

### 3. Molecular mass transport

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### 3.1 Introduction of Mass Transfer

When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimizing the concentration differences within a system. The transport of one constituent from a region of higher concentration to that of a lower concentration is called mass transfer.

The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial processes. Examples of such processes are:

- (i) Dispersion of gases from stacks
- (ii) Removal of pollutants from plant discharge streams by absorption
- (iii) Stripping of gases from waste water
- (iv) Neutron diffusion within nuclear reactors
- (v) Air conditioning

Many of our day-by-day experiences also involve mass transfer, for example:

- (i) A lump of sugar added to a cup of coffee eventually dissolves and then eventually diffuses to make the concentration uniform.
- (ii) Water evaporates from ponds to increase the humidity of passing-air-stream
- (iii) Perfumes presents a pleasant fragrance which is imparted throughout the surrounding atmosphere.

The mechanism of mass transfer involves both molecular diffusion and convection.

### 3.2 Properties of Mixtures

Mass transfer always involves mixtures. Consequently, we must account for the variation of physical properties which normally exist in a given system. When a system contains three or more components, as many industrial fluid streams do, the problem becomes unwidely very quickly. The conventional engineering approach to problems of multicomponent system is to attempt to reduce them to representative binary (i.e., two component) systems.

In order to understand the future discussions, let us first consider definitions and relations which are often used to explain the role of components within a mixture.

#### 3.2.1 Concentration of Species:

Concentration of species in multicomponent mixture can be expressed in many ways. For species A, mass concentration denoted by  $\rho_A$  is defined as the mass of A,  $m_A$  per unit volume of the mixture.

$$\rho_A = \frac{m_A}{V} \quad \text{-----} \quad (1)$$

The total mass concentration density  $\rho$  is the sum of the total mass of the mixture in unit volume:

$$\rho = \sum_i \rho_i$$

where  $\rho_i$  is the concentration of species i in the mixture.

Molar concentration of, A,  $C_A$  is defined as the number of moles of A present per unit volume of the mixture.

By definition,

$$\text{Number of moles} = \frac{\text{mass of } A}{\text{molecular weight of } A}$$

$$n_A = \frac{m_A}{M_A} \quad \text{----- (2)}$$

Therefore from (1) & (2)

$$C_A = \frac{n_A}{V} = \frac{\rho_A}{M_A}$$

For ideal gas mixtures,

$$n_A = \frac{p_A V}{RT} \quad [\text{from Ideal gas law } PV = nRT]$$

$$C_A = \frac{n_A}{V} = \frac{p_A}{RT}$$

where  $p_A$  is the partial pressure of species A in the mixture. V is the volume of gas, T is the absolute temperature, and R is the universal gas constant.

The total molar concentration or molar density of the mixture is given by

$$C = \sum_i C_i$$

### 3.2.2 Velocities

In a multicomponent system the various species will normally move at different velocities; and evaluation of velocity of mixture requires the averaging of the velocities of each species present.

If  $v_i$  is the velocity of species i with respect to stationary fixed coordinates, then mass-average velocity for a multicomponent mixture defined in terms of mass concentration is,

$$v = \frac{\sum_i \rho_i v_i}{\sum_i \rho_i} = \frac{\sum_i \rho_i v_i}{\rho}$$

By similar way, molar-average velocity of the mixture  $v^*$  is

$$v^* = \frac{\sum_i C_i V_i}{C}$$

For most engineering problems, there will be little difference in  $v^*$  and  $v$  and so the mass average velocity,  $v$ , will be used in all further discussions.

The velocity of a particular species relative to the mass-average or molar average velocity is termed as diffusion velocity

(i.e.) Diffusion velocity =  $v_i - v$

The mole fraction for liquid and solid mixture,  $x_A$ , and for gaseous mixtures,  $y_A$ , are the molar concentration of species A divided by the molar density of the mixtures.

$$x_A = \frac{C_A}{C} \quad (\text{liquids and solids})$$

$$y_A = \frac{C_A}{C} \quad (\text{gases}).$$

The sum of the mole fractions, by definition must equal 1;

$$(i.e.) \quad \sum_i x_i = 1$$

$$\sum_i y_i = 1$$

by similar way, mass fraction of A in mixture is;

$$w_A = \frac{\rho_A}{\rho}$$

10. The molar composition of a gas mixture at 273 K and  $1.5 \times 10^5$  Pa is:

O <sub>2</sub>	7%
CO	10%
CO <sub>2</sub>	15%
N <sub>2</sub>	68%

Determine

- a) the composition in weight percent
- b) average molecular weight of the gas mixture
- c) density of gas mixture
- d) partial pressure of  $O_2$ .

**Calculations:**

Let the gas mixture constitutes 1 mole. Then

$$\begin{aligned}O_2 &= 0.07 \text{ mol} \\CO &= 0.10 \text{ mol} \\CO_2 &= 0.15 \text{ mol} \\N_2 &= 0.68 \text{ mol}\end{aligned}$$

Molecular weight of the constituents are:

$$\begin{aligned}O_2 &= 2 * 16 = 32 \text{ g/mol} \\CO &= 12 + 16 = 28 \text{ g/mol} \\CO_2 &= 12 + 2 * 16 = 44 \text{ g/mol} \\N_2 &= 2 * 14 = 28 \text{ g/mol}\end{aligned}$$

Weight of the constituents are: (1 mol of gas mixture)

$$\begin{aligned}O_2 &= 0.07 * 32 = 2.24 \text{ g} \\CO &= 0.10 * 28 = 2.80 \text{ g} \\CO_2 &= 0.15 * 44 = 6.60 \text{ g} \\N_2 &= 0.68 * 28 = 19.04 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Total weight of gas mixture} &= 2.24 + 2.80 + 6.60 + 19.04 \\&= 30.68 \text{ g}\end{aligned}$$

