

# الجامعة التكنولوجية

## قسم الهندسة الكيميائية

### المرحلة الثالثة

### انتقال كتلة

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(\*) What is chemical Engineering ?

Chemical Engineering deals with industrial process in which raw materials are converted or separated into useful products.

(\*) Who is the chemical Engineer ?

An engineer, who apply the chemistry of a particular industrial process through the use of scientific and engineering principles.

He must **develop**, **design** and **engineer** both the industrial process and the equipment used.

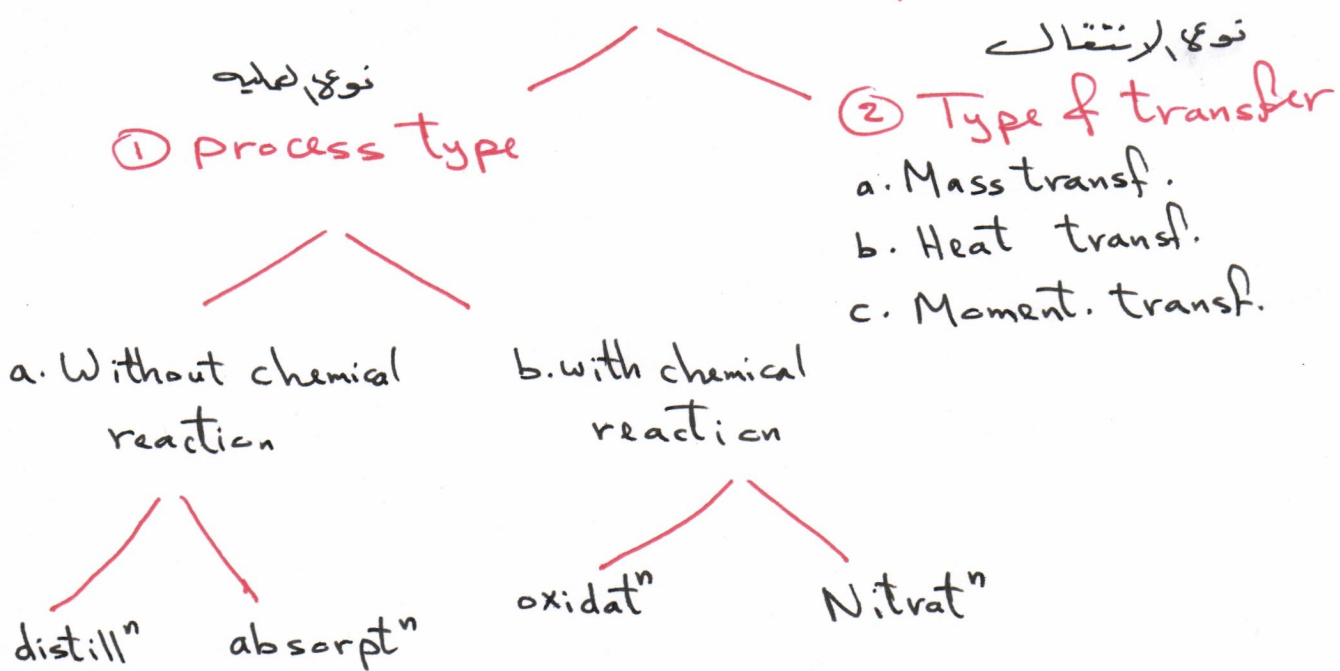
To do the above purposes, the chemical engineer need to know well about :-

1. Stoichiometry
2. Thermodynamics
3. Kinetic
4. Unit operation
5. Economic

(\*) What is Unit-Operation ?

The physical operation for manufacturing chemicals deals mainly with the transfer and change of materials and Energy principles by physical and physical-chemical means, such as :-  
Mass, heat and momentum transfer.

# - Classification of Unit-operation -



## \* Mass-Transfer and Diffusion.

When mass is being transferred from one distinct phase to another or through a single phase, the basic mechanism are the same wheather the phase is gas, liquid or Solid.

$$\text{Rate of transfer process} = \frac{\text{driving force}}{\text{resistance}}$$

i.e.  $\psi = -D \cdot \frac{dx}{dy}$

$$\therefore \psi = N_A = -D_{AB} \cdot \frac{dC_A}{dz}$$

$$\psi = q = -K \cdot \frac{dT}{dz}$$

$$\psi = \tau = -\mu \cdot \frac{du}{dz}$$

Mass Transfer

Fick's Law

Heat Transfer

Fourier's Law

Moment. Transf.

Newton's Law



## \* Subjects to be Studied are:-

- ① Diffusion
  - Steady
  - Unsteady
  - Binary System
  - Multi component
  - Gas
  - Liq.
  - Solid
- ② Absorption
  - Tray tower
  - Packed tower
  - Dilute solution.
  - Concent solution.
- ③ Distillation
  - Binary system
  - Multi component
  - Ideal
  - Non ideal
- ④ Mechanical separation or Size reduction.
- ⑤ Boundary Layer.



# Diffusion

The transport of molecules from a higher concentration to lower concentration is often called "diffusion".

Diffusion through

- ① Stagnant media called molecular diffusion
- ② Turbulent media called eddy or turbulent diffusion.

Molecular diffusion is important when the medium is stagnant or laminar flow flowing. But does not have a significant role to play if the medium is turbulent except in region very close to the phase boundary.

Example 2- vaporization of a layer of water

على سطح بحر طبقة ماء في الهواء ساكن، وفي الهواء متحرك

## Molecular - Diffusion

Since most of mass transfer operations are based on diffusional phenomena, the study of molecular diffusion is essential for understanding these phenomena.

Molecular diffusion or molecular transport can be defined as the transfer or movement of individual molecule through a fluid by means of the ~~new~~ random individual movement of the molecules.

Since the molecules travel in random path, it is often called (Random-Walk-process).

The rate of molecular diffusion is connected with :-

1. molecular velocity
2. concentration difference (driving or Potential force)

## \* Concentration, Velocity and Flux

① Concentration :- Generally expressed as :-

$$\rho_i = \text{mass - Conc}^n \text{ (kg/m}^3\text{)}.$$

$$\rho = \text{total mass : Conc}^n = \text{density (kg/m}^3\text{)} = \sum \rho_i$$

$$w_i = \rho_i / \rho = \text{mass fraction. } \sum w_i = 1$$

$$C_i = \text{molar. Conc}^n \text{ (kmol/m}^3\text{)}.$$

$$C = \text{Total molar. conc}^n \text{ (kmol/m}^3\text{)} = \sum C_i$$

$$x_i = C_i / C = \text{mole fraction. } \sum x_i = 1$$

We usually denote to :-

$$\text{gas mole fraction by } (y_i) = \rho_i / \rho$$

$$\text{liquid mole fraction by } (x_i) = C_i / C$$

## ② \* Mass average - velocity ( $u$ )

$$u = \frac{1}{\rho} \sum \rho_i u_i \quad \text{for } n\text{-component mixture}$$

## \* Molar - average - velocity ( $U$ )

$$U = \frac{1}{C} \sum C_i u_i$$

$$\begin{cases} v_i = \frac{N_i}{C} & \text{Species} \\ \text{or } v_m = \frac{N_T}{C_T} & \text{mixture} \end{cases}$$

Prove  $[u = U \text{ if the M.wt of all species are equal}]$ .

③ \* Species diffusion velocity relative to molar av. velocity

$$v_{iD} = v_i - v_m \Rightarrow v_i = v_{iD} + v_m$$

③ \* Flux :-

The net rate at which a species in a solution passes through a unit area in unit time. It is expressed in  $\text{kg/m}^2 \cdot \text{s}$  or  $\text{kmol/m}^2 \cdot \text{s}$

Flux  $\begin{cases} \text{mass flux} \\ \text{molar flux} \end{cases}$

④ mass flux

1. relative to a stationary observer  $\Rightarrow n_i = \rho_i u_i$
2. relative to an observer moving with mass avg. velocity  $\Rightarrow i_i = \rho_i (u_i - u)$
3. relative to an observer moving with molar. avg. velocity  $\Rightarrow j_i = \rho_i (u_i - u)$

⑤ Molar flux

1.  $N_i = C_i u_i$
2.  $I_i = C_i (u_i - u)$
3.  $J_i = C_i (u_i - u)$



Example (1):- A gas mixture ( $N_2 = 5\%$ ,  $H_2 = 15\%$ ,

$NH_3 = 76\%$  and  $Ar = 4\%$ ) flows through a pipe 25.4 mm in diameter at 4.05 bar total pressure.

If the velocities of the respective components are

0.03 m/s, 0.035 m/s, 0.03 m/s and 0.02 m/s.

Calculate:- mass. avg, molar avg and vol. avg. velocities of the mixture?

Take Mwt for:-

$N_2 = 28$ ,  $NH_3 = 17$ ,  $Ar = 40$

Solution:-

① to find mass. avg. velocity

$$u = \frac{1}{\rho} (P_1 u_1 + P_2 u_2 + P_3 u_3 + P_4 u_4)$$

$$\therefore P_i = P_i M_i / R.T, \quad P_T = P_T M_T / R.T$$

$$\therefore u = \frac{R.T}{P_T M_T} \left( \frac{P_1 M_1}{R.T} \cdot u_1 + \frac{P_2 M_2}{R.T} \cdot u_2 + \frac{P_3 M_3}{R.T} \cdot u_3 + \frac{P_4 M_4}{R.T} \cdot u_4 \right)$$

$$u = \frac{1}{M_T} \left( \frac{P_1}{P_T} M_1 u_1 + \frac{P_2}{P_T} M_2 u_2 + \frac{P_3}{P_T} M_3 u_3 + \frac{P_4}{P_T} M_4 u_4 \right)$$

$$\therefore P_i / P_T = y_i, \text{ therefore}$$

$$u = \frac{1}{M_T} (y_1 M_1 u_1 + y_2 M_2 u_2 + y_3 M_3 u_3 + y_4 M_4 u_4)$$

$$\therefore M_T = y_1 M_1 + y_2 M_2 + y_3 M_3 + y_4 M_4$$

$$= 0.05 \times 28 + 0.15 \times 2 + 0.76 \times 17 + 0.04 \times 40$$

$$\therefore M_T = 16.22$$

$$z-u = \frac{1}{16.22} [0.05 \times 28 \times 0.03 + 0.15 \times 2 \times 0.03 + 0.76 \times 17 \times 0.03 + 0.04 \times 40 \times 0.02]$$

$$u = 0.029 \text{ m/sec.}$$

② to find molar avg. velocity (U)

$$U = \frac{1}{C_T} [C_1 U_1 + C_2 U_2 + C_3 U_3 + C_4 U_4]$$

$$y_i = x_i = \frac{C_i}{C_T} \text{ for vap. and gas}$$

$$U = 0.05 \times 0.03 + 0.15 \times 0.035 + 0.76 \times 0.03 + 0.04 \times 0.02$$

$$U = 0.0303 \text{ m/sec}$$

③ Vol. avg. velocity = molar avg. velocity  
(for gases)

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H.W :- Show that  $U_m$  can be expressed as:-

$$U_m = x_A V_A + x_B V_B$$

# Fick's Law

The basic law of diffusion called "Fick's Law".

Flux of A in B  $\rightarrow \bar{J}_A \propto \frac{dC_A}{dz} \Rightarrow \bar{J}_A = -D_{AB} \frac{dC_A}{dz}$

where  $D_{AB}$  = diffusion coeff. or diffusivity.

Diffusion is a M.T. process occurs when conc<sup>n</sup> difference between two phases exists. Fick's Law express the molar flux ( $\bar{J}$ ) with respect to an observer moving with the molar avg. velocity. In practice, it is more useful to use expression for ( $N_A$ ) instead of ( $\bar{J}_A$ ).

$$\bar{J}_A = -D_{AB} \cdot \frac{dC_A}{dz} = C_A (u_A - u)$$

$$\begin{aligned} -D_{AB} \frac{dC_A}{dz} &= C_A u_A - C_A \cdot u \\ &= N_A - C_A \cdot \frac{1}{C} (C_A u_A + C_B u_B) \\ &= N_A - \frac{C_A}{C} (N_A + N_B) \end{aligned}$$

$N_A = \underbrace{\frac{C_A}{C} [N_A + N_B]}_{\text{bulk flow}} - \underbrace{D_{AB} \cdot \frac{dC_A}{dz}}_{\text{molecular diffusion}}$



For gas mixture:  $P = C \cdot R \cdot T \Rightarrow C = \frac{P}{RT} \Rightarrow C_A = \frac{P_A}{RT}$

$$dP = RT dC \Rightarrow dC = \frac{dP}{RT} \Rightarrow dC_A = \frac{dP_A}{RT}$$

$$N_A = \frac{P_A / RT}{P_T / RT} [N_A + N_B] - D_{AB} \frac{dP_A}{RT \cdot dz}$$

$\frac{dP_A}{P_T}$   
pressi

To convert  $(N_A)$  in terms of mole fraction  $(y_A)$

$$y_A = \frac{P_A}{P_T} \Rightarrow P_A = y_A P_T \Rightarrow dP_A = P_T dy_A$$

$$\therefore N_A = [N_A + N_B] \cdot y_A - \frac{D_{AB}}{R \cdot T} \cdot P_T \frac{dy_A}{dz}$$

$$\therefore N_A = [N_A + N_B] y_A - C_T D_{AB} \frac{dy_A}{dz}$$

$\frac{dy_A}{dz}$   
mole  
fraction

Note:- All the above equations for component (A) is derived in same way for species (B).

Then the total flux will be :-

$$N_T = N_A + N_B$$

# Diffusion in Gases

The most important cases to be studied are :-

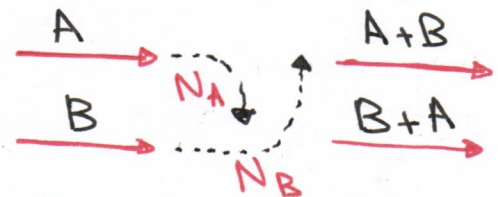
- ① Equimolar - Counter diffusion (EMD).
- ② Diffusion of species (A) through stagnant non-diffusing (B). } No bulk movement
- ③ Diffusion of gas (A) and (B) plus-convection.
- ④ Diffusion through a varying :-
  - (a) Path-length (time dependent).
  - (b) Cross-sectional area.

## ① Equimolar - Counter-diffusion (EMD)

For species (A, B), both diffuses at equal rates but in opposite direction.

A real life example for this case is :-

① (partical of carbon burning in air)



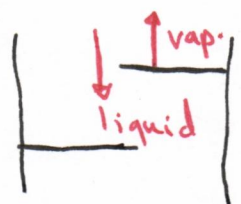
The particle is surrounded by an air-film, through which the molecules of oxygen diffuse and reach the surface of the particle to sustain combustion.

If  $[O_2]$  molecule diffuses to the surface, a molecule of  $CO_2$  is formed which diffuses out through the air-film.

So  $(O_2 \text{ and } CO_2)$  undergo (EMD).



② vapour rising in the distillation column remain in contact with the down-flowing liquid



$$N_A = -N_B$$

$$\therefore N_A = \frac{P_A}{P_T} [N_A + N_B] - \frac{D_{AB}}{RT} \frac{dP_A}{dz}$$

for stationary bulk flow

$$\therefore N_A = -D_{AB} / RT \frac{dP_A}{dz}$$

$$N_A \cdot dz = \frac{-D_{AB}}{RT} dP_A$$

by integration =

$$N_A = \frac{D_{AB}}{RT} \cdot \frac{P_{A1} - P_{A2}}{z}$$

for EMD

\* In this case, total pressure ( $P_T$ ) must be constant, therefore the net moles of (A) diffusing to the right must equal moles of (B) diffusing to the left.

$$* N_A = -N_B$$

$$\therefore -D_{AB} \frac{dC_A}{dz} = +D_{BA} \frac{dC_B}{dz}$$

$$C_T = C_A + C_B \Rightarrow dC_A + dC_B = dC_T = 0$$

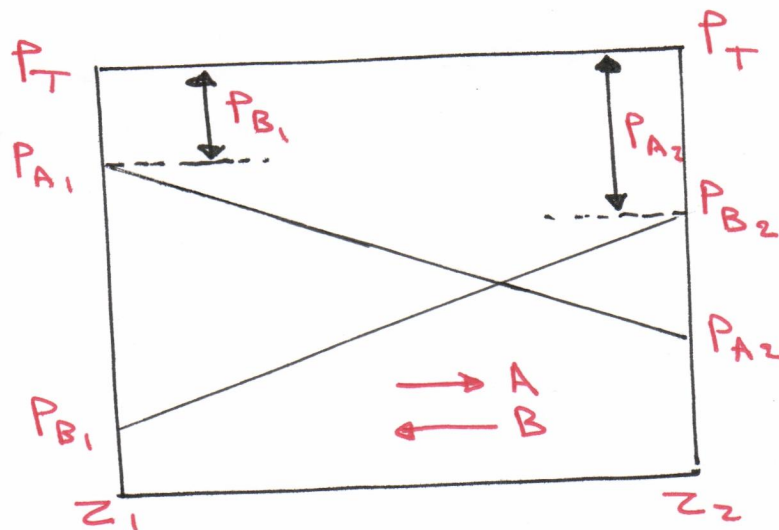
$$\therefore -dC_A = +dC_B$$

$$\therefore D_{AB} = D_{BA} = D$$

∴ for binary gas mixture the diffusivity of both (A) and (B) are the same.

