INTRODUCTION TO MASS TRANSFER CONT'D

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

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

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

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

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,

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

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

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 $6.75 * 10^{-5}$ 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

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

Therefore;

$$N_A = \frac{6.75 * 10^{-5}}{8.314 * 298 * 0.03}(55 - 15)\ \frac{kmol}{m^2.\text{sec}}$$
$$= 3.633 * 10^{-5}\ \frac{kmol}{m^2\ \text{sec}}$$

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

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

p_A = 28.33 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 $1.6 * 10^{-5}$ 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

2. 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) $N_A = -C D_{AB} \frac{d y_A}{d z} + y_A \left(N_A + N_B\right)$

Given

$N_B = - N_A$

Therefore $N_A = -C D_{AB} \frac{d y_A}{d z} = -D_{AB} \frac{d C_A}{d z}$

(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 $N_A = -D_{AB} \dfrac{d\left(p_A/RT\right)}{dz}$

For isothermal system, T is constant

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

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

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

where $Z = Z_2 - Z_1$

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

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

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

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

given: $N_B = -0.75 N_A$

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

$$= -C D_{AB} \frac{d y_A}{d z} + 0.25\, y_A N_A$$

$$N_A - 0.25\, y_A N_A = -C D_{AB} \frac{d y_A}{d z}$$

$$N_A\, d z = -C D_{AB} \frac{d y_A}{1 - 0.25\, y_A}$$

for constant N $_A$ and C

$$N_A \int_{Z_1}^{Z_2} d z = -C D_{AB} \int_{y_{A1}}^{y_{A2}} \frac{d y_A}{1 - 0.25\, y_A}$$

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

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

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

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),

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

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

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

Given: $N_B = 0$

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

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

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

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

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

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

= 1.059 Kmol / sec
= 3.814 mol/hr

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 diffusivity B:

N_A = constant , $N_B = 0$

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

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 :

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

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

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 $5.9 * 10^{-6}$ 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,

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

where C is the average molar density.

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

Conversion from weight fraction the Mole fraction:

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

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

Average molecular weight at 1 & 2:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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,

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

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.