Composition in weight percent:

$$\begin{aligned}O_2 &= \frac{2.24}{30.68} * 100 = 7.30\% \\CO &= \frac{2.80}{30.68} * 100 = 9.13\% \\CO_2 &= \frac{6.60}{30.68} * 100 = 21.51\% \\N_2 &= \frac{19.04}{30.68} * 100 = 62.06\%\end{aligned}$$

Average molecular weight of the gas mixture  $M = \frac{\text{Weight of gas mixture}}{\text{Number of moles}}$

$$M = \frac{30.68}{1} = 30.68 \text{ g/mol}$$

Assuming that the gas obeys ideal gas law,  
 $PV = nRT$

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

$\frac{n}{V}$  = molar density =  $\rho_m$

Therefore, density (or mass density) =  $\rho_m M$   
Where M is the molecular weight of the gas.

$$\text{Density} = \rho_m M = \frac{PM}{RT} = \frac{1.5 * 10^5 * 30.68}{8314 * 273} \text{ kg/m}^3$$
$$= 2.03 \text{ kg/m}^3$$

Partial pressure of  $O_2$  = [mole fraction of  $O_2$ ] \* total pressure

$$= \frac{7}{100} * (1.5 * 10^5)$$
$$= 0.07 * 1.5 * 10^5$$
$$= 0.105 * 10^5 \text{ Pa}$$

### 3.3 Diffusion flux

Just as momentum and energy (heat) transfer have two mechanisms for transport-molecular and convective, so does mass transfer. However, there are convective fluxes in mass transfer, even on a molecular level. The reason for this is that in mass transfer, whenever there is a driving force, there is always a net movement of the mass of a particular species which results in a bulk motion of molecules. Of course, there can also be convective mass transport due to macroscopic fluid motion. In this chapter the focus is on molecular mass transfer.

The mass (or 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

$$N_A = C_A v_A \quad \text{----- (1)}$$

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

$$N_A = C_A (v_A - v) + C_A v \quad \text{----- (2)}$$

By definition

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

Therefore, equation (2) becomes

$$\begin{aligned} N_A &= C_A (v_A - v) + \frac{C_A}{C} \sum_i C_i v_i \\ &= C_A (v_A - v) + y_A \sum_i C_i v_i \end{aligned}$$

For systems containing two components A and B,

$$\begin{aligned} N_A &= C_A (v_A - v) + y_A (C_A v_A + C_B v_B) \\ &= C_A (v_A - v) + y_A (N_A + N_B) \\ N_A &= C_A (v_A - v) + y_A N \quad \text{----- (3)} \end{aligned}$$

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.

### 3.3.1 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

$$J_A = -C D_{AB} \frac{dy_A}{dZ} \quad \text{----- (4)}$$

using this expression, Equation (3) could be written as

$$N_A = -C D_{AB} \frac{dy_A}{dZ} + y_A N \quad \text{----- (5)}$$

### 3.3.2 Relation among molar fluxes:

For a binary system containing A and B, from Equation (5),

$$N_A = J_A + y_A N$$

or  $J_A = N_A - y_A N \quad \text{----- (6)}$

Similarly,

$$J_B = N_B - y_B N \quad \text{----- (7)}$$

Addition of Equation (6) & (7) gives,

$$J_A + J_B = N_A + N_B - (y_A + y_B) N \quad \text{----- (8)}$$

By definition  $N = N_A + N_B$  and  $y_A + y_B = 1$ .

Therefore equation (8) becomes,

$$J_A + J_B = 0$$

$$J_A = -J_B$$

$$C D_{AB} \frac{dy_A}{dZ} = -C D_{BA} \frac{dy_B}{dZ} \quad \text{----- (9)}$$

From  $y_A + y_B = 1$   
 $dy_A = -dy_B$

Therefore Equation (9) becomes,

$$D_{AB} = D_{BA} \quad \text{----- (10)}$$



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

### 3.4 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,  $\nu = (\mu / \rho)$  in momentum transfer, and thermal diffusivity,  $\alpha (= k / \rho C_p)$  in heat transfer.

Diffusivity is normally reported in  $cm^2 / sec$ ; the SI unit being  $m^2 / sec$ .

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 :	$5 \times 10^{-6}$	-----	$1 \times 10^{-5}$	$m^2 / sec.$
Liquids :	$10^{-6}$	-----	$10^{-9}$	$m^2 / sec.$
Solids :	$5 \times 10^{-14}$	-----	$1 \times 10^{-10}$	$m^2 / sec.$

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

#### 3.4.1 Diffusivity in Gases:

Pressure dependence of diffusivity is given by

$$D_{AB} \propto \frac{1}{p} \quad (\text{for moderate ranges of pressures, upto 25 atm}).$$

And temperature dependency is according to

$$D_{AB} \propto T^{3/2}$$

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 Wilke is

$$D_{1-mixture} = \frac{1}{\frac{y'_2}{D_{1-2}} + \frac{y'_3}{D_{1-3}} + \dots + \frac{y'_n}{D_{1-n}}}$$

Where  $D_{1-mixture}$  is the diffusivity for component 1 in the gas mixture;  $D_{1-n}$  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

$$y'_2 = \frac{y_2}{y_2 + y_3 + \dots + y_n}$$

9. Determine the diffusivity of  $CO_2$  (1),  $O_2$  (2) and  $N_2$  (3) in a gas mixture having the composition:

$CO_2$  : 28.5 %,  $O_2$  : 15%,  $N_2$  : 56.5%,

The gas mixture is at 273 k and  $1.2 \times 10^5$  Pa. The binary diffusivity values are given as: (at 273 K)

$$D_{12} P = 1.874 \text{ m}^2 \text{ Pa/sec}$$

$$D_{13} P = 1.945 \text{ m}^2 \text{ Pa/sec}$$

$$D_{23} P = 1.834 \text{ m}^2 \text{ Pa/sec}$$

**Calculations:**

Diffusivity of  $CO_2$  in mixture

$$D_{1m} = \frac{1}{\frac{y'_2}{D_{12}} + \frac{y'_3}{D_{13}}}$$

$$\text{where } y'_2 = \frac{y_2}{y_2 + y_3} = \frac{0.15}{0.15 + 0.565} = 0.21$$

$$y'_3 = \frac{y_3}{y_2 + y_3} = \frac{0.565}{0.15 + 0.565} = 0.79$$

$$\text{Therefore } D_{1m} P = \frac{1}{\frac{0.21}{1.874} + \frac{0.79}{1.945}} = 1.93 \text{ m}^2 \cdot \text{Pa}/\text{sec}$$