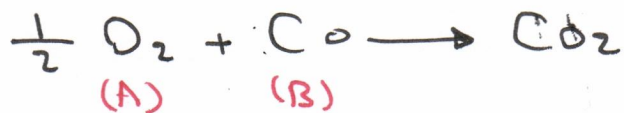


The distribution of the partial pressure of (A) and (B) along the diffusion path in this case are linear.



(\*) For a Non-equimolar-counter diffusion (NEMD)

Producing  $(CO_2)$  from  $(O_2)$  and hot-char-particle



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

$$N_A = (N_A + N_B) \cdot \frac{P_A}{P_T} + (-D_{AB}) \frac{dP_A}{dz}$$

Now substitute  $N_B = 2N_A$  and then integrate.

**Example (1) :-** A uniform tube (0.1) m long and (0.01 m di), containing  $N_2$  gas, Ammonia gas (A) diffusing through the pipe. At point (1),  $P_{A1} = 1.013 \times 10^4$  pas, and at point (2)  $P_{A2} = 0.507 \times 10^4$  pas. The total pressure is  $1.013 \times 10^5$  pas and the diffusivity  $D_{AB} = 0.23 \times 10^{-4} \text{ cm}^2/\text{sec}$ . Calculate :-  
 1- Fluxes of (A) and (B), at Temp = 298 K.  
 2- The rate of M.T for species (A) and (B).

**Solution :-**

1- Closed system with constant pressure and Temp., then the diffusion flow is EMD :-

$$\therefore N_A = \frac{D_{AB}}{RT} \cdot \frac{P_{A1} - P_{A2}}{Z_2 - Z_1}$$

$$= \frac{0.23 \times 10^{-4}}{8.314 \times 298} \cdot \frac{1.013 \times 10^4 - 0.507 \times 10^4}{0.1 - 0.0}$$

$$N_A = 4.7 \times 10^{-7} \text{ kgmol/m}^2 \cdot \text{Sec}$$

For species (B),  $P_{B2} = P_T - P_{A2}$ ,  $P_{B1} = P_T - P_{A1}$

$$\text{or } N_B = -4.7 \times 10^{-7} \text{ kgmol/m}^2 \cdot \text{Sec}.$$

2- mass transfer rate ( $n_A$ )

$$\therefore N_A = \frac{n_A}{\text{Area}} \Rightarrow n_A = N_A \times A$$

$$A = \frac{\pi}{4} d_i^2 \Rightarrow \frac{\pi}{4} (0.01)^2 \Rightarrow 7.8 \times 10^{-5} \text{ m}^2$$

$$\therefore n_A = 4.7 \times 10^{-7} \times 7.8 \times 10^{-5}$$

$$\therefore n_A = 36.66 \times 10^{-12} \frac{\text{kgmol}}{\text{Sec}}$$

$$\therefore n_B = -36.66 \times 10^{-12} \frac{\text{kgmol}}{\text{Sec}}$$

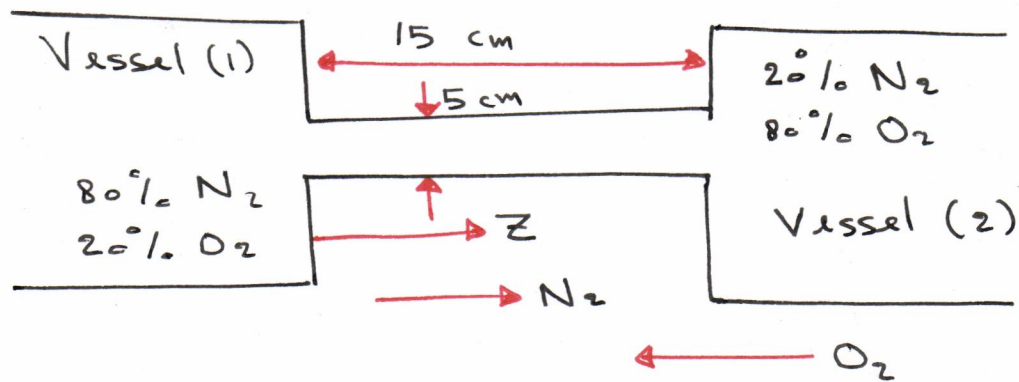
3- Try to calculate ( $U_A, U_B$ )

$$U_A = \frac{N_A}{C_A} \quad \& \quad C_A = \frac{P_A}{RT}$$

**Example (2) :-** Two large vessels are connected as shown in Figure. Vessel (1) contains 80%  $N_2$  (A) and 20%  $O_2$  (B), Vessel (2) contains 20%  $N_2$  and 80%  $O_2$ . The temp. ( $20^\circ C$ ) and the total pressure (2 atm). Calculate :-

- ① The flux and rate of transport of  $N_2$  from vessel 1 to 2, and same for  $O_2$ .
- ② The partial pressure of  $N_2$  and its gradient in the tube (0.05 m) from vessel (1). ( $dP_A/dz$ ).
- ③ The net mass flux ( $n_T$ ).

Given that diffusivity of  $N_2-O_2$  pair is  $1.01 \times 10^{-5} m^2/s$  at  $20^\circ C$  and 2 atm.



**Solution :-**

$$\textcircled{1} N_A = \frac{+D_{AB}}{RT} \frac{P_{A1} - P_{A2}}{z_2 - z_1}$$

$$D_{AB} = 1.01 \times 10^{-5} (m^2/s), R = 0.0821, T = 293 K$$

$$z = z_2 - z_1 = 0.15 m, \text{ To find } P_{A1}, P_{A2}$$

$$P_{A1} = y_{A1} \cdot P_T$$

$$= 0.8 \times 2$$

$$= 1.6 \text{ atm}$$

$$P_{A1} = 1.62 \times 10^5 \frac{N}{m^2}$$

$$P_{A2} = y_{A2} \cdot P_T$$

$$= 0.2 \times 2$$

$$= 0.4 \text{ atm}$$

$$P_{A2} = 0.406 \times 10^5 \frac{N}{m^2}$$



$$\therefore N_A = 3.3 \times 10^{-6} \text{ kmol/m}^2 \cdot \text{Sec.}$$

$$\text{rate of transport} = n_A = N_A \cdot \text{Area} \leftarrow \frac{\pi}{4} d_i^2 \leftarrow \frac{\pi}{4} (0.05)^2$$

$$= n_A = 6.6 \times 10^{-9} \text{ kmol/Sec.}$$

$$N_B = -N_A = -3.36 \times 10^{-6} \text{ kmol/m}^2 \cdot \text{s}$$

$$n_A = -n_B = -6.6 \times 10^{-9} \text{ kmol/Sec.}$$

② Partial press. changes linearly with diffusion Path.

$$\therefore \frac{dP}{dz} = \frac{P_{A2} - P_{A1}}{z} = \frac{(0.4 - 1.6)}{0.15} = -8 \text{ atm/m}$$

at point 0.05

$$P_A = P_T + \left[ \frac{dP_A}{dz} \right] \cdot \Delta z \quad \text{قانون هينري}$$

$$= 1.6 + (-8) \cdot 0.05$$

$$P_A \frac{dP}{dz} = 1.2 \text{ atm.}$$

$$\textcircled{3} n_T = N_A \cdot M_{wtA} + N_B M_{wtB}$$

$$= (3.36 \times 10^{-6} \times 28) - (3.36 \times 10^{-6} \times 32)$$

$$n_T = -1.344 \times 10^{-5} \text{ kmol/m}^2 \cdot \text{s}$$

## ② Diffusion of (A) through non-diffusing (B)

In this case one boundary at the end of the diffusion path is impermeable to other species, so it can not pass through.

A real life example: Dry air in sulphuric acid plant.

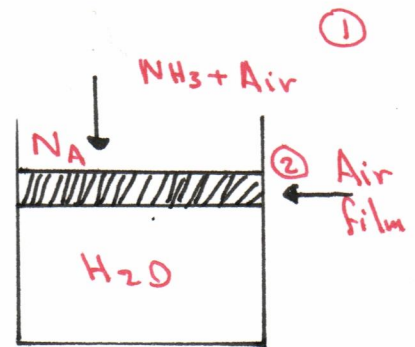
تحتاج الهواء الجاف لفصل هرق الكبريت في مصنع إنتاج حامض  $H_2SO_4$   
لذلك يمر الهواء الرطب على حامض كبريتيك مركز في زجاج محشوة، الرطوبة  
تنتقل خلال طبقة من الهواء وتصل إلى سطح الحامض وبعد هذا تمتص.  
لكن الهواء لا يزيد في الحامض وبالتالي لا يستطيع التناثر.

∴ moisture ( $H_2O$ ) has 
↗ Source (bulk of air)  
↘ Sink (the acid)

but (dry air) has (Source) but no (Sink).

- Another example ( $NH_3$  in Air) removal.

$NH_3$  diffuses easily across air film to water, but (Air) is insoluble.



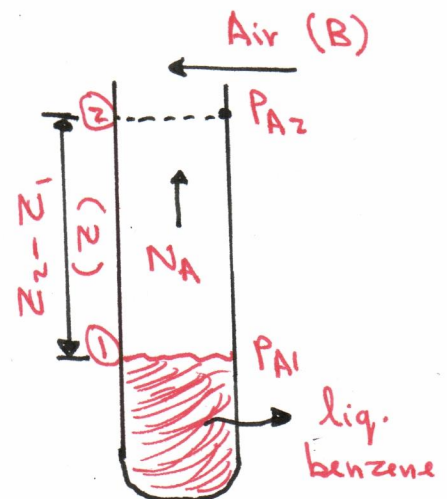
$$\therefore N_A = (N_A + N_B) \frac{P_A}{P_T} - \frac{D_{AB}}{RT} \frac{dP_A}{dz}$$

$$\therefore N_B = 0$$

$$\therefore N_A = N_A \frac{P_A}{P_T} - \frac{D_{AB}}{RT} \frac{dP_A}{dz}$$

$$\therefore N_A * dz = - \frac{D_{AB} P_T}{RT (P_T - P_A)} dP_A$$

integrating over  $z = 0, P_A = P_{A1}$   
and  $z = L, P_A = P_{A2}$



$$N_A = \frac{D_{AB} P_T}{RTZ} \ln \frac{\overbrace{P_T - P_{A2}}^{P_{B2}}}{\underbrace{P_T - P_{A1}}_{P_{B1}}}$$

It is more convenient to use [Log mean partial pressure]

$$N_A = \frac{D_{AB} P_T}{RTZ} \cdot \frac{P_{A1} - P_{A2}}{P_{BM}}$$

For  $N_B = 0$

$$\text{where } P_{BM} = \frac{P_{B2} - P_{B1}}{\ln \frac{P_{B2}}{P_{B1}}}$$

This equation expresses the flux in terms of driving force of species (A),  $(P_{A1} - P_{A2})$ .

We also can calculate the partial pressure ( $P_A$ ) of (A) at any intermediate point and the distribution of the partial pressure of (A) along the diffusion path, by using:-

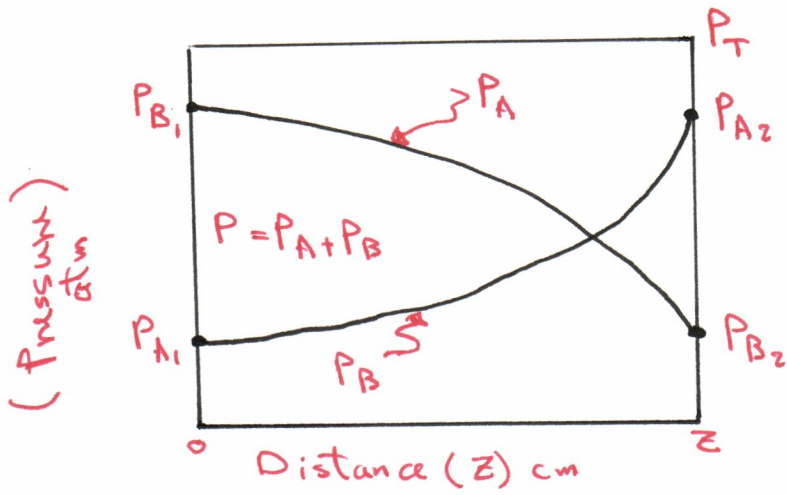
$$N_A = \frac{D_{AB} P_T}{RTZ} \ln \frac{P_T - P_A}{P_T - P_{A1}}$$

H.W 3 Try To Find

$$N_A = \frac{C_T D_{AB}}{Z_2 - Z_1} \cdot \frac{X_{A1} - X_{A2}}{X_{BM}}$$



Typical distribution of the partial pressure of the components along the diffusion path



هنا عندنا (A) ينفذ من  $Z=0$  الى  $Z=L$   
 كذلك (B) ينفذ من  $Z=0$  الى  $Z=L$   
 أي له  $\text{Press. gradient}$   
 ولكن نخت عندنا  $N_B = 0$   
 أي  $\text{flux} = 0$  مثال =

سوف تسبب بسرعة باتجاه معاكس لجريان الماء. فالذي نراه، انه لسوف  
 لا تتحرك تقريباً في الماء، ولكن في الحقيقة اننا لمحركه، ولكن  
 حركة الماء المعاكس تجمت سرعة لسوف وبالتالي نعتبر  
 $\text{flux}$  لها = صفر.

Example (3) :- Water in the bottom of a narrow metal tube, is held at a constant temp. of (293 K). The total pressure of dry air is  $1.0132 \times 10^5$  Pa. and Temp. = 293 K. Water evaporates and diffuses through the air, the diffusion path (0.15 m) long.

Calculate the rate of evaporation at steady state in  $\text{kmol/m}^2 \cdot \text{s}$ , given that  $D_{AB} = 0.25 \times 10^{-4} \text{ m}^2/\text{s}$ . and water-vap. press at  $20^\circ\text{C} = 17.54 \text{ mm Hg}$ .

Sol. :-

$$N_A = \frac{D_{AB} P_T}{RT} \cdot \frac{1}{Z_2 - Z_1} \frac{P_{A1} - P_{A2}}{P_{BM}}$$

$$P_{A1} = 17.54 \text{ mm Hg} = 0.0234 \text{ atm}$$

$$P_{A2} = \text{Zero (pure air and large bulk volume)}$$

$$P_{B1} = P_T - P_{A1} = 1 - 0.0231 \Rightarrow P_{B1} = 0.977 \text{ atm}$$

$$P_{B2} = P_T - P_{A2} = 1 - 0 \Rightarrow P_{B2} = 1.0 \text{ atm}$$

$$\therefore P_{B1} \approx P_{B2} \quad \therefore (P_{BM}) \text{ could be taken as the mean.}$$

$$P_{BM} = \frac{P_{B1} + P_{B2}}{2} = \frac{0.977 + 1}{2} = 0.9885 \text{ atm}$$

$$N_A = \frac{0.25 \times 10^{-4} \times 1.0132 \times 10^5}{8.312 \times 293} \cdot \frac{1}{0.15} \cdot \frac{0.0234}{0.9885}$$

$$N_A = 0.164 \times 10^{-3} \text{ kmol/m}^2 \cdot \text{s}$$

Example (4) :- Ammonia (A) diffuses through a stagnant layer of air (B) 1 cm thick at  $25^\circ\text{C}$  and 1 atm total press. The partial press. of (A) on the two sides of the air layer are  $P_{A_0} = 0.9 \text{ atm}$  and  $P_{A_1} = 0.1 \text{ atm}$ . Air is non diffusing.

Calculate :-

- The molar flux of  $\text{NH}_3$ .
- molar and mass-average velocity for each species.
- Plot the partial press. distribution of  $\text{NH}_3$  and air along the diffusion path.

