UNIT 3: Mass Transfer

Contents

3 MASS TRANSFER

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 air 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.

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.) $$\sum_i x_i = 1$$

$$\sum_i y_i = 1$$

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

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

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

$\frac{n}{V}$ = molar density = ρ_m

Therefore, density (or mass density) = $\rho_m M$

Where M is the molecular weight of the gas.

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

$$= 2.03\ kg/m^3$$

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

$$= \frac{7}{100} * \left(1.5 * 10^5\right)$$

$$= 0.07 * 1.5 * 10^5$$

$$= 0.105 * 10^5\ Pa$$

3.2 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

$$N_A = C_A \nu_A \qquad \text{---------- (1)}$$

This could be written interms of diffusion velocity of A, (i.e., $\nu_A - \nu$) and average velocity of mixture, ν, as

$$N_A = C_A (\nu_A - \nu) + C_A \nu \qquad \text{---------- (2)}$$

By definition

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

Therefore, equation (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 systems containing two components A and B,

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

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.

3.2.1 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

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

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.

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, $\nu\eta = (\mu / \rho)$ in momentum transfer, and thermal diffusivity, α $(= k / \rho C_\rho)$ 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, incease 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}	m^2 / sec.
Liquids :	10^{-6}	----------	10^{-9}	m^2 / sec.
Solids :	5×10^{-14}	----------	1×10^{-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.

Diffusivity in Gases:

Pressure dependence of diffusivity is given by

$$D_{AB} \propto \frac{1}{p}$$ (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

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

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

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

Diffusivity in liquids:

Diffusivity in liquid are exemplified by the values given in table … 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 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.

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 inturn 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.

3.2.2 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]

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

Problem. 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 ^{2}/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:

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

From Fick's law of diffusion,

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

Substituting this equation (1)

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

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,

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

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,

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

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

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

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:

$D_{AB} = 1.89 * 10^{-5}$ m^2/sec
P_t = 1 atm = $1.01325 * 10^5$ N/m^2
T = 25°C = 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)

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

3.3 Psuedo 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.

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

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

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

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

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

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

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

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

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

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

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

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

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

or $$N_A = -D_{AB}\frac{dC_A}{dz} + y_A(N_A + N_B) \qquad \text{-------- (1)}$$

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

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

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

at $z = z_1$ $C_A = C_{A1}$

and $z = z_2$ $C_A = C_{A2}$

Giving,

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

from which

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

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

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

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

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

$\frac{d}{dz}(N_A) = 0$ (Since N_A 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

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

Problem. 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 $6.75 * 10^{-5}$ m^2/sec.

i) calculate the flux of 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;

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

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

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

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

p_A = 28.33 kPa

Problem. 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 $1.6 * 10^{-5}$ kmol/m^2.sec, calculate the molecular diffusivity for the system.

Solution:

For equimolar counter current diffusion:

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

where

N_A = molar flux of A ($1.6 * 10^{-5}$ kmol/m^2.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, $D_{AB} = 3.898 * 10^{-5}$ m^2/sec

Problem. A tube 1 cm in inside diameter that is 20 cm long is filled with Co_2 and H_2 at a total pressure of 2 atm at 0°C. The diffusion coefficient of the $Co_2 – H_2$ system under these conditions is 0.275 cm^2/sec. If the partial pressure of 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 Co_2 through stagnant H_2 ($N_B = 0$)

i) $N_A = - C D_{AB} \frac{dy_A}{dz} + y_A\left(N_A + N_B\right)$

Given

$N_B = - N_A$

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

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

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

For isothermal system, T is constant

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

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

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

where $Z = Z_2 - Z_1$

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

$$N_A = \frac{0.275 * 10^{-4}}{8314 * 273 * 0.2}\left(1.5 * 1.01325 * 10^5 - 0.5 * 1.01325 * 10^5\right)$$
$$= 6.138 * 10^{-6}\ \frac{k\,mol}{m^2\,sec}$$

Rate of diffusion = $N_A S$

Where S is surface area

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

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

given: $N_B = -0.75\ N_A$

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

$$= -C D_{AB}\frac{dy_A}{dz} + 0.25\, y_A N_A$$

$$N_A - 0.25\, y_A N_A = -C D_{AB}\frac{dy_A}{dz}$$

$$N_A\, dz = -C D_{AB}\frac{dy_A}{1 - 0.25 y_A}$$

for constant N_A and C

$$N_A \int_{Z_1}^{Z_2} dz = -CD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1-0.25y_A}$$

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

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

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

Given:

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

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

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

Substituting these in equation (2),

$$N_A = \frac{4*0.0893*0.275*10^{-4}}{0.2}\left[\ln\frac{1-0.25*0.25}{1-0.25*0.75}\right]$$

$$= 7.028*10^{-6}\ \frac{kmol}{m^2\,\sec}$$

Rate of diffusion = $N_A S = 7.028 * 10^{-6} * \pi * (0.5 * 10^{-2})^2$

$= 5.52 * 10^{-10}$ kmol/sec

$= 1.987 * 10^{-3}$ mol/hr.

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

Given: $N_B = 0$

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

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

$$= \frac{CD_{AB}}{Z}\ln\left[\frac{1-y_{A2}}{1-y_{A1}}\right]$$

$$= \frac{0.0893*0.275*10^{-4}}{0.2}\left[\ln\left[\frac{1-0.25}{1-0.75}\right]\right]$$

$$= 1.349 * 10^{-5} \ \frac{kmol}{m^2 . \sec}$$

Rate of diffusion = $1.349\ 8\ 10^{-5} * \pi * (0.5 * 10^{-2})^2$

= 1.059 Kmol / sec
= 3.814 mol/hr

3.4 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, $\left[\frac{\rho}{M}\right]_{av}$.

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

N_A = 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

$$X_{BM} = \frac{X_{B2} - X_{B1}}{\ln\left[X_{B2} / X_{B1}\right]}$$

b) For steady – state equimolar counter diffusion :

$N_A = - N_B$ = const

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

Problem. 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 $5.9 * 10^{-6}$ cm^2/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.

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:

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

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

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

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

$$= 0.0517 \text{ gmol / cm}^3$$

$$= 51.7 \text{ kmol/m}^3$$

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

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

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

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

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

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

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

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

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

3.5 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 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 :

$$N_A = - D_{AB} \frac{dC_A}{dz} = \text{constant}$$, 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).

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.