Since  $P = 1.2 \cdot 10^5 \text{ Pa}$ ,

$$D_{1m} = \frac{1.93}{1.2 \cdot 10^5} = 1.61 \cdot 10^{-5} \text{ m}^2/\text{sec}$$

Diffusivity of  $O_2$  in the mixture,

$$D_{2m} = \frac{1}{\frac{y_1'}{D_{21}} + \frac{y_3'}{D_{23}}}$$

$$\text{Where } y_1' = \frac{y_1}{y_1 + y_3} = \frac{0.285}{0.285 + 0.565} = 0.335$$

(mole fraction on-2 free bases).

and

$$y_3' = \frac{y_3}{y_1 + y_3} = \frac{0.565}{0.285 + 0.565} = 0.665$$

and

$$D_{21} P = D_{12} P = 1.874 \text{ m}^2 \cdot \text{Pa}/\text{sec}$$

Therefore

$$D_{2m} P = \frac{1}{\frac{0.335}{1.874} + \frac{0.665}{1.834}} = 1.847 \text{ m}^2 \cdot \text{Pa}/\text{sec}$$

$$D_{2m} = \frac{1.847}{1.2 \cdot 10^5} = 1.539 \cdot 10^{-5} \text{ m}^2/\text{sec}$$

By Similar calculations Diffusivity of  $N_2$  in the mixture can be calculated, and is found to be,  $D_{3m} = 1.588 \cdot 10^{-5} \text{ m}^2/\text{sec}$ .

### 3.4.2 Diffusivity in liquids:

Diffusivity in liquid are exemplified by the values given in table ... Most of these values are nearer to  $10^{-5}$   $\text{cm}^2 / \text{sec}$ , and about ten thousand times slower 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  $\text{Na}^+$  and  $\text{Cl}^-$ . Though each ions 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 cations 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.

### 3.4.3 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 times 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.

## 3.5 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 (5) is [section 3.3.1]

$$N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A + N_B) \quad \text{--- (1)}$$

### 3.5.1 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.

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 tube, has a negligible solubility in liquid A, and is also chemically inert to A. (i.e. no reaction between A & B).

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  $S \Delta z$ , 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  $z + \Delta z$ ] – [Moles of A entering at  $z$ ] = 0.

$$(i.e.) \quad S N_A \Big|_{z+\Delta z} - S N_A \Big|_z = 0. \quad \text{----- (1)}$$

Dividing through by the volume,  $S\Delta z$ , and evaluating in the limit as  $\Delta z$  approaches zero, we obtain the differential equation

$$\frac{d N_A}{d z} = 0 \quad \text{----- (2)}$$

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,

$$\frac{d N_B}{d Z} = 0,$$

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 in 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) (of section 3.5)

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

Since  $N_B = 0$ ,

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

Rearranging,

$$N_A = \frac{-CD_{AB}}{1-y_A} \frac{dy_A}{dz} \quad \text{----- (3)}$$

This equation may be integrated between the two boundary conditions:

$$\begin{array}{ll} \text{at } z = z_1 & Y_A = Y_{A1} \\ \text{And at } z = z_2 & Y_A = y_{A2} \end{array}$$

Assuming the diffusivity is to be independent of concentration, and realizing that  $N_A$  is constant along the diffusion path, by integrating equation (3) we obtain

$$N_A \int_{z_1}^{z_2} dz = CD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{-dy_A}{1-y_A}$$

$$N_A = \frac{CD_{AB}}{z_2 - z_1} \ln \left( \frac{1-y_{A2}}{1-y_{A1}} \right) \quad \text{----- (4)}$$

The log mean average concentration of component B is defined as

$$y_{B,lm} = \frac{y_{B2} - y_{B1}}{\ln \left( \frac{y_{B2}}{y_{B1}} \right)}$$

Since  $y_B = 1 - y_A$ ,

$$y_{B,lm} = \frac{(1 - y_{A2}) - (1 - y_{A1})}{\ln\left(\frac{y_{A2}}{y_{A1}}\right)} = \frac{y_{A1} - y_{A2}}{\ln\left(\frac{y_{A2}}{y_{A1}}\right)} \quad \text{----- (5)}$$

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

$$N_A = \frac{CD_{AB}}{z_2 - z_1} \frac{(y_{A1} - y_{A2})}{y_{B,lm}} \quad \text{----- (6)}$$

For an ideal gas  $C = \frac{n}{V} = \frac{p}{RT}$ , and

$$\text{for mixture of ideal gases } y_A = \frac{p_A}{P}$$

Therefore, for an ideal gas mixture equation. (6) becomes

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

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 equation.

The concentration profile ( $y_A$  vs.  $z$ ) for this type of diffusion is shown in figure:

### Figure

12. 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.

- Derive the appropriate expression to calculate the flux oxygen. Define units of each term clearly.
- Calculate the flux of oxygen. Diffusivity of oxygen in nitrogen =  $1.89 \times 10^{-5} \text{ m}^2/\text{sec}$ .