Given :  $D_{AB} = 0.214 \frac{\text{cm}^2}{\text{sec}}$ ,  $R = 82.1 \frac{\text{cm}^3 \cdot \text{atm}}{\text{gmol} \cdot \text{K}}$

Sol. :- For stagnant layer of air (B),  $N_B = 0$

$$\textcircled{a} N_A = \frac{D_{AB} \cdot P_T}{R \cdot T} \cdot \frac{1}{\Delta z} \ln \frac{P_T - P_{A_1}}{P_T - P_{A_0}}$$

$$\therefore \Delta z = z_2 - z_1 = 1 \text{ cm}$$

$$= \frac{(0.214)(1)}{(82.1)(298)(1.0)} \ln \frac{1 - 0.1}{1 - 0.9}$$

$$N_A = 1.922 \times 10^{-5} \text{ gmol/cm}^2 \cdot \text{s}$$

$$\textcircled{b} N_T = U_m \cdot C_T \Rightarrow U_m = \frac{N_T}{C_T} \Rightarrow \frac{N_A + \cancel{N_B}}{C_T}$$

$$\therefore U_m = \frac{N_A}{C_T} = \frac{N_A}{P_T / RT}$$



$$U_m = \frac{1.922 \times 10^{-5}}{1.0} = 0.47 \text{ cm/sec (molar Avg. velo.)}$$

$$(82.1)(298)$$

$$N_A = U_A \cdot C_A \Rightarrow U_A = \frac{N_A}{C_A} = \frac{U_m C_T}{C_A} = \frac{U_m}{y_A}$$

$(C_A)$  varies along diffusion path

$\therefore U_A$  also varies.

$$y_A = \frac{P_A}{P_T} = \frac{0.9}{1.0} = 0.9$$

$$U_{A0} = \frac{0.47}{0.9} = 0.52 \text{ cm/s.}$$

$U_B = 0$  stationary (B)

$$\therefore \text{mass avg. velocity } (U) = \frac{U_A P_A + U_B P_B}{P_T}$$

$$U = \frac{U_A P_A}{P_T}$$

$$\therefore P_A = \frac{P_A M_{wt}(A)}{R \cdot T}, \quad P_T = \frac{P_T \cdot M_{wt}}{R \cdot T}$$

$$U = \frac{U_A \cdot P_A \cdot M_{wt}(A) / \cancel{RT}}{P_T \cdot M_{wt} / \cancel{RT}} \Rightarrow \frac{U_A \cdot \hat{P}_A \cdot (M_{wt}(A))}{(\hat{P}_T) (M_{wt}(\text{total}))}$$

$$U = \frac{U_A \cdot y_A \cdot M_{wt}(A)}{M_{wt}(\text{total})}$$

$$\begin{aligned}
 M_{wt}(\text{total}) &= M_{wt}(A) \cdot y_A + M_{wt}(B) \cdot y_B \\
 &= 17 * 0.9 + 29 * 0.1 \\
 &= 18.2
 \end{aligned}$$

$$\therefore U = \frac{(0.52)(0.9)(17)}{18.2} = 0.439 \text{ cm/Sec.}$$

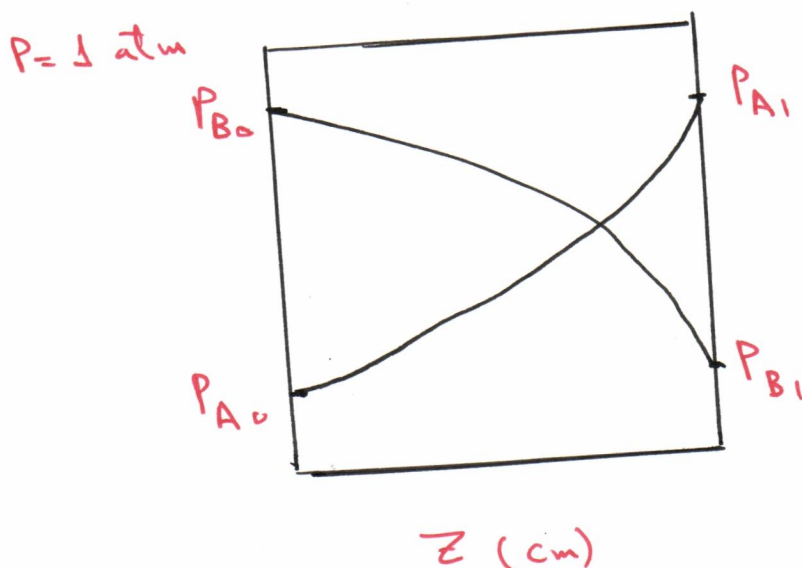
(C) To plot partial press. distrib<sup>n</sup>:-

$$N_A = 1.922 * 10^{-5} \frac{\text{gmol}}{\text{cm}^2 \cdot \text{Sec}} = \frac{(0.214)(1.0)}{(82.1)(298)} \cdot \frac{1}{Z} \ln \frac{1-P_A}{1-0.9}$$

rearrange above equ<sup>n</sup>. to get:-

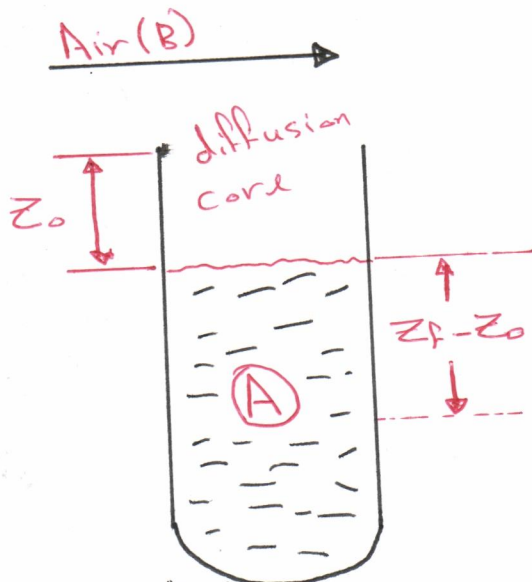
$$P_A = 1 - (0.1) \exp(2.197 \cdot Z) \quad \text{for species(A)}$$

$$P_B = (P_T - P_A) \quad \text{for species(B)}$$



④ Diffusion through a varying path length.

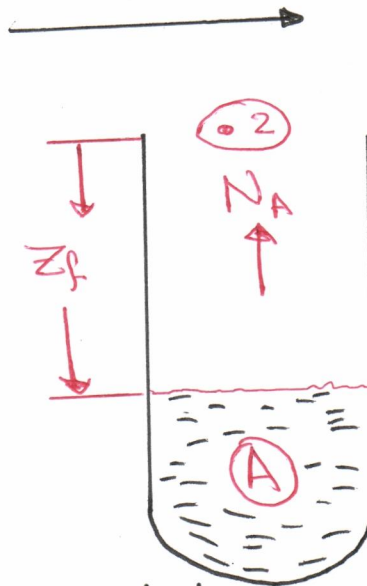
① Usually used to determine the time required to drop the level to liquid to a certain height.



at  $t=0$

A = Acetone

B = Air



at  $t=t_f$

② At the surface,  $P_{A1} = P_A^0$

$$X_{A1} = P_A^0 / P_T$$

③ At point (2),  $P_{A2} = 0$

لأنه كسالة سطح، سطح، سطح  
 ① هي فقط، نافذة، نافذة  
 ② لا تنفذ، لذلك يبقى تركيز  
 ③ هو 1، سطح، سطح  
 Binary

$[C_A]$  remain constant always.

For stationary non-diffusing (B) :-  $N_B = 0$

$$N_A = \frac{-D_{AB}}{RT} \cdot \frac{P_T}{P_{BM}} \cdot \frac{P_{A2} - P_{A1}}{z_2 - z_1}$$

∴ we can find (time) from ( $N_A$ )

$$N_A = u_A \cdot C_A \Rightarrow N_A = \frac{dz}{dt} \cdot \frac{\rho_A}{M_A}$$



Sub. For  $(N_A)$ :-

$$\frac{dz}{dt} \frac{P_A}{M_A} = \frac{-D_{AB}}{RT} \cdot \frac{P_T}{P_{BM}} \cdot \frac{P_{A2} - P_{A1}}{z}$$

put  $z_2 - z_1 = z$

separating variables, then solve equation above:-

$$t = \frac{P_A}{M_A} \left[ \frac{RT}{D_{AB}} \cdot \frac{P_{BM}}{P_T (P_{A1} - P_{A2})} \right] \int_{z_0}^{z_f} z \cdot dz$$

↳ Used to determine the time required to drop the level to a certain height.

H.W. (4) :- Find the equation to measure time required to drop level of liquid to certain height, where  $(N_A = -N_B)$ . (EMD).

#### ④ Diffusion through a varying cross-sectional area

③ All cases previously mentioned,  $(N_A)$  was assumed almost constant, because area of diffusion is constant. Now for a varying cross-sectional area, then we get:-

$$N_A = \frac{\bar{N}_A}{A} \quad \text{where } (\bar{N}_A) \text{ is constant at steady state} \\ (N_A) \text{ is not constant}$$

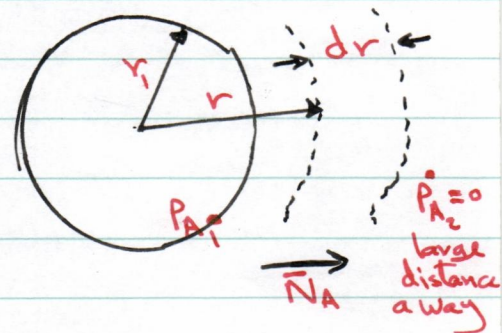
To study this case, two examples will be taken.

- 1 - Diffusion from a sphere material.
- 2 - Diffusion in conical vessel.

① Species (A) diffusing through stagnant (B)

$$N_A = \frac{\bar{N}_A}{A} = \frac{\bar{N}_A}{4\pi r^2}$$

$$\therefore N_A = N_A \frac{P_A}{P_T} - \frac{D_{AB}}{RT} \frac{dP_A}{dz}$$



$$N_A \left(1 - \frac{P_A}{P_T}\right) = -\frac{D_{AB}}{RT} \frac{dP_A}{dz} \Rightarrow N_A = \frac{-D_{AB}}{RT} \frac{dP_A}{\left(1 - \frac{P_A}{P_T}\right) dz}$$

$$\frac{\bar{N}_A}{4\pi r^2} = \frac{-D_{AB}}{RT} \frac{dP_A}{\left(1 - \frac{P_A}{P_T}\right) dr} \Rightarrow \text{Arrange and solve}$$

$$\frac{\bar{N}_A}{4\pi} \left[ \frac{1}{r_1} - \frac{1}{r_2} \right] = \frac{D_{AB}}{RT} P_T \ln \frac{P_T - P_{A2}}{P_T - P_{A1}} \dots (*)$$

↳ used to find  $P_{A2}$  for certain  $r_2$



1 - For  $r_2 \gg r_1 \Rightarrow \frac{1}{r_2} \approx 0$

and dividing by  $r_1$ , then:-

$$\frac{\bar{N}_A}{4\pi r_1^2} = N_{A,1} = \frac{D_{AB}}{R.T. \cdot r_1} P_T \frac{P_{A1} - P_{A2}}{P_{BM}}$$

General form  
for sphere only

2 - For  $P_{A1} \ll P_T$  then  $P_{BM} = P_1$  (dilute solution)

$$\frac{\bar{N}_A}{4\pi r_1^2} = \frac{D_{AB}}{R.T. \cdot r_1} \cancel{P_T} \frac{P_{A1} - P_{A2}}{\cancel{P_T}}$$

and  $D_1 = 2r_1$ , then:-

$$\bar{N}_A = 2\pi \cdot D_1 \cdot D_{AB} (C_{A1} - C_{A2})$$

$$\therefore N_A = \frac{2 D_{AB}}{D_1} (C_{A1} - C_{A2})$$

Can be used for  
gas and liquids

$$N_{A,1} = \frac{D_{AB}}{R.T. \cdot r_1} (P_{A1} - P_{A2}) \quad \text{Gases}$$

$$N_{A,1} = \frac{D_{AB}}{r_1} (C_{A1} - C_{A2}) \quad \text{liquids}$$



Ex(1):- A sphere of Naphthalene having radius of 2.0 mm, is suspended in a large volume of still air at 318°K and  $1.013 \times 10^5$  pas. The surface temp. of the sphere can be assumed to be at 318°K, and vapour pressure is 0.55 mmHg.  $D_{AB}$  for naphthalene in air at 318°K is  $6.92 \times 10^{-6}$  m<sup>2</sup>/sec. Calculate the rate of evaporation of naphthalene at the surface? given that  $R = 8314$  m<sup>3</sup>.Pa / Kmol. K.

$$\underline{\underline{Sol.}} \quad N_{A_1} = \frac{D_{AB}}{R \cdot T \cdot r_1} \cdot P_T \frac{P_{A_1} - P_{A_2}}{P_{BM}}$$

$$P_{A_1} = \frac{0.55 \text{ mmHg}}{760} \times 1.0132 \times 10^5 = 73.32 \text{ Pas.}$$

$$\text{Since } P_{A_1} \ll P_T \quad \therefore P_{BM} = P_T$$

$$N_{A_1} = \frac{D_{AB}}{R \cdot T \cdot r_1} P_{A_1} \quad \text{where } P_{A_2} = 0 \text{ [large distance]}$$

$$N_{A_1} = \frac{6.92 \times 10^{-6} \times 73.32}{8314 \times 318 \times 2 \times 10^{-3}} = \frac{507.37 \times 10^{-6}}{5287.7}$$

$$N_{A_1} = 9.6 \times 10^{-8} \text{ Kgmol / m}^2 \cdot \text{Sec.}$$

Note:- if it was required to find the partial pressure after a certain distance, then we can use eq. (\*) to find ( $P_{A_2}$ ) at ( $r_2$ )

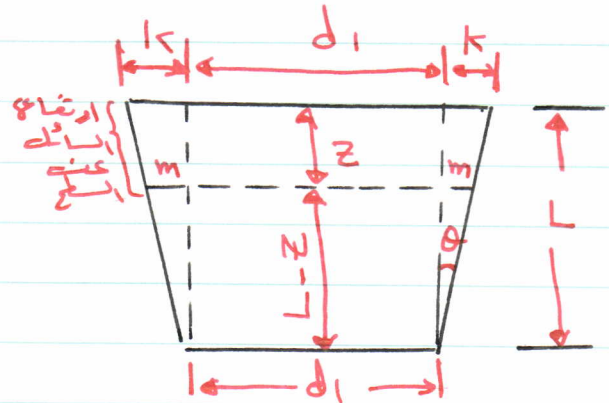
$$\frac{\bar{N}_A}{4\pi} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) = \frac{D_{AB}}{R \cdot T} P_T \ln \frac{P_T - P_{A_2}}{P_T - P_{A_1}}$$

## ② Diffusion in Conical vessel

For non-diffusing gas (B)  
we have find :-

$$N_A = x_A N_A - C_T D_{AB} \frac{dx_A}{dz}$$

$$N_A = \frac{-D_{AB}}{R \cdot T} \frac{P_T}{P_T - P_A} \cdot \frac{dP_A}{dz}$$



$$(N_A) = \frac{-D_{AB}}{R \cdot T} \frac{P_T}{P_T - P_A} \frac{dP_A}{dz}$$

( $N_A$ ) now is not constant, but varies with ( $z$ ), then we have to find a relation between them

$$\therefore N_A = \frac{\bar{N}_A}{A} \Rightarrow \frac{\bar{N}_A}{A} = \frac{-D_{AB}}{R \cdot T} \frac{P_T}{P_T - P_A} \frac{dP_A}{dz}$$

$$\bar{N}_A \int_{z_1}^{z_2} \frac{dP_A}{A} = \frac{-D_{AB} \cdot P_T}{R \cdot T} \int_{P_{A1}}^{P_{A2}} \frac{dP_A}{P_T - P_A}$$

$$\therefore A = \frac{\pi}{4} d^2 \quad (\text{a relation between } (z) \text{ and } (d))$$

$$\tan \theta = \frac{k}{L} = \frac{m}{L - z} \quad \therefore m = \frac{k(L - z)}{L}$$

Total diameter at height ( $z$ ) =  $d$

$$d = d_1 + 2m \rightarrow \text{نصف قطر القاعدة} + 2 \times \text{نصف قطر المقطع عند الارتفاع } z$$

$$d = d_1 + \frac{2k(L - z)}{L}$$

$$\therefore \bar{N}_A \int_{z_1}^{z_2} \frac{dz}{\frac{\pi}{4} \left( d_1 + \frac{2K(L-z)}{L} \right)^2} = \frac{-D_{AB} \cdot P_T}{R \cdot T} \int_{P_{A1}}^{P_{A2}} \frac{dP_A}{P_T - P_A}$$

Ex. (2) :- An open conical vessel is filled with water up to 0.5 cm from top. Calculate the time required to drop level by (1 cm), given that  $D_{AB} = 0.256 \text{ cm}^2/\text{s}$ , at 1 atm and  $25^\circ\text{C}$ . The vapor pressure of water at  $25^\circ\text{C}$  is 0.0313 atm. Figures shown below

