}}{Z}\left(C_{A1} - C_{A2}\right) = \frac{D_{AB}}{Z}\left(\frac{\rho}{M}\right)_{av}\left(x_{A1} - x_{A2}\right)$$ ------------------- (1.42)

Example 1.5 *Calculate the rate of diffusion of butanol at 20°C under unidirectional steady state conditions through a 0.1 cm thick film of water when the concentrations of butanol at the opposite sides of the film are, respectively 10% and 4% butanol by weight. The diffusivity of butanol in water solution is $5.9 * 10^{-6}$ cm²/sec. The densities of 10% and 4% butanol solutions at 20°C may be taken as 0.971 and 0.992 g/cc respectively. Molecular weight of butanol (C_4H_9OH) is 74, and that of water 18.*

Solution:
For steady state unidirectional diffusion,

$$N_A = \frac{D_{AB}}{z}C\frac{\left(x_{A1} - x_{A2}\right)}{x_{B,lm}}$$

where C is the average molar density.

$$= \left(\frac{\rho}{M}\right)_{avg}$$

Conversion from weight fraction the Mole fraction:

$$x_{A1} = \frac{\left(0.1/74\right)}{\left(0.1/74 + 0.9/18\right)} = 0.026$$

$$x_{A2} = \frac{\left(0.04/74\right)}{\left(0.04/74 + 0.96/18\right)} = 0.010$$

Average molecular weight at 1 & 2:

$$M_1 = \frac{1}{\left(0.1/74 + 0.9/18\right)} = 19.47\,kg/Kmol$$

$$M_2 = \frac{1}{\left(0.04/74 + 0.96/18\right)} = 18.56\,kg/Kmol$$

$$\left(\frac{\rho}{M}\right)_{avg} = \frac{\left(\rho_1/M_1 + \rho_2/M_2\right)}{2}$$

$$= \frac{0.971/19.47 + 0.992/18.56}{2}$$

$$= 0.0517 \ gmol \ / \ cm^3$$

$$= 51.7 \ kmol/m^3$$

$$x_{B,lm} = \frac{x_{B2} - x_{B1}}{\ln\left(x_{B2}/x_{B1}\right)} = \frac{\left(1 - x_{A2}\right) - \left(1 - x_{A1}\right)}{\ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)}$$

(i.e.)

$$x_{B,lm} = \frac{\left(1 - 0.01\right) - \left(1 - 0.026\right)}{\ln\left(\frac{1 - 0.01}{1 - 0.026}\right)}$$

$$= \frac{0.016}{0.0163} = 0.982$$

Therefore

$$N_A = \frac{D_{AB}}{2}\left(\frac{\rho}{M}\right)_{avg}\frac{\left(x_{A1} - x_{A2}\right)}{x_{B,lm}}$$

$$= \frac{5.9 * 10^{-6} * 10^{-4} * 51.7}{0.1 * 10^{-2}} * \frac{(0.026 - 0.010)}{0.982}$$

$$= 4.97 * 10^{-7} \frac{kmol}{m^2 \ sec}$$

$$= 1.789 \frac{gmol}{m^2.hr.} = 1.789 \times 74 \frac{g}{m^2.hr.}$$

$$N_A = 132.4 \frac{g}{m^2.hr.}$$

1.5.5 DIFFUSION IN SOLIDS

In certain unit operation of chemical engineering such as in drying or in absorption, mass transfer takes place between a solid and a fluid phase. If the transferred species is distributed uniformly in the solid phase and forms a homogeneous medium, the diffusion of the species in the solid phase is said to be structure independent. In this case diffusivity or diffusion coefficient is direction – independent.

At steady state, and for mass diffusion which is independent of the solid matrix structure, the molar flux in the z direction is:

$$N_A = -D_{AB} \frac{dC_A}{dz} = \text{constant}, \text{ as given by Fick's law.}$$

Integrating the above equation,

$$N_A = \frac{D_{AB}\left(C_{A1} - C_{A2}\right)}{z} \qquad \text{-------------------- (1.43)}$$

Which is similar to the expression obtained for diffusion in a stagnant fluid with no bulk motion (i.e. N= 0).

- **DIFFUSION IN PROCESS SOLIDS**

    In some chemical operations, such as heterogeneous catalysis, an important factor, affecting the rate of reaction is the diffusions of the gaseous component through a porous solid. The effective diffusivity in the solid is reduced below what it could be in a free fluid, for two reasons. First, the tortuous nature of the path increases the distance, which a molecule must travel to advance a given distance in the solid. Second, the free cross – sectional area is restricted. For many catalyst pellets, the effective diffusivity of a gaseous component is of the order of one tenth of its value in a free gas.

    If the pressure is low enough and the pores are small enough, the gas molecules will collide with the walls more frequently than with each other. This is known as Knudsen flow or Knudsen diffusion. Upon hitting the wall, the molecules are momentarily absorbed and then given off in random directions. The gas flux is reduced by the wall collisions.

    By use of the kinetic flux is the concentration gradient is independent of pressure; whereas the proportionality constant for molecular diffusion in gases (i.e. Diffusivity) is inversely proportional to pressure.

    Knudsen diffusion occurs when the size of the pore is of the order of the mean free path of the diffusing molecule.

1.6 TRANSIENT DIFFUSION

    Transient processes, in which the concentration at a given point varies with time, are referred to as unsteady state processes or time – dependent processes. This variation in concentration is associated with a variation in the mass flux.

These generally fall into two categories:
  (i)   The process which is in an unsteady state only during its initial startup, and
  (ii)   The process which is in a batch operation throughout its operation.

In unsteady state processes there are three variables-concentration, time, and position. Therefore, the diffusion process must be described by partial rather than ordinary differential equations.

Although the differential equations for unsteady state diffusion are easy to establish, most solutions to these equations have been limited to situations involving simple geometries and boundary conditions, and a constant diffusion coefficient.

Many solutions are for one-directional mass transfer as defined by Fick's second law of diffusion:

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

------------------- (1.44)

This partial differential equation describes a physical situation in which there is no bulk–motion contribution, and there is no chemical reaction. This situation is encountered when the diffusion takes place in solids, in stationary liquids, or in system having equi-molar counter diffusion. Due to the extremely slow rate of diffusion within liquids, the bulk motion contribution of flux equation (i.e., $y_A \sum N_i$) approaches the value of zero for dilute solutions; accordingly, this system also satisfies Fick's second law of diffusion.

The solution to Fick's second law usually has one of the two standard forms. It may appear in the form of a trigonometric series which converges for large values of time, or it may involve series of error functions or related integrals which are most suitable for numerical evaluation at small values of time. These solutions are commonly obtained by using the mathematical techniques of separation of variables or Laplace transforms.