**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  $J_A$ :

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

From Fick's law of diffusion,

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

Substituting this equation (1)

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

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

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

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

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

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

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

Therefore,

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



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

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

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:**

- $D_{AB} = 1.89 * 10^{-5} \text{ m}^2/\text{sec}$
- $P_t = 1 \text{ atm} = 1.01325 * 10^5 \text{ N/m}^2$
- $T = 25^\circ\text{C} = 273 + 25 = 298 \text{ K}$
- $z = 2 \text{ mm} = 0.002 \text{ m}$
- $P_{A1} = 0.2 * 1 = 0.2 \text{ atm}$  (From Ideal gas law and additive pressure rule)
- $P_{A2} = 0.1 * 1 = 0.1 \text{ atm}$

Substituting these in equation (6)

$$N_A = \frac{(1.89 * 10^{-5})(1.01325 * 10^5)}{(8314)(298)(0.002)} \ln \left( \frac{1 - 0.1}{1 - 0.2} \right)$$

$$= 4.55 * 10^{-5} \text{ kmol/m}^2.\text{sec}$$

### 3.5.2 Pseudo steady state diffusion through a stagnant film:

In many mass transfer operations, one of the boundaries may move with time. If the length of the diffusion path changes a small amount over a long period of time, a pseudo steady state diffusion model may be used. When this condition exists, the equation of steady state diffusion through stagnant gas' can be used to find the flux.

**figure**

If the difference in the level of liquid A over the time interval considered is only a small fraction of the total diffusion path, and  $t_0 - t$  is relatively long period of time,

at any given instant in that period, the molar flux in the gas phase may be evaluated by

$$N_A = \frac{C D_{AB} (y_{A1} - y_{A2})}{z y_{B,lm}} \text{----- (1)}$$

where  $z$  equals  $z_2 - z_1$ , the length of the diffusion path at time  $t$ .

The molar flux  $N_A$  is related to the amount of A leaving the liquid by

$$N_A = \frac{\rho_{A,L}}{M_A} \frac{dz}{dt} \text{----- (2)}$$

where  $\frac{\rho_{A,L}}{M_A}$  is the molar density of A in the liquid phase

under Pseudo steady state conditions, equations (1) & (2) can be equated to give

$$\frac{\rho_{A,L}}{M_A} \frac{dz}{dt} = \frac{C D_{AB} (y_{A1} - y_{A2})}{z y_{B,lm}} \text{----- (3)}$$

Equation. (3) may be integrated from  $t = 0$  to  $t$  and from  $z = z_{t0}$  to  $z = z_t$  as:

$$\int_{t=0}^t dt = \frac{\rho_{A,L} y_{B,lm} / M_A}{C D_{AB} (y_{A1} - y_{A2})} \int_{z_{t0}}^{z_t} z dz$$

yielding

$$t = \frac{\rho_{A,L} y_{B,lm} / M_A}{C D_{AB} (y_{A1} - y_{A2})} \left( \frac{z_t^2 - z_{t0}^2}{2} \right) \text{----- (4)}$$

This shall be rearranged to evaluate diffusivity  $D_{AB}$  as,

$$D_{AB} = \frac{\rho_{A,L} y_{B,lm}}{M_A C (y_{A1} - y_{A2}) t} \left( \frac{z_t^2 - z_{t0}^2}{2} \right)$$

**1. A vertical glass tube 3 mm in diameter is filled with liquid toluene to a depth of 20mm from the top openend. After 275 hrs at 39.4 °C and a total**

pressure of 760 mm Hg the level has dropped to 80 mm from the top.  
Calculate the value of diffusivity.

Data:

vapor pressure of toluene at 39.4°C = 7.64 kN / m<sup>2</sup>,

density of liquid toluene = 850 kg/m<sup>3</sup>

Molecular weight of toluene = 92

(C<sub>6</sub> H<sub>6</sub> CH<sub>3</sub>)

$$D_{AB} = \frac{\rho_{A,L} Y_{B,lm}}{M_A C (y_{A1} - y_{A2}) t} \left( \frac{Z_t^2 - Z_{t0}^2}{2} \right)$$

figure

$$\text{where } y_{B,lm} = \frac{y_{B2} - y_{B1}}{\ln \left( \frac{y_{B2}}{y_{B1}} \right)}$$

$$y_{B2} = 1 - y_{A2}$$

$$y_{B1} = 1 - y_{A1}$$

$$y_{A1} = \frac{\rho_{A1}}{P} = \frac{7.64}{101.3}$$

$$(760 \text{ mm Hg} = 101.3 \text{ kN/m}^2)$$

$$= 0.0754$$

$$y_{B1} = 1 - 0.0754 = 0.9246$$

$$y_{A2} = 0$$

$$y_B = 1 - y_{A2} = 1$$

$$\text{Therefore } y_{B,lm} = \frac{1 - 0.9246}{\ln \left( \frac{1}{0.9246} \right)} = 0.9618$$

$$C = \frac{P}{RT} = \frac{1.01325 * 10^5}{8314 * (273 + 39.4)}$$

$$= 0.039 \text{ k mol /m}^3$$

Therefore

$$D_{AB} = \frac{850 * 0.9618}{92 * 0.039 * (0.0754 - 0) * 275 * 3600} \left( \frac{0.08^2 - 0.02^2}{2} \right)$$

$$= 1.5262 * 10^{-3} (0.08^2 - 0.02^2)$$

$$= 9.1572 * 10^{-6} \text{ m}^2/\text{sec.}$$

### 3.5.3 Equimolar 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 
$$N_A = -D_{AB} \frac{dC_A}{dz} + y_A (N_A + N_B) \quad \text{----- (1)}$$

with the substitution of  $N_B = -N_A$ , Equation (1) becomes,

$$N_A = -D_{AB} \frac{dC_A}{dz} \quad \text{----- (2)}$$

For steady state diffusion Equation. (2) may be integrated, using the boundary conditions:

$$\begin{array}{ll} \text{at } z = z_1 & C_A = C_{A1} \\ \text{and } z = z_2 & C_A = C_{A2} \end{array}$$

Giving,

$$N_A \int_{z_1}^{z_2} dz = -D_{AB} \int_{C_{A1}}^{C_{A2}} dC_A$$

from which

$$N_A = \frac{D_{AB}}{z_2 - z_1} (C_{A1} - C_{A2}) \quad \text{----- (3)}$$

For ideal gases,  $C_A = \frac{n_A}{V} = \frac{p_A}{RT}$ . Therefore Equation. (3) becomes

$$N_A = \frac{D_{AB}}{RT(z_2 - z_1)} (P_{A1} - P_{A2}) \quad \text{----- (4)}$$

This is the equation of molar flux for steady-state equimolar counter diffusion.