Sol. :-

$$\bar{N}_A \int_{z_1}^{z_2} \frac{dz}{A} = \frac{-D_{AB} \cdot P_T}{R \cdot T} \int_{P_{A1}}^{P_{A2}} \frac{dP_A}{P_T - P_A}$$

we must find relation between (d) and (z)

$$\tan \theta = \frac{1}{\sqrt{3}} = \frac{1 \text{ cm}}{L} = \frac{r}{L-z}$$

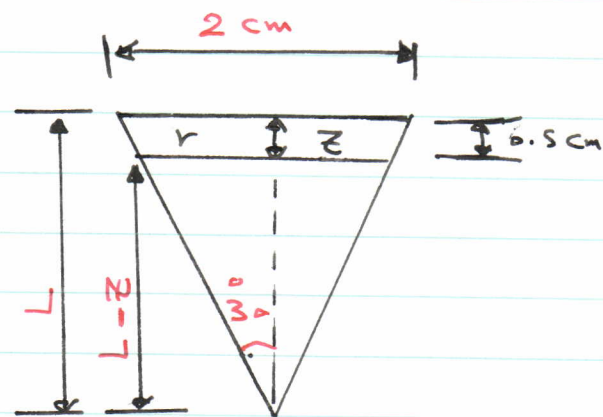
$$\therefore L = \sqrt{3}$$

$$\frac{1}{\sqrt{3}} = \frac{r}{\sqrt{3} - z}$$

$$\therefore r = \frac{\sqrt{3} - z}{\sqrt{3}}$$

$$d = 2r$$

$$d = \frac{2(\sqrt{3} - z)}{\sqrt{3}}$$





$$\therefore A = \frac{\pi}{4} d^2 \Rightarrow A = \frac{\pi}{4} \left[ \frac{2(\sqrt{3} - z)}{\sqrt{3}} \right]^2$$

$$\therefore A = \frac{\pi}{3} (\sqrt{3} - z)^2 \text{ used to solve for } (t)$$

Solving  $(\bar{N}_A)$  equation after substitution (A) and  $P_{A2} = 0$ ,  $(\bar{N}_A)$  can be found:-

$$\bar{N}_A \int_{z_1}^{z_2} \frac{dz}{\frac{\pi}{3} (\sqrt{3} - z)^2} = \frac{-D_{AB} P_T}{R \cdot T} \ln \frac{P_T - P_{A2}}{P_T - P_{A1}}$$

$$\therefore \bar{N}_A = 4.41 \times 10^{-5} \text{ kmol/sec.}$$

Note:- To find the time required to drop the level to a certain new level.

$$N_A = \frac{\bar{N}_A}{A} = v_A \cdot C_A = \frac{dz}{dt} \cdot \frac{P_A}{M_A}$$

$$\bar{N}_A \int_0^t dt = \frac{P_A}{M_A} \int_{z_0}^{z_F} A \cdot dz$$

$$t = \frac{1}{\bar{N}_A} \cdot \frac{P_A}{M_A} \cdot \int_{z_0}^{z_F} \frac{\pi}{3} (\sqrt{3} - z)^2 dz$$

$$= \frac{\pi}{3 \bar{N}_A} \cdot \frac{P_A}{M_A} \int_{z_0}^{z_F} (3 - 2\sqrt{3}z + z^2) dz$$

$$t = \frac{\pi}{3 \bar{N}_A} \frac{P_A}{M_A} \left[ 3z - \sqrt{3} z^2 + \frac{z^3}{3} \right]_{0.5}^{10.5}$$

$$\therefore t =$$

## Diffusivity in gases and vapours

Two kinds of diffusivities can be computed.

- ① Kinematic diffusivity ( $D_{AB}$ ).
- ② Dynamic diffusivity ( $\delta_{AB}$ ).

( $D_{AB}$ ) is mainly proportional to [Temp. and press.]

① Kinematic diffusivity  $\therefore (D_{AB})$ .

Ⓐ Gilliland diffusivity equation.

$$D_{AB} = \frac{b \cdot T^{3/2}}{P_T [\nu_A^{1/3} + \nu_B^{1/3}]^2} \cdot \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad \text{Lil}$$

$D_{AB}$  = diffusivity  $\text{m}^2/\text{sec}$ .

$b$  = constant = 0.0043

$P_T$  = Total system pressure (Pa), ( $\text{N/m}^2$ )

$T$  = Temp. in ( $^{\circ}\text{K}$ ).

$\nu_A, \nu_B$  = molar volume of (A and B) at normal boiling point ( $\text{cm}^3/\text{gmol}$ ).

$M_A, M_B$  = molecular weight.

Ⓑ Andrussov equation.

$$D_{AB} = \frac{b \cdot T^{1.78} (1 + \sqrt{M_A + M_B})}{P_T (\nu_A^{1/3} + \nu_B^{1/3}) \cdot \sqrt{M_A + M_B}}$$

$$b = 7.98 \times 10^{-4}$$

## ① Fuller-equation

$$D_{AB} = \frac{B \cdot (T)^{1.75}}{P_T \sqrt{M_{AB}} (\sum v_A^{1/3} + \sum v_B^{1/3})^2}$$

where:-

$$M_{AB} = \frac{1}{(1/M_A + 1/M_B)}, \quad B = 1 \times 10^{-7}$$

$\sum v_A$  = summation of the atomic and structural diffusion volumes

ex.  $C_6H_6 \Rightarrow 6 \times C + 6 \times H + \text{aromatic ring.}$

but for non-cyclic :- No. of atoms  $\times$  activity  
+ Hetro-cyclic ring.

## ② Dynamic diffusivity ( $S_{AB}$ ).

where  $S_{AB} = D_{AB} \cdot C = D_{AB} / v_m$

$$S_{AB} = \frac{b \cdot T^{3/2}}{v_m \cdot P_T (\sum v_A^{1/3} + \sum v_B^{1/3})^2} \cdot \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

for ideal gas  $v_m \times P_T = R \cdot T$ ,  $b = 0.0043$

$$S_{AB} = \frac{b \cdot T^{1/2}}{R (\sum v_A^{1/3} + \sum v_B^{1/3})^2} \cdot \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$



Now to correct  $(D_{AB})$  or  $(S_{AB})$  at different conditions

$$\frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{1.5} \cdot \frac{P_2}{P_1}$$

$$\text{or } \frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{1.75} \frac{P_2}{P_1}$$

$$\text{and } (S_{AB})_T = (S_{AB})_{\text{Ref.}} \cdot \sqrt{\frac{T}{T_{\text{ref}}}}$$

Ex(1) :- Normal Butanol (A) is diff using through air (B) at (1 atm). Estimate the diffusivity  $(D_{AB})$  for the following conditions :-  
a - For  $0^\circ\text{C}$ , b -  $25.9^\circ\text{C}$ , c -  $0^\circ\text{C}$  and 2 atm.

Sol. :- (a) Take  $M_A = 74.1$ ,  $M_B = 29$   
From Table (8.3) Perry) and using ① Fuller-equation  
 $P = 1 \text{ atm}$ ,  $T = 273 \text{ K}$

$$\nu_C = 16.5, \nu_{H_2} = 1.98, \nu_{O_2} = 5.48$$

$$\sum \nu_A = 4(16.5) + 1(1.98) + 1(5.48)$$

$$= 91.28$$

$$\sum \nu_B = 20.1$$

$$D_{AB} = \frac{1.0 \times 10^{-7} (273)^{1.75}}{1.0 \left[ (91.28)^{1/3} + (20.1)^{1/3} \right]^2} \cdot \left[ \frac{1}{74.1} + \frac{1}{29} \right]^{0.5}$$

$$D_{AB} = 7.73 \times 10^{-6} \text{ m}^2/\text{sec}$$

② Using Gilliland corr.

$$D_{AB} = 7.078 \times 10^{-6} \text{ m}^2/\text{sec}.$$

⑥ For  $T = 25.9 = 298.9 \text{ K}$

$$D_{AB} \text{ at } 25.4 = D_{AB} \text{ at } 20^\circ\text{C} \left[ \frac{T_{25.9^\circ\text{C}}}{T_{20^\circ\text{C}}} \right]^{1.75}$$

$$= 7.73 \times 10^{-6} \left( \frac{298.9}{273} \right)^{1.75}$$

$$D_{AB} = 9.07 \times 10^{-6} \text{ m}^2/\text{sec}.$$

⑦ For  $T = 0^\circ\text{C}$  and  $P_2 = (2 \text{ atm})$ .

$$D_{AB} = D_{AB} \left( \frac{P_1}{P_2} \right) = 7.73 \times 10^{-6} \left( \frac{1}{2} \right)$$

$$D_{AB} = 3.87 \times 10^{-6} \text{ m}^2/\text{sec}.$$

## Maxwell's Law of diffusion For Binary System

Maxwell's postulated that the pressure gradient ( $dp_A$ ) in the direction of diffusion for a constituent of two components gaseous mixture was proportional to:

A) The relative velocity of the molecules in the direction of diffusion.

B) The product of the molar concentration of the component.

Thus;

$$-dp_A \propto C_A C_B (v_A - v_B) dz$$

$$-dp_A = \alpha_{AB} C_A C_B (v_A - v_B) dz$$

Where  $v_A$  &  $v_B$  = mean molecule of (A) & (B) respectively.

$C_A$  &  $C_B$  = molar concentration of the component (A) & (B) respectively.

At equilibrium, the partial pressure gradient of the diffusing gas =  $dp_A / dz$ .

$$\frac{-dp_A}{dz} = \alpha_{AB} \left( \frac{\rho_A}{M_A} \right) \left( \frac{\rho_B}{M_B} \right) (v_A - v_B)$$

$$N_A = v_A \cdot C_A \rightarrow N_A = v_A \cdot \left( \frac{\rho_A}{M_A} \right), \quad N_B = v_B \cdot \left( \frac{\rho_B}{M_B} \right)$$

$$v_A = N_A \cdot \frac{M_A}{\rho_A}, \quad v_B = N_B \cdot \frac{M_B}{\rho_B}$$

$$\frac{-dp_A}{dz} = \alpha_{AB} \left( \frac{\rho_A}{M_A} \right) \left( \frac{\rho_B}{M_B} \right) \left( N_A \cdot \frac{M_A}{\rho_A} - N_B \cdot \frac{M_B}{\rho_B} \right)$$

$$\frac{-dp_A}{dz} = \alpha_{AB} \left( N_A \cdot \frac{\rho_B}{M_B} - N_B \cdot \frac{\rho_A}{M_A} \right)$$

For ideal gas law;  $P \cdot V = n \cdot R \cdot T$ ,  $C_A = \frac{P_A}{R \cdot T} = \frac{\rho_A}{M_A}$

$$\frac{-dp_A}{dz} = \alpha_{AB} \left( N_A \cdot \frac{P_B}{R \cdot T} - N_B \cdot \frac{P_A}{R \cdot T} \right)$$

$$\frac{-dp_A}{dz} = \frac{\alpha_{AB}}{R \cdot T} (N_A \cdot P_B - N_B \cdot P_A)$$

$$\frac{-dp_A}{dz} = \frac{\alpha_{AB}}{R \cdot T} (N_A \cdot (P_T - P_A) - N_B \cdot P_A)$$

$$\text{Diffusivity coefficient } (D_{AB}) = \frac{R^2 \cdot T^2}{\alpha_{AB} \cdot P_T}$$



$$\frac{-dp_A}{dz} = \frac{R.T}{D_{AB} P_T} (N_A \cdot P_T - N_A \cdot P_A - N_B \cdot P_A)$$

The above equation is Maxwell-equation.

Where: R=gas constant, T=temperature in °K, °R.

P<sub>A</sub>, P<sub>B</sub>=partial pressure, P<sub>T</sub>=total pressure.

Now, applying the two cases that have been considered before, *i.e.* equimolar diffusion, and diffusion through stagnant layer, then we can reach to the final equation.

a) For equimolar-counter-diffusion (EMD).

$$N_A = -N_B$$

$$\frac{-dp_A}{dz} = \frac{R.T}{D_{AB} P_T} (N_A \cdot P_T)$$

$$N_A = \left( \frac{-D_{AB}}{R.T} \right) \left( \frac{P_{A2} - P_{A1}}{Z_2 - Z_1} \right) \quad [\text{Maxwell eq. for EMD}]$$

b) For N<sub>B</sub> = 0

$$-dp_A = N_A \left( \frac{R.T}{D_{AB} P_T} \right) (P_T - P_A) dz$$

$$N_A = \left( \frac{-D_{AB}}{R.T} \right) \left( \frac{P_T}{(Z_2 - Z_1)} \right) \ln \left( \frac{P_T - P_{A2}}{P_T - P_{A1}} \right)$$

Note: P<sub>T</sub> = P<sub>A1</sub> + P<sub>B1</sub> and P<sub>T</sub> = P<sub>A2</sub> + P<sub>B2</sub>,

$$P_{A1} + P_{B1} = P_{A2} + P_{B2} \rightarrow P_{A1} - P_{A2} = P_{B2} - P_{B1}$$

Therefore:

$$N_A = \left( -\frac{D_{AB} \cdot P_T}{R \cdot T} \right) \left( \frac{P_T}{P_{BM}} \right) \left( \frac{P_{A2} - P_{A1}}{Z_2 - Z_1} \right) \quad [\text{Maxwell eq. for } N_B=0]$$

Where:  $\left( \frac{P_T}{P_{BM}} \right)$  = Drift factor.

Drift factor  $\left( \frac{P_T}{P_{BM}} \right)$  = Represent the enhancement effect on mass transfer due to thenon diffusing component (B) and to total flow in the direction of diffusion.

## Maxwell's Law for Multi-Component Mass Transfer

Consider the transfer of component (A) through a stationary gas consisting of component B, C, D ...

Suppose that the total partial pressure gradient can be regarded as being made up of series of terms, each represent the contribution of the individual component gases,

$$-dp_A = \alpha_{AB} C_A C_B (v_A - v_B) dz \quad (\text{for binary system})$$

But now we have:

$$\frac{-dp_A}{dz} = \alpha_{AB} C_A C_B (v_A - v_B) + \alpha_{AC} C_A C_C (v_A - v_C) + \alpha_{AD} C_A C_D (v_A - v_D) + \dots\dots\dots$$

For stationary gas (B, C, D) velocities of (B, C, D) = 0

$$N_A = v_A \cdot C_A \rightarrow v_A = \frac{N_A}{C_A}$$

$$\frac{-dp_A}{dz} = [\alpha_{AB} C_B + \alpha_{AC} C_C + \alpha_{AD} C_D] \cdot N_A$$

Since  $P_B = C_B \cdot R \cdot T$ ,  $P_C = C_C \cdot R \cdot T$ ,  $P_D = C_D \cdot R \cdot T$

$$\frac{-dp_A}{dz} = \left( \frac{N_A}{R \cdot T} \right) [\alpha_{AB} P_B + \alpha_{AC} P_C + \alpha_{AD} P_D]$$

When  $\alpha_{AB} = \frac{R \cdot T^2}{D_{AB} \cdot P_T}$ , therefore:

$$\frac{-dp_A}{dz} = N_A \left( \frac{R \cdot T}{P_T} \right) \left[ \frac{P_B}{D_{AB}} + \frac{P_C}{D_{AC}} + \frac{P_D}{D_{AD}} \right]$$

$$N_A = \left( \frac{-P_T}{R \cdot T} \right) \left[ \frac{1}{\frac{P_B}{D_{AB}} + \frac{P_C}{D_{AC}} + \frac{P_D}{D_{AD}}} \right] \frac{dp_A}{dz} \dots\dots\dots (*)$$

$$N_A = \left( \frac{-P_T}{R \cdot T} \right) D \frac{dp_A}{dz}$$

$$\text{Put } \frac{1}{D^*} = \frac{P_B}{D_{AB}} + \frac{P_C}{D_{AC}} + \frac{P_D}{D_{AD}}$$

Divided equation (\*) by  $\frac{(P_T - P_A)}{(P_T - P_A)}$ :

$$N_A = \frac{-1}{R.T} \frac{P_T}{(P_T - P_A)} \left[ \frac{1}{\frac{y_B^*}{D_{AB}} + \frac{y_C^*}{D_{AC}} + \frac{y_D^*}{D_{AD}}} \right] \frac{dp_A}{dz}$$

$$\text{Where } \frac{1}{D^*} = \frac{y_B^*}{D_{AB}} + \frac{y_C^*}{D_{AC}} + \frac{y_D^*}{D_{AD}}$$

$D^*$  = effective Diffusivity = function of mole fraction

$$N_A = \frac{-D^*}{R.T} \frac{P_T}{(P_T - P_A)} \frac{dp_A}{dz}$$

$$-\int_{P_A}^{P_T} \frac{dp_A}{(P_T - P_A)} = \left( \frac{R.T}{D^* \cdot P_T} \right) N_A \int_{Z_1}^{Z_2} dz$$

After the integration:

$$N_A = \left( \frac{-D^*}{R.T} \right) \left( \frac{P_T}{P_{im}} \right) \left( \frac{P_{A2} - P_{A1}}{Z_2 - Z_1} \right) [\text{for multi-component gas system}]$$

Where:

$$P_T = P_A + P_B + P_C + P_D \quad [\text{diffusing + nondiffusing}]$$

$$P_t = (P_T - P_A) = P_B + P_C + P_D \quad [\text{nondiffusing only}]$$

$$y_B^* = P_B/P_t, \quad y_C^* = P_C/P_t, \quad y_D^* = P_D/P_t$$

$$\text{and } P_{im} = \frac{(P_T - P_{A2}) - (P_T - P_{A1})}{\ln \frac{(P_T - P_{A2})}{(P_T - P_{A1})}}$$



### **Example 1:**

Oxygen (O<sub>2</sub>) (A) is diffusing through non-diffusing gas mixture of methane (CH<sub>4</sub>)(B) and hydrogen (H<sub>2</sub>) (C) in the volume ratio of 2:1. The total pressure is  $1 \times 10^5 \text{ N/m}^2$  and the temperature is  $0^\circ \text{C}$ . The partial pressure of oxygen at two planes (2 mm) is  $13 \text{ kN/m}^2$  and  $6.5 \text{ kN/m}^2$ . The diffusivity of Oxygen in Hydrogen ( $D_{O_2/H_2}$ ) =  $6.99 \times 10^{-5} \text{ m}^2/\text{s}$  and the diffusivity of Oxygen in Methane ( $D_{O_2/CH_4}$ ) =  $1.88 \times 10^{-5} \text{ m}^2/\text{s}$ . Calculate the rate of diffusion of oxygen in  $\text{kmol/m}^2\text{s}$  through each square meter of the two planes.

### **Solution:**

$$N_A = \left( \frac{-D}{R.T} \right) \left( \frac{P_T}{P_{im}} \right) \left( \frac{P_{A2} - P_{A1}}{Z_2 - Z_1} \right)$$

$$D = \frac{1}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}}}$$

$$y_B = \frac{2}{3} = 0.667, y_C = \frac{1}{3} = 0.333$$

$$D = 2.46 \times 10^{-5} \text{ m}^2/\text{s}$$

$$P_{im} = \frac{(P_T - P_{A2}) - (P_T - P_{A1})}{\ln \frac{(P_T - P_{A2})}{(P_T - P_{A1})}} = \frac{(1 \times 10^5 - 6500) - (1 \times 10^5 - 13000)}{\ln \frac{(1 \times 10^5 - 6500)}{(1 \times 10^5 - 13000)}} = 9 \times 10^4 \text{ N/m}^2$$

$$\text{Sub. For } Z_2 - Z_1 = 2 \times 10^{-3} \text{ m}$$

$$N_A = 3.91 \times 10^{-5} \text{ kmol/m}^2.\text{sec.}$$

## Molecular Diffusion in Liquid Phase

Molecular diffusion in liquid phase takes place in many separation operations, such as:

- 1- Liquid – liquid extraction.
- 2- Gas absorption.
- 3- Distillation.
- 4- Oxygenation of rivers by air.
- 5- Diffusion of salts in blood.

Some important notes in liquid diffusion, these are:

- 1- Slower than in gas phase because of the density and attractive forces between molecules.
- 2- Diffusivities are dependent on the concentration of the diffusing component.

General form for diffusing equation is :

$$N_A = -D_L \left( \frac{dC_A}{dz} \right) + \frac{C_A}{C_T} (N_A + N_B)$$

1-forequimolar diffusion (EMD), where  $N_A = -N_B$ , then:

$$N_A = -D_L \left( \frac{C_{A2} - C_{A1}}{Z_2 - Z_1} \right), \text{ Or}$$

$$N_A = -D_L \cdot C_{av} \frac{(X_{A2} - X_{A1})}{(Z_2 - Z_1)}$$

Where:-

$D_L$ : diffusivity of solute (A) in (B) ( $\text{m}^2/\text{s}$ ).

$X_A$ : mole fraction of (A) at any point.

$$C_{av} = \frac{1}{2} \left[ \frac{\rho_1}{Mwt_1} + \frac{\rho_2}{Mwt_2} \right]$$

Where:-

$C_{av}$ : average concentration of (A+B) in ( $\text{kmol}/\text{m}^3$ ).

$Mwt_1$  &  $Mwt_2$ : average molecular weight of the solution at points 1 & 2 respectively ( $\text{kg}/\text{kmol}$ ).

$\rho_1$  &  $\rho_2$ : average density of the solution at points 1 & 2 in ( $\text{kg}/\text{m}^3$ ).

2- When  $N_B = 0$  (stationary).

$$N_A = -D_L \left( \frac{C_{av}}{X_{BLM}} \right) \frac{(X_{A2} - X_{A1})}{(Z_2 - Z_1)}$$

$$\text{Where } X_{BLM} = \frac{(X_{B2} - X_{B1})}{\ln \frac{X_{B2}}{X_{B1}}}$$

An important note, that is  $X_{A1} + X_{B1} = X_{A2} + X_{B2} = 1$  and for dilute solution:

$X_{BLM} \sim 1.0$ , then:

$$N_A = -D_L \left( \frac{C_{A2} - C_{A1}}{Z_2 - Z_1} \right) \text{ (Dilute solution only)}$$

## **Diffusivities in Liquids:**

Diffusion coefficient in liquids at 293 K is given in table (10.7) in volume (1) of chemical engineering by (Coulson, J.M.; Richardson, J.F.) fifth edition (page 506).

1- Wilke & Chang equation:

$$D_{AB} = \frac{7.4 \times 10^{-8} (\varphi_B \cdot Mwt_B)^{0.5} \cdot T}{\mu_B \cdot v_A^{0.6}}$$

Where:

$D_{AB}$  = diffusivity of solute (A) in very dilute solution in solvent (B), (cm<sup>2</sup>/s).

$Mwt_B$  = molecular weight of solvent (B).

$T$  = temperature (K).

$\mu_B$  = viscosity of solvent (B), (Cp or gm/cm.s).

$v_A$  = Solute molar volume at its normal boiling point (cm<sup>3</sup>/mol).

## **Diffusion of (A) Through Multi-Component Stagnant Layer Mixture.**

$$N_A = D^- \left( \frac{-C_T}{C_{RM}} \right) \left( \frac{C_{A2} - C_{A1}}{Z_2 - Z_1} \right), \quad \text{Or, } N_A = D^- \left( \frac{-C_{av}}{X_{RM}} \right) \left( \frac{X_{A2} - X_{A1}}{Z_2 - Z_1} \right)$$

$$\text{Where: } D^- = \frac{1}{\frac{X_B}{D_{AB}} + \frac{X_C}{D_{AC}} + \frac{X_D}{D_{AD}}}$$

$X_{RM}$  (same as  $P_{im}$ ) = remaining mole fraction log mean. (all component except (A)).



### **Example:**

Calculate the rate of diffusion of  $\text{CH}_3\text{COOH}$  (A) across a film of non-diffusing water (B) solution (1 mm) thick at  $17^\circ\text{C}$  when the concentration on opposite sides of the film are 9 and 3 wt% respectively. The  $D_{AB} = 0.95 \times 10^{-9} \text{ m}^2/\text{s}$ .

Give that:-

$$M_A = 60, M_B = 18.$$

$$\rho = 1012 \text{ kg/m}^3 \quad (9\% \text{ solution}).$$

$$\rho = 1003 \text{ kg/m}^3 \quad (3\% \text{ solution}).$$

### **Solution:**

$$N_A = -D_L \cdot \left( \frac{C_{av}}{X_{BLM}} \right) \frac{(X_{A2} - X_{A1})}{(Z_2 - Z_1)}$$

$$X_{A1} = \frac{\frac{0.09}{60}}{\frac{0.09}{60} + \frac{0.91}{18}} = 0.0288 \quad \text{at position (2).}$$

$$X_{A2} = \frac{\frac{0.03}{60}}{\frac{0.03}{60} + \frac{0.97}{18}} = 0.0092 \quad \text{at position (1).}$$

$$\frac{1}{M_1} = \frac{0.09}{60} + \frac{0.91}{18} \rightarrow M_1 = 19.8 \text{ kg/kmol}$$

$$\frac{1}{M_2} = \frac{0.03}{60} + \frac{0.97}{18} \rightarrow M_2 = 18.4 \text{ kg/kmol}$$

$$C_{av} = \frac{1}{2} \left[ \frac{\rho_1}{M_{wt_1}} + \frac{\rho_2}{M_{wt_2}} \right] \rightarrow \frac{1}{2} \left[ \frac{1012}{19.8} + \frac{1003}{18.4} \right]$$

$$C_{av} = 52.8 \text{ kmol/m}^3.$$

$$X_{B1} = 1 - X_{A1} \rightarrow 1 - 0.0288 \rightarrow X_{B1} = 0.9712$$

$$X_{B2} = 1 - X_{A2} \rightarrow 1 - 0.009 \rightarrow X_{B1} = 0.9908$$

$$X_{BLM} = \frac{(X_{B2} - X_{B1})}{\ln \frac{X_{B2}}{X_{B1}}} \rightarrow \frac{(0.9908 - 0.971)}{\ln \frac{0.9908}{0.971}}, \quad X_{BLM} = 0.98$$

$$N_A = -0.95 \times 10^{-9} * \frac{52.8}{0.98} * \frac{0.0092 - 0.0283}{0.001}$$

$$N_A = 0.977 \times 10^{-6} \text{ kmol/m}^2 \cdot \text{sec}$$

## Molecular Diffusion in Solid Phase

Diffusion in solids takes place by different mechanisms depending on the diffusing atom, molecule, or ion; the nature of the solid structure, whether it be porous or nonporous, crystalline, or amorphous; and the type of solid material, whether it be metallic, ceramic, polymeric, biological, or cellular. Diffusion in solid phase can be classified as:

- 1- Diffusion which follows Fick's law and does not depend on the structure of solid.
- 2- Diffusion in which the structure of solid are important.

### 1- Diffusion that follows Fick's law:

That is

$$N_A = -D_{AB} \left( \frac{dC_A}{dZ} \right)$$

Where:

$D_{AB}$  = Diffusivity of fluid A in solid B in  $m^2/s$ . It is independent of pressure, but a function of Temperature.

#### A) For diffusion through a solid slab at steady – state:

$$N_A = -D_{AB} \left( \frac{C_{A_2} - C_{A_1}}{Z_2 - Z_1} \right)$$

#### B) For diffusion through a solid hollow cylinder of $r_1$ (inner radius) and $r_2$ (outer radius) with length L:

$$N_A = \frac{\bar{N}_A}{A} = \frac{\bar{N}_A}{2\pi r L} = -D_{AB} \left( \frac{dC_A}{dZ} \right)$$

$$\bar{N}_A = -D_{AB} (C_{A_2} - C_{A_1}) \frac{2\pi L}{\ln \frac{r_2}{r_1}}$$

#### C) For diffusion through a solid hollow spherical shape of $r_1$ (inner radius) and $r_2$ (outer radius):

$$N_A = \frac{\bar{N}_A}{A} = \frac{\bar{N}_A}{4\pi r^2} = -D_{AB} \left( \frac{dC_A}{dZ} \right)$$

$$\frac{\bar{N}_A}{4\pi} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) = D_{AB} (C_{A_2} - C_{A_1})$$

Where:

$C_{A_2}$  &  $C_{A_1}$  = concentrations at opposite side of the sphere.

In the case that gas diffuses through a solid, then the solubility of the gas in the solid is directly proportional to the partial pressure of solute.

The solubility of a solute gas (A) in a solid is expressed as (S) in  $\text{cm}^3$  solute (at STP, e.g.  $0^\circ\text{C}$ , and 1 atm) per  $\text{cm}^3$  solid per (atm, partial pressure of solute A), then:

$$S = \frac{\text{cm}^3 (\text{STP}) \text{ of A}}{\text{cm}^3 \text{ solid} \cdot \text{atm}}$$

To convert the solubility (S) of A to concentration ( $C_A$ ):

$$C_A = S * \frac{1}{22.414} * P_A$$

Where:

$$C_A = \frac{\text{mol A}}{\text{cm}^3}, S = \frac{\text{cm}^3 (\text{STP}) \text{ of A}}{\text{atm} \cdot \text{cm}^3 (\text{solid})}, P_A = \text{atm, and } 22.414 = \frac{\text{cm}^3 \text{ A}}{\text{mol}}$$

In many cases the experimental data for diffusion of gases in solid are given as permeability ( $P_M$ ) in  $\text{cm}^3$  of solute gas (A) at STP  $\{0^\circ\text{C}$ , and 1 atm $\}$  per diffusing per second per  $\text{cm}^2$  cross-sectional area through of solid of 1 cm thick under a pressure difference of 1 atm.

$$N_A = -D_{AB} \left( \frac{C_{A2} - C_{A1}}{Z_2 - Z_1} \right)$$

Applying (Eq. 84), then

$$C_{A1} = \frac{S \cdot P_{A1}}{22.414} \text{ \& } C_{A2} = \frac{S \cdot P_{A2}}{22.414}, \text{ then:}$$

$$N_A = -\frac{D_{AB} \cdot S}{22.414} \left( \frac{P_{A2} - P_{A1}}{Z_2 - Z_1} \right) = \frac{P_m (P_{A1} - P_{A2})}{22.414 (Z_2 - Z_1)}$$

Where:

$$P_m = D_{AB} \cdot S = \frac{\text{cm}^3 (\text{STP}) \text{ of A}}{\text{cm}^2 \cdot S \cdot \frac{\text{atm}}{1\text{cm}}}$$

If series of solids are presented in series 1, 2, 3, ..., etc of thickness of each  $L_1, L_2, L_3, \dots$ , etc respectively, then:

$$N_A = \frac{(P_{A1} - P_{A2})}{22.414} \left( \frac{1}{\frac{L_1}{P_{m1}} + \frac{L_2}{P_{m2}} + \frac{L_3}{P_{m3}} + \dots} \right)$$

Where:

$(P_{A1} - P_{A2})$  is the overall partial pressure difference.



## **Diffusion in which the structure of solid are important:**

### ***Porous Solids***

When solids are porous, predictions of the diffusivity of gaseous and liquid solute species in the pores can be made. This type of diffusion is also of great importance in the analysis and design of reactors using porous solid catalysts. It is sufficient to mention here that any of the following four mass transfer mechanisms or combinations thereof may take place:

1. Ordinary molecular diffusion through pores, which present tortuous paths and hinder the movement of large molecules when their diameter is more than 10% of the pore diameter.
2. Knudsen diffusion, which involves collisions of diffusing gaseous molecules with the pore walls when the pore diameter and pressure are such that the molecular mean free path is large compared to the pore diameter.
3. Surface diffusion involving the jumping of molecules, adsorbed on the pore walls, from one adsorption site to another based on a surface concentration-driving force.
4. Bulk flow through or into the pores.

When treating diffusion of solutes in porous materials where diffusion is considered to occur only in the fluid in the pores, it is common to refer to an effective diffusivity,  $D_{eff}$ , which is based on (1) the total cross-sectional area of the porous solid rather than the cross-sectional area of the pore and (2) on a straight path, rather than the pore path, which may be tortuous. If pore diffusion occurs only by ordinary molecular diffusion, the effective diffusivity can be expressed in terms of the ordinary diffusion coefficient,  $D$ , by

$$D_{eff} = \frac{D_{AB} \epsilon}{\tau}$$

And the rate of diffusion is calculated by

$$N_A = -D_{eff} \left( \frac{C_{A2} - C_{A1}}{Z_2 - Z_1} \right)$$

Where  $\epsilon$  the fractional porosity (typically 0.5) of the solid and  $\tau$  is the pore-path tortuosity (typically 2 to 3), which is the ratio of the pore length to the length if the pore were straight in the direction of diffusion.

### Example

A sintered solid of silica (2mm) thick is porous with void fraction of 0.3 and tortuosity of 4. the pores are filled with water at 298 K. at one face the concentration of KCl is held at 0.1 mol / liter and fresh water flow rapidly by other face. Neglecting any other resistance but that in porous solid, calculate the diffusion of KCl at steady state. Given the diffusivity  $D_{AB}$  is equal to  $1.98 \times 10^{-9} \text{ m}^2/\text{s}$ .