Concentration profile in these equimolar counter diffusion may be obtained from,

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

And from equation. (2)

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

Therefore

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

or 
$$\frac{d^2 C_A}{dz^2} = 0.$$

This equation may be solved using the boundary conditions to give

$$\frac{C_A - C_{A1}}{C_{A1} - C_{A2}} = \frac{z - z_1}{z_1 - z_2} \quad \text{----- (5)}$$

Equation, (5) indicates a linear concentration profile for equimolar counter diffusion.

3. 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  $6.75 \times 10^{-5} \text{ m}^2/\text{sec}$ .

- i) calculate the flux of  $\text{CH}_4$  at steady state for equimolar counter diffusion.
- ii) Calculate the partial pressure at a point 0.02 m apart from point 1.

**Calculation:**

For steady state equimolar counter diffusion, molar flux is given by

$$N_A = \frac{D_{AB}}{RTz} (p_{A1} - p_{A2}) \quad \text{----- (1)}$$

Therefore;

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

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

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

$$3.633 * 10^{-5} = \frac{6.75 * 10^{-5}}{8.314 * 298 * 0.02} (55 - p_A)$$

$$p_A = 28.33 \text{ kPa}$$

11. In a gas mixture of hydrogen and oxygen, steady state equimolar counter diffusion is occurring at a total pressure of 100 kPa and temperature of 20°C. If the partial pressures of oxygen at two planes 0.01 m apart, and perpendicular to the direction of diffusion are 15 kPa and 5 kPa, respectively and the mass diffusion flux of oxygen in the mixture is  $1.6 * 10^{-5} \text{ kmol/m}^2 \cdot \text{sec}$ , calculate the molecular diffusivity for the system.

**Solution:**

For equimolar counter current diffusion:

$$N_A = \frac{D_{AB}}{RTz} (p_{A1} - p_{A2}) \text{----- (1)}$$

where

- $N_A$  = molar flux of A ( $1.6 * 10^{-5} \text{ kmol/m}^2 \cdot \text{sec}$ ):
- $D_{AB}$  = molecular diffusivity of A in B
- R = Universal gas constant (8.314 kJ/kmol.k)
- T = Temperature in absolute scale (273 + 20 = 293 K)
- z = distance between two measurement planes 1 and 2 (0.01 m)
- $P_{A1}$  = partial pressure of A at plane 1 (15 kPa); and
- $P_{A2}$  = partial pressure of A at plane 2 (5 kPa)

Substituting these in equation (1)

$$1.6 * 10^{-5} = \frac{D_{AB}}{(8.314)(293)(0.01)} (15 - 5)$$

Therefore,  $D_{AB} = 3.898 \times 10^{-5} \text{ m}^2/\text{sec}$

2. A tube 1 cm in inside diameter that is 20 cm long is filled with  $\text{Co}_2$  and  $\text{H}_2$  at a total pressure of 2 atm at  $0^\circ\text{C}$ . The diffusion coefficient of the  $\text{Co}_2 - \text{H}_2$  system under these conditions is  $0.275 \text{ cm}^2/\text{sec}$ . If the partial pressure of  $\text{Co}_2$  is 1.5 atm at one end of the tube and 0.5 atm at the other end, find the rate of diffusion for:

- i) steady state equimolar counter diffusion ( $N_A = -N_B$ )
- ii) steady state counter diffusion where  $N_B = -0.75 N_A$ , and
- iii) steady state diffusion of  $\text{Co}_2$  through stagnant  $\text{H}_2$  ( $N_B = 0$ )

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

Given

$$N_B = -N_A$$

$$\text{Therefore } N_A = -CD_{AB} \frac{dy_A}{dz} = -D_{AB} \frac{dC_A}{dz}$$

(For ideal gas mixture  $C_A = \frac{p_A}{RT}$  where  $p_A$  is the partial pressure of A; such that  $p_A + p_B = P$ )

$$\text{Therefore } N_A = -D_{AB} \frac{d(p_A/RT)}{dz}$$

For isothermal system, T is constant

$$\text{Therefore } N_A = \frac{-D_{AB}}{RT} \frac{dp_A}{dz}$$

$$(i.e.) N_A \int_{Z_1}^{Z_2} dz = -\frac{D_{AB}}{RT} \int_{P_{A1}}^{P_{A2}} dp_A$$

$$N_A = \frac{D_{AB}}{RT Z} (p_{A1} - p_{A2}) \text{ ----- (1)}$$

where  $Z = Z_2 - Z_1$

Given:  $D_{AB} = 0.275 \text{ cm}^2/\text{sec} = 0.275 \times 10^{-4} \text{ m}^2/\text{sec}$ ;  $T = 0^\circ\text{C} = 273 \text{ k}$

$$N_A = \frac{0.275 * 10^{-4}}{8314 * 273 * 0.2} (1.5 * 1.01325 * 10^5 - 0.5 * 1.01325 * 10^5)$$

$$= 6.138 * 10^{-6} \frac{k mol}{m^2 sec}$$

Rate of diffusion =  $N_A S$

Where S is surface area

$$\begin{aligned} \text{Therefore rate of diffusion} &= 6.138 * 10^{-6} * \pi r^2 \\ &= 6.138 * 10^{-6} * \pi (0.5 * 10^{-2})^2 \\ &= 4.821 * 10^{-10} \text{ k mol/sec} \\ &= 1.735 * 10^{-3} \text{ mol/hr.} \end{aligned}$$