### Solution

Since neglecting any other resistance but that in porous solid, then ordinary diffusion is occurred

$$N_A = -D_{eff} \left( \frac{C_{A_2} - C_{A_1}}{Z_2 - Z_1} \right)$$

And  $D_{eff}$  is calculated by equation 89

$$D_{eff} = \frac{D_{AB} \epsilon}{\tau} = \frac{1.98 \times 10^{-9} * 0.3}{4} = 1.4025 \times 10^{-10} \frac{\text{m}^2}{\text{s}}$$

$$N_A = -1.4025 \times 10^{-10} \left( \frac{0 - 0.1}{0.002} \right) = 7.01 \times 10^{-9} \frac{\text{kmol KCl}}{\text{m}^2 * \text{s}}$$

## Convective Mass Transfer for Binary gas Mixture

In previous sections we have considered molecular diffusion in stagnant fluid (laminar flow) where the rate of diffusion is slow. To increase the rate of mass transfer, the fluid velocity is increased until turbulent mass transfer occurs. As given before in equation (1):

$$N_i = X_i N + \text{molecular diffusion flux of } i + \text{eddy diffusion flux of } i \quad \dots (1)$$

The eddy diffusion flux term is given by:

$$J_{A_z}^* = -E_d \frac{dC_A}{dz} \quad \dots (2)$$

Then

$$N_A = -C_T^* (D_{AB} + E_D) * \left( \frac{dX_A}{dz} \right) + X_A (N_A + N_B) \quad \dots (3)$$

This is the general equation used to calculate the mass transfer.

1- For equi - molar mass transfer

A) For gases:

$$N_A = \frac{-(D_{AB} + E_D) * \frac{dP_A}{dz} + \frac{P_A}{P_T} * (N_A + N_B)}{R * T} \quad \dots (4)$$

For equi - molar transfer: ( $N_A = -N_B$ )

Then :

$$N_A = \frac{-(D_{AB} + E_D) * \frac{dP_A}{dz}}{R * T} \quad \dots (5)$$

By integrating equation (5) from  $P_{A_1}$  at  $Z_1$  to  $P_{A_2}$  and  $Z_2$  then:

$$N_A = \frac{(D_{AB} + E_D) * (P_{A_1} - P_{A_2})}{R * T (Z_2 - Z_1)} \quad \dots (6)$$

Because the film thickness can not be measured or is not known, then the value ( $Z_2 - Z_1$ ) is not known (the distance of the path), also the amount of  $E_D$  can not be measured, then, the term (individual mass transfer coefficient) is used as shown below:

$$N_A = K'_G (P_{A_1} - P_{A_2}) \quad \dots (7)$$

Where:

$$K'_G = \frac{(D_{AB} + E_D)}{R * T (Z_2 - Z_1)} \quad \dots (8)$$

Also for gases another form of equation (8) can be written as:

$$N_A = K'_y (y_{A_1} - y_{A_2}) \quad \dots (9)$$

A) For Liquids:

Similar to what done for gases, the rate of mass transfer is:

$$N_A = K'_L (C_{A_1} - C_{A_2}) = K'_x (X_{A_1} - X_{A_2}) \quad \dots (10)$$





The general form for the mass transfer is:

$$N_A = K'_C (C_{A_1} - C_{A_2}) \dots\dots (11)$$

All these individual mass transfer coefficients are related to each other.

For gases:

$$N_A = K'_C (C_{A_1} - C_{A_2}) = K'_G (P_{A_1} - P_{A_2}) = K'_y (y_{A_1} - y_{A_2}) \dots\dots (12)$$

So

$$K'_C = k'_G \cdot \frac{R \cdot T}{C_T} = \frac{K'_y}{C_T}$$

Home work: find the relations for the liquid phase.

2- For uni - molecular mass transfer

A) For gases:

$$N_A = \frac{-(D_{AB} + E_D)}{R \cdot T} * \frac{dP_A}{dZ} + \frac{P_A}{P_T} * (N_A + N_B) \dots\dots (4)$$

For uni - molar transfer: ( $N_B = 0$ )

Then equation (4) will be:

$$N_A = \frac{-(D_{AB} + E_D)}{R \cdot T} * \frac{dP_A}{dZ} + \frac{P_A}{P_T} * (N_A) \dots\dots (13)$$

By integrating equation (13) from  $P_{A_1}$  at  $Z_1$  to  $P_{A_2}$  and  $Z_2$  then

$$N_A = \frac{(D_{AB} + E_D) * P_T}{R * T * P_{BLM}} * \frac{(P_{A_1} - P_{A_2})}{(Z_2 - Z_1)} \dots\dots (14)$$

Similarly as done in section 1:

$$N_A = K_G (P_{A_1} - P_{A_2}) = K_y (y_{A_1} - y_{A_2}) = K_C (C_{A_1} - C_{A_2}) \dots\dots (15)$$

B) For Liquids:

Similar to what done for gases, the rate of mass transfer is:

$$N_A = K_L (C_{A_1} - C_{A_2}) = K_x (X_{A_1} - X_{A_2}) \dots\dots (16)$$

The general form for the mass transfer is:

$$N_A = K_C (C_{A_1} - C_{A_2}) \dots\dots (17)$$

Home work: find the relations for the gas phase and liquid phase. Also write the units of each coefficient.



## Methods to Determine the Mass transfer Coefficient

The mass transfer coefficient can be evaluated using empirical correlations involving dimensionless numbers. These empirical equations were obtained from experimental data using various types of fluids, different velocities, and different geometrics. The most important groups (dimensionless numbers) are:

1- Reynolds Number (Re No.):

Re. No indicate the degree of turbulence.

$$Re No = \frac{\rho u d}{\mu} = \frac{\text{interfial force}}{\text{viscous force}}$$

Where:

$\rho$  = density of flowing mixture fluid (solute A and solvent B).

$\mu$  = viscosity of flowing mixture fluid (solute A and solvent B).

$d$  = diameter of the pipe in which the fluid is flow.

$D_p$  May be used in Reynolds number equation instead of  $d$  when flow across a sphere, also  $L$  may be used if the flow was above a flat plate.

$U$  = mean average velocity in the pipe.

If the flow was across a packed bed,  $U$  will be substituted by:

$$U = \frac{\bar{U}}{\epsilon}$$

Where

$\bar{U}$  is the superficial velocity of empty cross- section of packed bed column.

$\epsilon$  = void fraction.

2- Schmidt Number (Sc No.):

$$Sc No = \frac{\mu}{\rho D_{AB}} = \frac{\nu}{D_{AB}} = \frac{\text{momentum diff usivity}}{\text{molecular diff usivity}}$$

3- Sherwood Number (Sh No.):

$$Sh No = \frac{K'_C L}{D_{AB}}$$

4- Stanton Number (St No.):

$$Sh No = \frac{Sh}{Re * Sc} = \frac{K'_C}{u} = \frac{K'_C \rho}{G_m}, \text{ where } G_m = \frac{\rho \cdot u}{M_{avg.}} = u \cdot C_{avg.} \dots (1)$$

(flow rate)

5- J-factor

In general  $j$ -factors are uniquely determined by the geometric configuration and the Reynolds number.





Now after introducing the dimensionless groups, now we will present the correlations used to calculate the mass transfer coefficient.

1- Using the analogy or similarity of momentum, heat, and mass transfer using Chilton – Colburn Analogy:

$$j_M = j_H = j_D = \frac{f}{2} = \frac{K'_C \cdot \rho}{G_m} (Sc)^{2/3} = \frac{k'_C}{u} (Sc)^{2/3} = \frac{k'_G P_T}{G_m} (Sc)^{2/3} \dots\dots (2)$$

2- For flow inside pipe

For both gases and liquids, where  $Re > 2100$

$$Sh No = \frac{K'_C d}{D_{AB}} = 0.023(Re)^{0.833} (Sc)^{0.333} \dots\dots (3) \text{ (For turbulent)}$$

**Note:**

$Sc = 0.5 - 3$  for gases

$Sc > 100$  for liquids

Or

$$j_M = j_H = j_D = 0.023(Re)^{-0.2} \dots\dots (4)$$

For  $10000 < Re < 1000000$

$$Sh = k_L \frac{d}{D_{AB}} = 1.62 \left[ (Re)(Sc) \frac{d}{L} \right]^{1/3} \dots\dots (5) \text{ (For Laminar)}$$

3- For flow parallel to flat plate of length L

A- for gases

$$j_M = j_H = j_D = 0.664(Re)^{-0.5} \dots\dots (6)$$

For  $Re < 15000$  where  $Re = \frac{L U \rho}{\mu}$

And

$$j_M = j_H = j_D = 0.036(Re)^{-0.2} \dots\dots (7)$$

For  $15000 < Re < 300000$  where  $Re = \frac{L U \rho}{\mu}$

B- for liquids

$$j_M = j_H = j_D = 0.99(Re)^{-0.5} \dots\dots (8)$$

For  $600 < Re < 50000$  where  $Re = \frac{L U \rho}{\mu}$

For both gases and liquids

$$j_M = j_H = j_D = 0.037(Re)^{-0.2} \dots\dots (9)$$

For  $500000 < Re < 5 \cdot 10^8$  where  $Re = \frac{L U \rho}{\mu}$



4- For flow normal to a long circular cylinder of diameter  $D$ , where the drag coefficient includes both form drag and skin friction, but only the skin friction contribution applies to the analogy:

$$(j_M)_{\text{skin friction}} = j_H = j_D = 0.193(\text{Re})^{-0.382} \quad \dots \dots (10)$$

$$\text{For } 4000 < \text{Re} < 40000 \text{ where } \text{Re} = \frac{D_{\text{cylind}} U \rho}{\mu}$$

$$(j_M)_{\text{skin friction}} = j_H = j_D = 0.0266(\text{Re})^{-0.195} \quad \dots \dots (11)$$

$$\text{For } 40000 < \text{Re} < 250000 \text{ where } \text{Re} = \frac{D_{\text{cylind}} U \rho}{\mu}$$

5- For flow past a single sphere of diameter  $D_p$

$$(j_M)_{\text{skin friction}} = j_H = j_D = 0.37 * (\text{Re})^{-0.4} \quad \dots \dots (12)$$

$$\text{For } 20 < \text{Re} < 100000 \text{ where } \text{Re} = \frac{D_p u \rho}{\mu}$$

The above equation is used for both gases and liquids. Another method is used to calculate the mass transfer coefficient.

For very low Re No. ( $\text{Re} < 1$ ) the Sh No. approach a value of 2, then:

$$\text{Sh No} = \frac{K'_C d}{D_{AB}} = 2$$

$$\therefore K'_C = \text{Sh} * \frac{D_{AB}}{D_p} = \frac{2 * D_{AB}}{D_p} \quad \dots \dots (13)$$

For gases where  $\text{Re} = 1 - 48000$  and  $\text{Sc} = 0.6 - 2.7$ , a modified equation can be used:

$$\text{Sh No} = \frac{K'_C d}{D_{AB}} = 2 + \left( 0.552 \text{Re}^{0.53} * \text{Sc}^{0.333} \right) \quad \dots \dots (14)$$

For liquids:

$$\text{Sh No} = \frac{K'_C d}{D_{AB}} = 2 + \left( 0.95 \text{Re}^{0.5} * \text{Sc}^{0.333} \right) \quad \dots \dots (15)$$

For  $\text{Re} = 2 - 2000$

And also for liquids

$$\text{Sh No} = \frac{K'_C d}{D_{AB}} = 2 + \left( 0.347 \text{Re}^{0.62} * \text{Sc}^{0.333} \right) \quad \dots \dots (16)$$

For  $\text{Re} = 2000 - 17000$





6- For flow through beds packed with spherical particles of uniform size  $D_p$

$$j_H = j_D = 1.17(\text{Re})^{-0.415} \quad \dots (17)$$

For  $10 < \text{Re} < 2500$  where  $\text{Re} = \frac{D_p U \rho}{\mu}$

For other shapes of packing a correction factor can be used such as:

$$j_D (\text{cylinder}) = 0.79 * j_D (\text{sphere})$$

$$j_D (\text{cube}) = 0.71 * j_D (\text{sphere})$$

7- For fluidized beds of packed with sphere, for both gases and liquids:

$$j_D = 0.01 + \frac{0.86}{\text{Re}^{0.58} - 0.483} \quad \dots (18)$$



## Methods for Mass transfer at Fluid – Fluid Interface (Phase Boundary)

In the previous sections, diffusion and mass transfer within solids and fluids were considered, where the interface was a smooth solid surface. Of greater interest in separation processes is mass transfer across an interface between a gas and a liquid or between two liquid phases. Such interfaces exist in absorption, distillation, extraction, and stripping. At fluid-fluid interfaces, turbulence may persist to the interface. Mass transfer rate between two fluid phases will depend on:-

- 1-Physical properties of the two phases.
- 2-Concentration difference  $\Delta C$ .
- 3-Interfacial area.
- 4-Degree of turbulence.

The following theoretical models have been developed to describe mass transfer from a fluid to such an interface.

### Film Theory

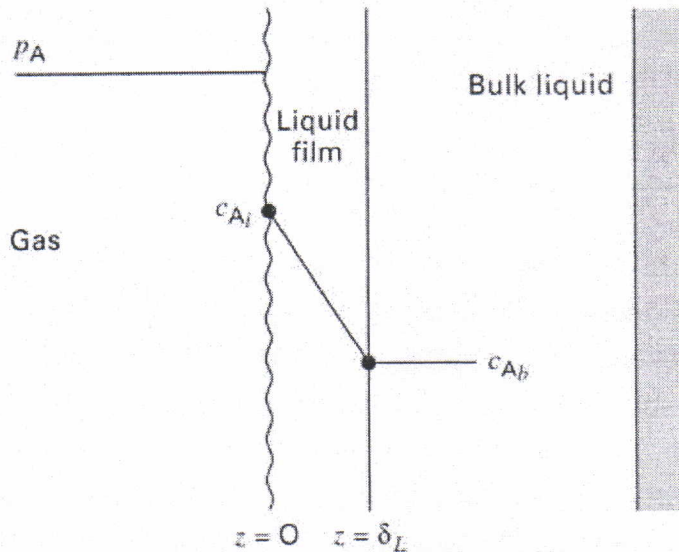
A simple theoretical model for turbulent mass transfer to or from a fluid-phase boundary was suggested in 1904 by Nernst, who postulated that the entire resistance to mass transfer in a given turbulent phase is in a thin, stagnant region of that phase at the interface, called a film. This film is similar to the laminar sub – layer that forms when a fluid flows in the turbulent regime parallel to a flat plate. This is shown schematically in Figure 4. For the case of a gas-liquid interface, where the gas is pure component A, which diffuses into nonvolatile liquid B. Thus, a process of absorption of A into liquid B takes place, without desorption of B into gaseous A. Because the gas is pure A at total pressure  $P = P_A$ , there is no resistance to mass transfer in the gas phase. At the gas-liquid interface, equilibrium is assumed so the concentration of A,  $C_{Ai}$  is related to the partial pressure of A,  $P_A$ , by some form of Henry's law, for





example,  $C_{Ai} = H_A P_A$ . In the thin stagnant liquid film of thickness  $\delta$ , molecular diffusion only occurs with a driving force of  $(C_{Ai} - C_{Ab})$ . Since the film is assumed to be very thin, the entire diffusing A passes through the film and into the bulk liquid. If, in addition, bulk flow of A is neglected, the concentration gradient is linear as in Figure . Accordingly, Fick's first law, for the diffusion flux integrates to:

$$J_A = \frac{D_{AB}}{\delta} (C_{Ai} - C_{Ab}) = \frac{C_T^* D_{AB}}{\delta} (X_{Ai} - X_{Ab}) \quad \text{--- (1)}$$



**Figure 1** Film theory for mass transfer from a fluid – fluid interface into a liquid.

If the liquid phase is dilute in A, the bulk-flow effect can be neglected and (Eq. 1 ) applies to the total flux:

$$N_A = \frac{D_{AB}}{\delta} (C_{Ai} - C_{Ab}) = \frac{C_T^* D_{AB}}{\delta} (X_{Ai} - X_{Ab}) \quad \text{--- (2)}$$

If the bulk-flow effect is not negligible, then,

$$N_A = \frac{C \cdot D_{AB}}{Z_2 - Z_1} \ln \left( \frac{1 - X_{Ab}}{1 - X_{Ai}} \right) = \frac{C \cdot D_{AB}}{\delta (1 - X_A)_{LM}} (X_{Ai} - X_{Ab}) \quad \text{--- (3)}$$

Where:

$$(1 - x_A)_{LM} = \frac{x_{Ai} - x_{Ab}}{\ln[(1 - x_{Ab})/(1 - x_{Ai})]} = (x_B)_{LM}$$

In practice, the ratios  $D_{AB}/\delta$  in (Eq. 2 ) and  $D_{AB}/\delta^*(1 - X_A)_{LM}$  in (Eq. 3 ) are replaced by mass transfer coefficients and  $K'_c$  and  $K_c$ , respectively, because the film thickness,  $\delta$ , which depends on the flow conditions, is not known.



The film theory, which is easy to understand and apply, is often criticized because it appears to predict that the rate of mass transfer is directly proportional to the molecular diffusivity. This dependency is at odds with experimental data, which indicate a dependency of  $D^n$ , where  $n$  ranges from about 0.5 to 0.75. However, if  $D_{AB}/\delta$  is replaced with  $K'_c$ , which is then estimated from the Chilton-Colburn analogy, (Eq. <sup>PAGE 51</sup> 2), we obtain  $K'_c$  proportional to  $D_{AB}^{2/3}$ , which is in better agreement with experimental data. In effect,  $\delta$  depends on  $D_{AB}$  (Sc No.). Regardless of whether the criticism of the film theory is valid, the theory has been and continues to be widely used in the design of mass transfer separation equipment.





## Example

A wetted wall column of inside diameter (2 in) contains air and CO<sub>2</sub> flowing at 3 ft/s. at a certain point in the column, the CO<sub>2</sub> concentration in the air is 0.1 mol fraction, at the same point in the column, the concentration of CO<sub>2</sub> in the water at the water – air interface is 0.005 mole fraction. The column operates at 10 atm and 25 °C. Calculate the mass transfer coefficient and the mass flux at the point of consideration, given the following data:

The diffusivity of CO<sub>2</sub> in air at 25 °C and 1 atm = 0.164 cm<sup>2</sup>/s

The density of air at STP = 0.0808 lb/ft<sup>3</sup>

The viscosity of air at 25 °C and 10 atm = 0.018 cP

Henry constant = 1640 atm / mol fraction

## Solution

Since we are dealing with a case of fluid flow inside a pipe, then to calculate the mass transfer coefficient use the following equation:

$$Sh No = \frac{K'_C d}{D_{AB}} = 0.023(Re)^{0.833} (Sc)^{0.333}$$

But we are dealing with mass transfer through stagnant layer (transfer of CO<sub>2</sub> from air to water only), then

$$K_C = K'_C \frac{P_T}{P_{B_{LM}}}$$

Or

$$Sh No = \frac{K_C * P_{B_{LM}} * d}{P_T * D_{AB}} = 0.023(Re)^{0.833} (Sc)^{0.333}$$

And

$$K_C = \frac{P_T * D_{AB}}{P_{B_{LM}} * d} * 0.023(Re)^{0.833} (Sc)^{0.333}$$

To calculate the dimensionless groups we must first correct the physical properties from their conditions to the operation condition (10 atm and 25 °C), also we must convert all the units of all the quantities to the SI system.

$$u = 3 \frac{ft}{s} * \frac{1m}{3.28 ft} = 0.915 \frac{m}{s}$$

$$d = 2in = 2in * \frac{2.54cm}{in} * \frac{1m}{100cm} = 0.0508m$$

$$\mu = 0.018cP = 0.018 * 10^{-3} \frac{kg}{m * s}$$



$$\rho = \frac{p^* mwt}{R * T}$$

Then

$$\frac{(\rho_2)_{298K, 10atm}}{(\rho_1)_{STP}} = \frac{\left(\frac{P_2}{T_2}\right)}{\left(\frac{P_1}{T_1}\right)} = \frac{\frac{10}{298}}{\frac{1}{273}}$$

$$\rho_1 = 0.0808 \frac{lb}{ft^3} = 0.0808 \frac{lb}{ft^3} * \frac{1kg}{2.2lb} * \left(\frac{3.28ft}{1m}\right)^3 = 1.296 \frac{kg}{m^3}$$

$$\therefore \rho_2 = 1.296 \frac{kg}{m^3} * \frac{10 * 273}{298} = 11.973 \frac{kg}{m^3}$$

$$\frac{(D_{AB})_2}{(D_{AB})_1} = \left(\frac{P_1}{P_2}\right) * \left(\frac{T_2}{T_1}\right)^{1.5}$$

$$(D_{AB})_1 = 0.164 \frac{cm^2}{s} = 0.164 \frac{cm^2}{s} * \left(\frac{1m}{100cm}\right)^2 = 1.64 * 10^{-5} \frac{m^2}{s}$$

$$(D_{AB}) = 1.64 * 10^{-5} * \left(\frac{1}{10}\right) * \left(\frac{298}{273}\right)^{1.5} = 1.64 * 10^{-6} \frac{m^2}{s}$$

$$P_{B_{Lm}} = \frac{P_{B_2} - P_{B_1}}{\ln\left(\frac{P_{B_2}}{P_{B_1}}\right)}$$

$$P_{A_1} = y_1 * P_T = 0.1 * 10 = 1atm$$

$$P_{B_1} = 10 - 1 = 9atm$$

$P_{A_2}$  can be estimated from Henry law

$$P_A = x_A * H$$

$$P_{A_2} = 0.005 * 1640 = 8.2atm$$

$$P_{B_2} = 10 - 8.2 = 1.8atm$$

$$\therefore P_{B_{LM}} = \frac{1.8 - 9}{\ln\left(\frac{1.8}{9}\right)} = 4.473612$$

Now we can calculate the mass transfer coefficient





$$K_C = \frac{P_T * D_{AB}}{P_{B_{LM}} * d} * 0.023(Re)^{0.833} (Sc)^{0.333}$$

$$K_C = \frac{P_T * D_{AB}}{P_{B_{LM}} * d} * 0.023 * \left( \frac{\rho * u * d}{\mu} \right)^{0.833} \left( \frac{\mu}{\rho * D_{AB}} \right)^{0.333}$$

$$K_C = \frac{10 * 1.64 * 10^{-6} * 0.023}{4.473612 * 0.0508} * \left( \frac{11.973 * 0.915 * 0.0508}{0.018 * 10^{-3}} \right)^{0.833} * \left( \frac{0.018 * 10^{-3}}{11.973 * 1.64 * 10^{-6}} \right)^{0.333}$$

$$K_C = 0.008868 \frac{m}{s}$$

$$N_A = K_g (P_{A_1} - P_{A_2})$$

$$K_g = \frac{K_C}{R * T} = 0.008868 \frac{m}{s} * \frac{1}{0.082 \frac{atm * l}{mol * K} * \frac{m^3}{1000l} * \frac{1000mol}{kmol} * 298K}$$

$$K_g = 3.62642 * 10^{-4} \frac{kmol}{m^2 * s * atm}$$

$$N_A = 3.62642 * 10^{-4} * (8.2 - 1) = 2.611 * 10^{-3} \frac{kmol}{m^2 * s}$$



	Rate equation		Units of coefficient
	(EMD)	Non-diffusing (B)	
For Gas	$N_A = K_G \cdot \Delta P_A$	$N_A = K_G \cdot \Delta P_A$	$\frac{\text{Moles transferred}}{(\text{time}) (\text{area}) (\text{press.})}$
	$N_A = K_y \cdot \Delta y_A$	$N_A = K_y \cdot \Delta y_A$	$\frac{\text{Moles transferred}}{(\text{time}) (\text{area}) \left(\frac{\text{mole}}{\text{fraction}}\right)}$
	$N_A = K_C \cdot \Delta C_A$	$N_A = K_C \cdot \Delta C_A$	$\frac{\text{Moles transferred}}{(\text{time}) (\text{area}) \left(\frac{\text{mole}}{\text{vol.}}\right)}$
conversions	$F = K_G \cdot P_{BM} = K_y \frac{P_{BM}}{P_T} = K_C \cdot \frac{P_{BM}}{R \cdot T} = K_G \cdot P_T = K_y = K_C \frac{P_T}{R \cdot T} = K_C \cdot G_T$		
For Liquid	$N_A = K_L \cdot \Delta C_A$	$N_A = K_L \cdot \Delta C_A$	$\frac{\text{Moles transferred}}{(\text{time}) (\text{area}) \left(\frac{\text{mole}}{\text{vol.}}\right)}$
	$N_A = K_X \cdot \Delta X_A$	$N_A = K_X \cdot \Delta X_A$	$\frac{\text{Moles transferred}}{(\text{time}) (\text{area}) \left(\frac{\text{mole}}{\text{fraction}}\right)}$
conversions	$F = K_X \cdot X_{BM} = K_L \cdot X_{BM} \cdot C_T = K_L \cdot C_T = K_L \frac{\rho}{M} = K_X$		

Relations among mass – transfer – coefficients.

Conversions	
$(N_B = 0)$	$(N_A = -N_B)$
$K_C = K_G \cdot R \cdot T$	$K_C = K_y \cdot \frac{R \cdot T}{P_T}$
$K_y = K_G \cdot P_T$	$K_C = K_G \cdot R \cdot T$
$K_X = K_L \cdot \left(\frac{\rho}{M_{WT}}\right)_{\text{avg.}}$	$K_X = K_L \cdot C_{\text{avg.}}$ $= K_L \cdot \left(\frac{\rho}{M_{WT}}\right)_{\text{avg.}}$



## Film – Penetration theory

Toor and Marchello, in 1958, combined features of the film, penetration, and surface renewal theories to develop a film-penetration model, which predicts a dependency of the mass transfer coefficient  $K_c$  on the diffusivity, that varies from  $\sqrt{D_{AB}}$  to  $D_{AB}$ . Their theory assumes that the entire resistance to mass transfer resides in a film of fixed thickness  $\delta$ . Eddies move to and from the bulk fluid and this film. Age distributions for time spent in the film are of the Higbie or Danckwerts type.

Fick's second law, (Eq. 100), still applies, but the boundary conditions are now

$$\begin{array}{lll} \text{At } t = 0 & 0 \leq Z \leq \infty & C_A = C_{Ab} \\ t > 0 & Z = 0 & C_A = C_{Ai} \quad (C_{Ai} : \text{initial concentration}) \\ t > 0 & Z = \delta & C_A = C_{Ab} \end{array}$$

Infinite-series solutions are obtained by the method of Laplace transforms. The rate of mass transfer is then obtained in the usual manner by applying Fick's first law at the fluid-fluid interface.

$$N_A = -D_{AB} \left. \frac{\partial C_A}{\partial Z} \right|_{Z=0} = K_c (C_{Ai} - C_{A0})$$

## Two – Film Theory

Separation processes that involve contacting two fluid phases generally require consideration of mass transfer resistances in both phases. In 1923, Whitman suggested an extension of the film theory to two fluid films in series. Each film presents a resistance to mass transfer, but concentrations in the two fluids at the interface are in equilibrium. That is, there is no additional interfacial resistance to mass transfer. This concept has found extensive application in modeling of steady-state gas-liquid and liquid-liquid separation processes, when the fluid phases are in laminar or turbulent flow. The assumption of equilibrium at the interface is satisfactory unless mass transfer rates are very high or surfactants accumulate at the interface.

### Gas- Liquid Case

Consider the steady-state mass transfer of A from a gas phase, across an interface, into liquid phase. It could be postulated, as shown in Figure 2a, that a thin gas film exists on one side of the interface and a thin liquid film exists on the other side with the controlling factors being molecular diffusion through each of the films. However, this postulation is not necessary, because instead of writing the mass transfer rate as:

$$N_A = \frac{(D_{AB})_G}{\delta_G} (C_{Ab} - C_{Ai})_G = \frac{(D_{AB})_L}{\delta_L} (C_{Ai} - C_{Ab})_L \quad \dots \text{--- (4)}$$

We can express the rate of mass transfer in terms of mass transfer coefficients that can be determined from any suitable theory, with the concentration gradients visualized more realistically as in Figure 2b. In addition, we can use any number of different

mass transfer coefficients, depending on the selection of the driving force for mass transfer.

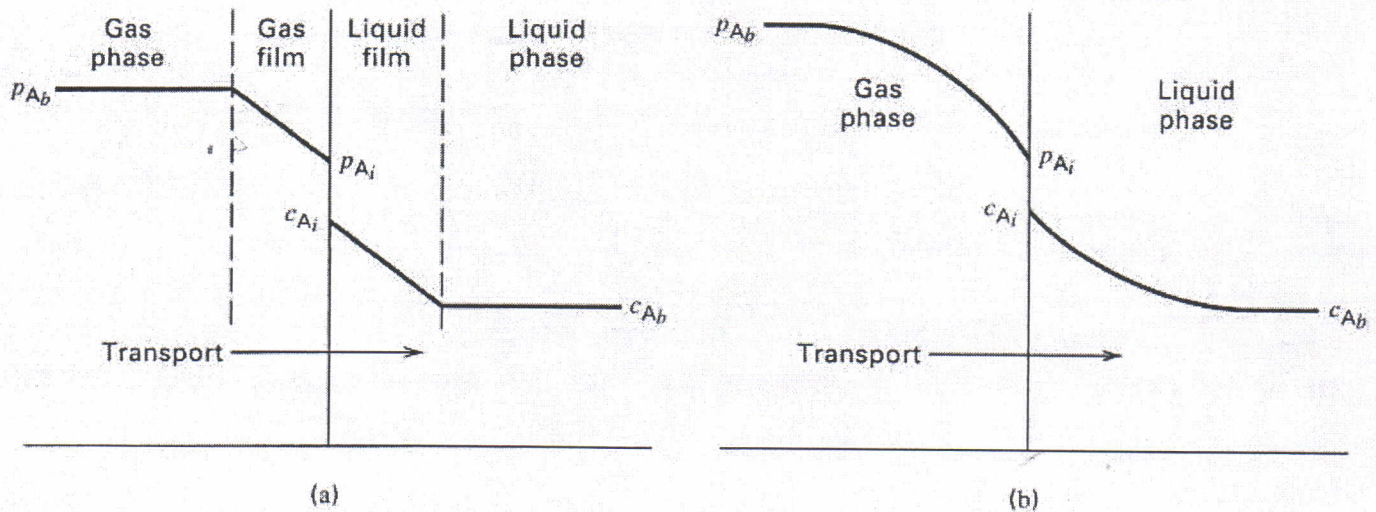


Figure 2 Concentration gradients for two – resistance theory: (a) film theory; (b) more realistic gradients.

For gas phase, under dilute or equimolar counter diffusion (EMD) conditions, we write the mass transfer rate in terms of partial pressure:

$$N_A = K'_g (P_{A_b} - P_{A_i}) \quad \text{----- (5)}$$

Or for stagnant layer mass transfer (non – volatile liquid), the rate of mass transfer can be written as:

$$N_A = K_g (P_{A_b} - P_{A_i}) \quad \text{--- (6)}$$

Where ( ' ) refers to the equimolar counter diffusion case.

The above equations can be written in terms of mole fractions as:

$$N_A = \frac{K'_g}{P_T} (y_{A_b} - y_{A_i}) = K'_y (y_{A_b} - y_{A_i}) \quad \text{--- (7)}$$

And

$$N_A = \frac{K_g}{P_T} (y_{A_b} - y_{A_i}) = K_y (y_{A_b} - y_{A_i}) \quad \text{--- (8)}$$

For the liquid phase, we might use molar concentrations:

$$N_A = K'_l (C_{A_i} - C_{A_b}) \quad \text{----- (9) for equi – molar mass transfer}$$

$$N_A = K_l (C_{A_i} - C_{A_b}) \quad \text{--- (10) for uni – molar mass transfer}$$

Also can be written in terms of mole fractions:



$$N_A = \frac{K_l'}{C_T} (x_{A_i} - x_{A_b}) = K_x' (x_{A_i} - x_{A_b}) \quad \text{--- (11) for equi-molar mass transfer}$$

And

$$N_A = \frac{K_l}{C_T} (x_{A_i} - x_{A_b}) = K_x (x_{A_i} - x_{A_b}) \quad \text{--- (12) for uni-molar mass transfer}$$

At the phases interface,  $C_{A_i}$  and  $P_{A_i}$  are in equilibrium. Applying a version of Henry's law:

$$C_{A_i} = H_A * P_{A_i} \quad \text{--- (13)}$$

Equations ( 5 ), ( 9 ) and ( 13 ) are a commonly used combination for vapor-liquid mass transfer. Computations of mass transfer rates are generally made from knowledge of bulk concentrations, which in this case are  $C_{A_b}$  and  $P_{A_b}$ .

The equilibrium relationship for dilute solution (Henry's law) is:

$$P_A^* = H * x_A \quad \text{--- (14)}$$

And for gases (Dalton's Law):

$$P_A = P_T * y_A \quad \text{--- (15)}$$

Then

$$y_A^* = \frac{H}{P_T} * x_A = m * x_A \quad \text{--- (16)}$$

Or

$$y_A = m * x_A^* \quad \text{--- (17)}$$

And for the interface

$$y_i = m * x_i \quad \text{--- (18)}$$

Equilibrium data can be presented as a curve (for concentrated solution) and straight line (for dilute solution).

The task now is how to calculate the interfacial concentration (interfacial mole fraction) because we need them in the calculation of mass transfer rate.

Depending on the two film theory, and as shown in above sections we have two cases, the EMD (for example distillation), and the UMD (absorption through non-volatile liquid).