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

$$\text{given: } N_B = -0.75 N_A$$

$$\text{Therefore } N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A - 0.75 N_A)$$

$$= -CD_{AB} \frac{dy_A}{dz} + 0.25 y_A N_A$$

$$N_A - 0.25 y_A N_A = -CD_{AB} \frac{dy_A}{dz}$$

$$N_A dz = -CD_{AB} \frac{dy_A}{1 - 0.25 y_A}$$

for constant  $N_A$  and C

$$N_A \int_{z_1}^{z_2} dz = -CD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1 - 0.25 y_A}$$

$$\left[ \int \frac{dx}{a + bx} = \frac{1}{b} \ln(a + bx) \right]$$

$$N_A z = (-CD_{AB}) \left( \frac{-1}{0.25} \right) \left[ \ln(1 - 0.25 y_A) \right]_{y_{A1}}^{y_{A2}}$$



$$N_A = -\frac{4CD_{AB}}{z} \ln \left( \frac{1-0.25y_{A2}}{1-0.25y_{A1}} \right) \text{----- (2)}$$

**Given:**

$$C = \frac{p}{RT} = \frac{2 * 1.01325 * 10^5}{8314 * 273} = 0.0893 \text{ K mol/m}^3$$

$$y_{A1} = \frac{p_{A1}}{P} = \frac{1.5}{2} = 0.75$$

$$y_{A2} = \frac{p_{A2}}{P} = \frac{0.5}{2} = 0.25$$

Substituting these in equation (2),

$$\begin{aligned} N_A &= \frac{4 * 0.0893 * 0.275 * 10^{-4}}{0.2} \left[ \ln \frac{1-0.25 * 0.25}{1-0.25 * 0.75} \right] \\ &= 7.028 * 10^{-6} \frac{\text{kmol}}{\text{m}^2 \text{ sec}} \end{aligned}$$

$$\begin{aligned} \text{Rate of diffusion} = N_A S &= 7.028 * 10^{-6} * \pi * (0.5 * 10^{-2})^2 \\ &= 5.52 * 10^{-10} \text{ kmol/sec} \\ &= 1.987 * 10^{-3} \text{ mol/hr.} \end{aligned}$$

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

**Given:**  $N_B = 0$

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

$$\begin{aligned} N_A \int_{Z_1}^{Z_2} dz &= -CD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1-y_A} \\ &= \frac{CD_{AB}}{Z} \ln \left( \frac{1-y_{A2}}{1-y_{A1}} \right) \\ &= \frac{0.0893 * 0.275 * 10^{-4}}{0.2} \left[ \ln \left( \frac{1-0.25}{1-0.75} \right) \right] \end{aligned}$$

$$= 1.349 \times 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{sec}}$$

$$\text{Rate of diffusion} = 1.349 \times 10^{-5} \times \pi \times (0.5 \times 10^{-2})^2$$

$$= 1.059 \text{ Kmol / sec}$$

$$= 3.814 \text{ mol/hr}$$

### 3.5.4 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.

#### a) Evaporation of a spherical Droplet:

As an example of such problems, we shall 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 figure. At any moment, when the radius

**Figure**  
**Evaporation of a raindrop**

of the drop is  $r_0$ , the flux of water vapor at any distance  $r$  from the center is given by

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

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

Therefore,

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

Rearranging,

$$N_A = \frac{-CD_{AB}}{1-y_A} \frac{dy_A}{dr} \quad \text{----- (1)}$$

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 rate at  $r$  and  $r + \delta r$  are the same.

This could be written as,

$$A N_A|_r = A N_A|_{r+\delta r} \quad \text{_____} \quad (2)$$

where A = surface area of sphere at r or r + δr.

Substituting for A = 4 π r<sup>2</sup> in equation (2),

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

or

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

$$\text{ss} \quad \frac{d}{dr} (r^2 N_A) = 0 \quad \text{_____} \quad (3)$$

Integrating,

$$r^2 N_A = \text{constant} \quad \text{_____} \quad (4)$$

From equation (4),  $r^2 N_A = r_0^2 N_{A_0}$

Substituting for N<sub>A</sub> from equation (1),

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

$$r_0^2 N_{A_0} \int \frac{dr}{r^2} = -C D_{AB} \int \frac{dy_A}{1-y_A} \quad \text{_____} \quad (5)$$

Boundary condition :

$$\text{At } r = r_0 \quad y_A = y_{AS}$$

And

$$\text{At } r = \infty \quad y_A = y_{A\infty}$$

Therefore equation (5) becomes,

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

Simplifying,

$$N_{A_0} = \frac{C D_{AB}}{r_0} \ln \left( \frac{1-y_{A\infty}}{1-y_{AS}} \right) \quad \text{_____} \quad (6)$$

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

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

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

$$= -4\pi r_0^2 \frac{\rho_L}{M_A} \frac{dr_0}{dt} \quad \text{_____ (7)}$$

Substituting for  $N_{A0}$  from equation (6) in equation (7),

$$\frac{CD_{AB}}{r_0} \ln \left( \frac{1-y_A}{1-y_{AS}} \right) = \frac{-\rho_L}{M_A} \frac{dr_0}{dt} \quad \text{_____ (8)}$$

Initial condition :

When  $t = 0$   $r_0 = r_1$

Integrating equation (8) with these initial condition,

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

$$t = \frac{\rho_L}{M_A} \frac{1}{2CD_{AB}} \frac{r_1^2}{\ln \left( \frac{1-y_{A\infty}}{1-y_{AS}} \right)} \quad \text{_____ (9)}$$

Equation (9) gives the total time  $t$  required for complete evaporation of spherical droplet of initial radius  $r_1$ .