Case 1:

For equi-molecular counter diffusion

$$\text{Let } y_A = y_{Ab}$$

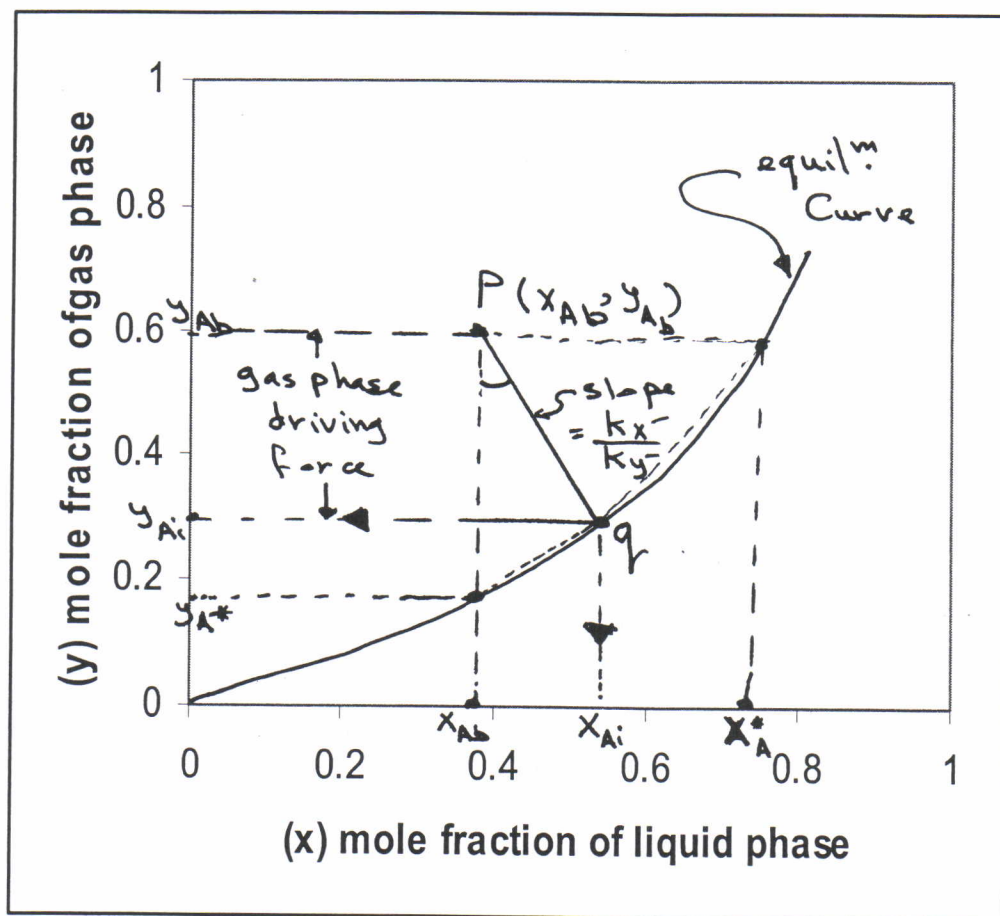
$$\text{and } x_A = x_{Ab}$$

$$N_A = K_y' (y_A - y_{A_i}) = K_x' (x_{A_i} - x_A) \quad \text{--- (19)}$$

Then

$$-\frac{K'_x}{K'_y} = \frac{(y_A - y_{A_i})}{(x_A - x_{A_i})} \quad \dots \dots \dots (20)$$

Assume a column where a gas and a liquid are contacted. At any point (P) in the column, the gas phase has a mole fraction of A (certain composition of A) that is  $y_A$ . And the liquid has a mole fraction of A (certain composition of A) that is  $x_A$ . Then at that point an equilibrium between the gas phase and the liquid phase exist at  $y_{A_i}$  and  $x_{A_i}$  at point (m)



In the above figure plot the equilibrium data and also and point (p). Draw a straight line from point (P) to intersect the equilibrium curve at point (1), let it be q.

The slop of this straight line (pq) is:

$$Slop = \frac{y_A - y_{A_i}}{x_A - x_{A_i}} = -\frac{K'_x}{K'_y}$$

Then, to estimate the interface composition, we must know the mass transfer coefficient for both gas phase and liquid phase also the equilibrium data must be known.

The equilibrium data are presented by a curve for concentrated solution, and by a straight line for dilute solution.

Case 2:

For uni-molecular diffusion (mass transfer of A through stagnant layer of B)

Let  $y_A = y_{Ab}$

and  $x_A = x_{Ab}$

$$N_A = K_y (y_A - y_{A_i}) = K_x (x_{A_i} - x_A) \quad \text{--- (21)}$$

Or

$$N_A = \frac{K'_y}{y_{A_{iLM}}} (y_A - y_{A_i}) = \frac{K'_x}{x_{A_{iLM}}} (x_{A_i} - x_A) \quad \text{--- (22)}$$

Then

$$-\frac{K_x}{K_y} = \frac{(y_A - y_{A_i})}{(x_A - x_{A_i})} \quad \text{--- (23)}$$

But the slop of the drawn between points (P) & (m) is

$$\text{Slop} = \frac{y_A - y_{A_i}}{x_A - x_{A_i}} = -\frac{K'_x}{K'_y}$$

Therefore substitute  $K_y$  and  $K_x$  by there equivalents as

$$K_y = \frac{K'_y}{y_{A_{iLM}}}$$

And

$$K_x = \frac{K'_x}{x_{A_{iLM}}}$$

These relations must be found from the previous section

Therefore the slop for this case is:

$$\text{Slop} = -\frac{K'_x / x_{A_{iLM}}}{K'_y / y_{A_{iLM}}} = \frac{y_A - y_{A_i}}{x_A - x_{A_i}}$$

Where



$$x_{A_{iLM}} = \frac{(1 - x_A) - (1 - x_{A_i})}{\ln \frac{(1 - x_A)}{(1 - x_{A_i})}}$$

And

$$y_{A_{iLM}} = \frac{(1 - y_{A_i}) - (1 - y_A)}{\ln \frac{(1 - y_{A_i})}{(1 - y_A)}}$$

From the slop equation we can conclude that there is a difficulty in calculating the interface composition ( $y_{A_i}$  and  $x_{A_i}$ ), because they are already exist in the left hand side of the slop equation. This problem will be solved by trail and error by following these steps:

- 1- Assume a value for ( $y_{A_{iLM}}$  and  $x_{A_{iLM}}$ ) and let it be equal to (1).
- 2- Calculate the slop.
- 3- Plot the line (pq).
- 4- From the intersection point read  $x_{Ai}$  and  $y_{Ai}$ .
- 5- Calculate ( $y_{A_{iLM}}$  and  $x_{A_{iLM}}$ ), then recalculate the slop of the line (pq) and let it be (slop)<sub>2</sub> if the value of the two slops are equal then the assumed values of ( $y_{A_{iLM}}$  and  $x_{A_{iLM}}$ ) is correct. If not, then use the value of (slop)<sub>2</sub> to estimate a new values of  $x_{Ai}$  and  $y_{Ai}$  by repeating steps (3-5) until you will reach not more the 10% change in the value of the slop.

Note:

For dilute solutions ( $y_{A_{iLM}}$  and  $x_{A_{iLM}}$ ) are equal to (1)

### Overall driving force and overall mass transfer coefficient

Because of difficulties in measuring the interface composition and the individual mass transfer coefficients in some cases, another driving force and coefficients are used, that is the overall driving force and the overall mass transfer coefficient.

Again, assume a column where a gas and a liquid are contacted. At any point (P) in the column, the gas phase has a mole fraction of A (certain composition of A) that is  $y_A$ , and the liquid has a mole fraction of A (certain composition of A) that is  $x_A$ . Then at that point which we will call point (1), equilibrium between the gas phase and the liquid phase exist at  $y_{A_i}$  and  $x_{A_i}$ . From point P plot a vertical line to intersect the equilibrium curve at point (2), where  $y = y_A^*$  and  $x = x_A$ . And plot a horizontal line

from point (p) to intercept the equilibrium curve at point (3) at this point  $y = y_A$  and  $x = x_A^*$ .

$(y_A - y_A^*)$  is called the overall driving force for the gas phase, and

$(x_A^* - x_A)$  is called the overall driving force for the liquid phase.

The slope of the equilibrium curve at point (1) is  $m_1$ :

$$m_1 = \frac{y_A - y_{A_i}}{x_A - x_{A_i}}$$

The slope of the equilibrium curve at point (2) is  $m_2$ :

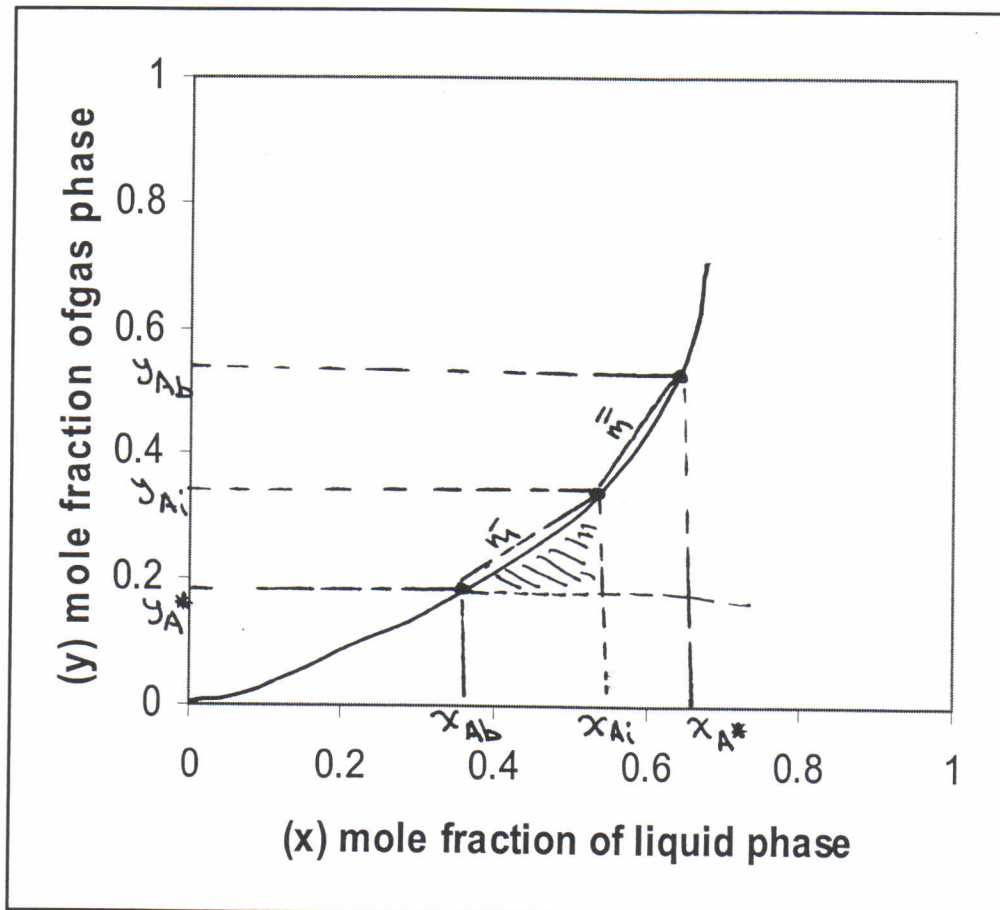
$$m_2 = \frac{y_{A_i} - y_A^*}{x_A - x_{A_i}}$$

The slope of the equilibrium curve at point (3) is  $m_3$ :

$$m_3 = \frac{y_A - y_{A_i}}{x_A^* - x_{A_i}}$$

The slopes of the equilibrium curve at points 1, 2, and 3 are equivalent if the solution is a dilute solution, that is

$$m_1 = m_2 = m_3$$



Now, the rate of mass transfer which will be calculated based on overall driving force can be written as follow:

A) For EMD

$$N_A = K'_{oy}(y_A - y_A^*) \quad \text{--- (24)}$$

B) For UMD

$$N_A = K_{oy}(y_A - y_A^*) \quad \text{--- (25)}$$

Where

$K'_{oy}$  and  $K_{oy}$  are the overall mass transfer coefficients with units (kmol/m<sup>2</sup>. s.mol fract), which are based on the overall driving force in the gas phase.

$y_A^*$  : is the value of the mole fraction of A in the gas phase that would be in equilibrium with  $x_A$ .

Or, and for the two cases

$$N_A = K'_{ox}(x_A^* - x_A) \quad \text{--- (26)}$$

$$N_A = K_{ox}(x_A^* - x_A) \quad \text{--- (27)}$$

Where

$K'_{ox}$  and  $K_{ox}$  are the overall mass transfer coefficients with units (kmol/m<sup>2</sup>. s.mol fract), which are based on the overall driving force in the liquid phase.

$x_A^*$  : is the value of the mole fraction in the liquid phase that would be in equilibrium with  $y_A$ .

The relationship between the overall mass transfer coefficient and the individual mass transfer coefficient

A) Case 1 EMD

We can write the overall driving force as follow by adding and subtracting  $y_{A_i}$ , that is:

$$y_A - y_A^* = (y_A - y_{A_i}) + (y_{A_i} - y_A^*)$$

But

$$m_2 = \frac{y_{A_i} - y_A^*}{x_A - x_{A_i}}$$

Then

$$y_A - y_A^* = (y_A - y_{A_i}) + m_2(x_A - x_{A_i})$$

Substitute each driving force by its equivalent in the EMD case, that is:

$$(67)$$



$$\frac{N_A}{K'_{oy}} = \frac{N_A}{K'_y} + \frac{m_2^* N_A}{K'_x}$$

Finally

$$\frac{1}{K'_{oy}} = \frac{1}{K'_y} + \frac{m_2}{K'_x} \quad \text{--- (28)}$$

Equation 174 can be explained as follow:

The total resistance for mass transfer is equal to the summation of individual resistance for each phase (the gas phase & the liquid phase).

The same procedure could be made to find the relationship between the over all mass transfer coefficient for the liquid phase and the individual mass transfer coefficients, the relation is:

$$\frac{1}{K'_{ox}} = \frac{1}{m_3 K'_y} + \frac{1}{K'_x} \quad \text{--- (29)}$$

For the dilute solutions:

$$m_1 = m_2 = m_3 = m$$

Then:

$$\frac{1}{K'_{oy}} = \frac{1}{K'_y} + \frac{m}{K'_x} \quad \text{--- (30)}$$

$$\frac{1}{K'_{ox}} = \frac{1}{m K'_y} + \frac{1}{K'_x} \quad \text{--- (31)}$$

B) Case 1 UMD

In this case only solute A is transferred through the interface and no B is transferred. As shown in above:

$$K_y = \frac{K'_y}{y_{A_{iLM}}}$$

And

$$K_x = \frac{K'_x}{x_{A_{iLM}}}$$

Then

$$N_A = \frac{K'_y}{y_{A_{iLM}}} (y_A - y_{A_i}) = \frac{K'_x}{x_{A_{iLM}}} (x_{A_i} - x_A) \quad \text{--- (32)}$$

For the over all driving force, and by using the over all mass transfer coefficient, the mass transfer rate is calculated by:

(68)



$$N_A = \frac{K'_{oy}}{y_{A_{LM}}^*} (y_A - y_A^*) = \frac{K'_{ox}}{x_{A_{LM}}^*} (x_A^* - x_A) \quad \text{--- (33)}$$

Where:

$$x_{A_{LM}}^* = \frac{(1 - x_A) - (1 - x_A^*)}{\ln \frac{(1 - x_A)}{(1 - x_A^*)}}$$

And

$$y_{A_{LM}}^* = \frac{(1 - y_A) - (1 - y_A^*)}{\ln \frac{(1 - y_A)}{(1 - y_A^*)}}$$

Using the same procedure done in the EMD, we can find the relationship between the overall mass transfer coefficient and the individual mass transfer coefficients, as shown:

For the gas phase:

$$\frac{y_{A_{LM}}^*}{K'_{oy}} = \frac{y_{A_{iLM}}}{K'_y} + \frac{m_2 x_{A_{iLM}}}{K'_x} \quad \text{--- (34)}$$

For the liquid phase:

$$\frac{x_{A_{LM}}^*}{K'_{ox}} = \frac{y_{A_{iLM}}}{m_3 K'_y} + \frac{x_{A_{iLM}}}{K'_x} \quad \text{--- (35)}$$

Again for dilute solution when:

$$m_1 = m_2 = m_3 = m$$

Then

$$x_{A_{LM}}^* = y_{A_{LM}}^* = x_{A_{iLM}} = y_{A_{iLM}} = 1$$

Question:

Is there an overall mass transfer coefficient base on partial pressure for the gas phase, and other one based on concentration for the liquid phase?

Answer:

Yes, these are presented as  $K_{og}$ , and  $K_{ol}$ .

Question:

Find the relationships between these overall mass transfer coefficients and the individual mass transfer coefficient?

(69)