### b) Combustion of a coal particle:

The problem of combustion of spherical coal particle is similar to evaporation of a drop with the exception that chemical reaction (combustions) occurs at the surface of the particle. During combustion of coal, the reaction



occurs. According to this reaction for every mole of oxygen that diffuses to the surface of coal (maximum of carbon), react with 1 mole of carbon, releases 1 mole of carbon dioxide, which must diffuse away from this surface. This is a case of equimolar counter diffusion of  $CO_2$  and  $O_2$ . Normally air (a mixture of  $N_2$  and  $O_2$ ) is used for combustion, and in this case  $N_2$  does not takes part in the reaction, and its flux is zero. (i.e.  $N_{N_2} = 0$ ).

The molar flux of  $O_2$  could be written as

$$N_{O_2} = -CD_{O_2-gas} \frac{dy_{O_2}}{dr} + y_{O_2} (N_{O_2} + N_{CO_2} + N_{N_2}) \quad \text{_____ (1)}$$

Where  $D_{O_2-gas}$  is the diffusivity of  $O_2$  in the gas mixture.

Since  $N_{N_2} = 0$ , and from stoichiometry  $N_{O_2} = -N_{CO_2}$ , equation (1) becomes

$$N_{O_2} = -CD_{O_2-gas} \frac{dy_{O_2}}{dr} \quad \text{_____ (2)}$$

For steady state conditions,

$$\frac{d}{dr} (r^2 N_{O_2}) = 0 \quad \text{_____ (3)}$$

Integrating,

$$r^2 N_{O_2} = \text{constant} = r_0^2 N_{O_2s} \quad \text{_____ (4)}$$

Where  $r_0$  is the radius of coal particle at any instant, and  $N_{O_2s}$  is the flux of  $O_2$  at the surface of the particle.

Substituting for  $N_{O_2}$  from equation (2) in equation (4),

$$-r^2 CD_{O_2-gas} \frac{dy_{O_2}}{dr} = r_0^2 N_{O_2s} \quad \text{_____ (5)}$$

Boundary condition :

$$\text{At } r = r_0 \quad y_{O_2} = y_{O_2s}$$

And

$$\text{At } r = \infty \quad y_{O_2} = y_{O_2\infty}$$

With these boundary condition, equation (5) becomes

$$r_0^2 N_{A_0} \int_{r_0}^{\infty} \frac{dr}{r^2} = -CD_{O_2-gas} \int_{y_{O_2s}}^{y_{O_2\infty}} dy_{O_2}$$

which yields

$$N_{O_2s} = \frac{CD_{O_2-gas}}{r_0} (y_{O_2s} - y_{O_2\infty}) \quad \text{_____ (6)}$$

For fast reaction of  $O_2$  with coal, the mole fraction of  $O_2$  at the surface of particle is zero. (i.e.,)  $y_{O_2s} = 0$ .

And also at some distance away from the surface of the particle  $y_{O_2} = y_{O_2\infty} = 0.21$  (because air is a mixture of 21 mole %  $O_2$  and 79 mole %  $N_2$ )

With these conditions, equation (6) becomes,

$$N_{O_2 s} = \frac{0.21 CD_{O_2 - gas}}{r_0} \quad \text{----- (7)}$$

**Figure**  
**Combustion of a particle of coal**

5. 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 318 K is 0.555 mm Hg. The  $D_{AB}$  of naphthalene in air at 318 K is  $6.92 \times 10^{-6} \text{ m}^2/\text{sec}$ . Calculate the rate of evaporation of naphthalene from the surface.

**Calculation**

Steady state mass balance over a element of radius  $r$  and  $r + \delta r$  leads to

$$S N_A \Big|_r - S N_A \Big|_{r + \delta r} = 0 \quad \text{----- (1)}$$

where  $S$  is the surface are ( $= 4 \pi r^2$ )

dividing (1) by  $S\delta r$ , and taking the limit as  $\delta r$  approaches zero, gives:

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

Integrating  $r^2 N_A = \text{constant}$  (or)  $4 \pi r^2 N_A = \text{constant}$

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,

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

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

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

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

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

$W_A = \text{Rate of evaporation} = 4 \pi r^2 N_A \big|_R = \text{constant.}$

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

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

Boundary condition:

$$\text{At } r = R \quad y_A = \frac{0.555}{760} = 7.303 \times 10^{-4}$$

$$\ln(1 - y_A) = -7.3 \times 10^{-4}$$

$$\text{At } r = \infty \quad y_A = 0 \quad \ln(1 - y_A) = 0$$

$$\text{Therefore } W_A \int_R^{\infty} \frac{dr}{r^2} = 4 \pi D_{AB} C \int_{-7.3 \times 10^{-4}}^0 d[\ln(1 - y_A)]$$

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

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

$$W_A = 4 \pi R D_{AB} C \cdot 7.3 \times 10^{-4}$$

$$C = \frac{P}{\text{Gas constant} \cdot T} = \frac{1.01325 \times 10^5}{8314 \cdot 318} = 0.0383 \text{ kmol/m}^3$$

Initial rate of evaporation:

$$\begin{aligned} \text{Therefore } W_A &= 4 \cdot 3.142 \cdot 2 \cdot 10^{-3} \cdot 6.92 \cdot 10^{-6} \cdot 0.0383 \cdot 7.3 \cdot 10^{-4} \\ &= 4.863 \cdot 10^{-12} \text{ kmol/sec} \\ &= 1.751 \cdot 10^{-5} \text{ mol/hr.} \end{aligned}$$

### 3.5.5 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,  $\left( \frac{\rho}{M} \right)_{av}$ .

a) For steady – state diffusion of A through non diffusivity B:

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

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

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

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

b) For steady – state equimolar counter diffusion :

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

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

4. 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  $5.9 \times 10^{-6} \text{ cm}^2/\text{sec}$ . 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 ( $\text{C}_4\text{H}_9\text{OH}$ ) is 74, and that of water 18.

### Calculations

For steady state unidirectional diffusion,

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

where C is the average molar density.

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

Conversion from weight fraction the Mole fraction:

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

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

Average molecular weight at 1 & 2:



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

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

$$\begin{aligned} \left(\frac{\rho}{M}\right)_{avg} &= \frac{(\rho_1/M_1 + \rho_2/M_2)}{2} \\ &= \frac{0.971/19.47 + 0.992/18.56}{2} \\ &= 0.0517 \text{ gmol / cm}^3 \\ &= 51.7 \text{ kmol/m}^3 \end{aligned}$$

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

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

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

$$\begin{aligned} \text{Therefore } N_A &= \frac{D_{AB}}{2} \left(\frac{\rho}{M}\right)_{avg} \frac{(x_{A1} - x_{A2})}{x_{B,lm}} \\ &= \frac{5.9 * 10^{-6} * 10^{-4} * 51.7}{0.1 * 10^{-2}} * \frac{(0.026 - 0.010)}{0.982} \\ &= 4.97 * 10^{-7} \frac{\text{kmol}}{\text{m}^2 \text{ sec}} \\ &= 1.789 \frac{\text{gmol}}{\text{m}^2 \cdot \text{hr.}} \\ &= 1.789 * 74 \frac{\text{g}}{\text{m}^2 \cdot \text{hr.}} \\ &= 132.4 \frac{\text{g}}{\text{m}^2 \cdot \text{hr.}} \end{aligned}$$

**Mass diffusion with homogeneous chemical reaction:**

Absorption operations involves contact of a gas mixture with a liquid and preferential dissolution of a component in the contacting liquid. Depending on the chemical nature of the involved molecules, the absorption may or may not involve chemical reaction.

The following analysis illustrates the diffusion of a component from the gas phase into the liquid phase accompanied by a chemical reaction in the liquid phase. Consider a layer of absorbing medium (liquid) as shown in diagram.

### Figure

At the surface of the liquid, the composition of A is  $C_{A0}$ . The thickness of the film,  $\delta$  is so defined, that beyond this film the concentration of A is always zero ; that is  $C_{A\delta} = 0$ . If there is very little fluid motion within the film,

$$N_A = -D_{AB} \frac{dC_A}{dz} + \frac{C_A}{C} (N_A + N_B) \quad \text{_____ (1)}$$

If concentration of A in the film,  $C_A$  is assumed small, equation (1) becomes

$$N_A = -D_{AB} \frac{dC_A}{dz} \quad \text{_____ (2)}$$

The molar flux  $N_A$  changes along the diffusion path. This change is due to the reaction that takes place in the liquid film. This changes could be written as

$$\frac{d}{dz} (N_A) - r_A = 0 \quad \text{_____ (3)}$$

where  $-r_A$  is the rate of disappearance of A. For a first order reaction,



with the substitution from equation (4) and (2) in equation (3),

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

For constant Diffusivity,

$$-D_{AB} \frac{d^2 C_A}{dz^2} + k C_A = 0 \quad \text{_____ (5)}$$

which is a second order ordinary differential equation. The general solution to this equation is

$$C_A = C_1 \cos h \left( \sqrt{\frac{k}{D_{AB}}} z \right) + C_2 \sin h \left( \sqrt{\frac{k}{D_{AB}}} z \right) \quad \text{_____ (6)}$$

The constants of this equation can be evaluated from the boundary conditions:

at  $Z = 0$   $C_A = C_{A0}$   
 And at  $Z = \delta$   $C_A = 0$ .

The constant  $C_1$  is equal to  $C_{A0}$ , and  $C_2$  is equal to  $-C_{A0} / \tanh\left(\sqrt{k/D_{AB}} \delta\right)$  with this substitution equation (6) becomes,

$$C_A = C_{A0} \cosh\left(\sqrt{k/D_{AB}} z\right) - \frac{C_{A0} \sinh\left(\sqrt{k/D_{AB}} z\right)}{\tanh\left(\sqrt{k/D_{AB}} \delta\right)} \quad (7)$$

This equation gives the variation of concentration of A with  $z$  (i.e. concentration profile of A in the liquid). The molar flux at the liquid surface can be determined by differentiating equation (7), and evaluating the derivative  $dC_A/dz$  at  $z = 0$

Differentiating  $C_A$  with respect to  $z$ ,

$$\frac{dC_A}{dz} = C_{A0} \sqrt{k/D_{AB}} \sinh\left(\sqrt{k/D_{AB}} z\right) - \frac{C_{A0} \sqrt{k/D_{AB}} \cosh\left(\sqrt{k/D_{AB}} z\right)}{\tanh\left(\sqrt{k/D_{AB}} \delta\right)} \quad (8)$$

Substituting  $z = 0$  in equation (8) and from equation (2),

$$N_A|_{z=0} = \frac{D_{AB} C_{A0}}{\delta} \left[ \frac{\sqrt{k/D_{AB}} \delta}{\tanh\left(\sqrt{k/D_{AB}} \delta\right)} \right] \quad (9)$$

For absorption with no chemical reaction, the flux of A is obtained from equation (2) as

$$N_A = \frac{D_{AB} C_{A0}}{\delta} \quad (10)$$

which is constant throughout the film of liquid. On comparison of equation (9) and

(10), it is apparent that the term  $\left[ \frac{\sqrt{k/D_{AB}} \delta}{\tanh\left(\sqrt{k/D_{AB}} \delta\right)} \right]$  shows

the influence of the chemical reactions. This term a dimensionless quantity, is often called as Hatta Number.

### 3.5.7 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 cases 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,

$$N_A = \frac{D_{AB} (C_{A1} - C_{A2})}{z}$$

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.

### 3.6 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 :

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2} \quad \text{_____ (1)}$$

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 equimolar 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.