

# CHAPTER 1

# MASS TRANSFER

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## **1.1 Introduction To Mass Transfer**

Generally in a nature there is a tendency for any species or matter to slowly move from places of high concentration to lower concentration.

e.g.

when population grows, city dwellers tend to build houses and settle outside on peripheries of main cities.

Another general examples of mass transfer process

- a) Liquid in an open pail of water evaporates into still air because of the difference in concentration of water vapor at the water surface and the surrounding air. There is driving force from the water surface to the surrounding air
- b) A piece of sugar added to a cup of coffee eventually dissolves by itself and diffuses to the surrounding solution.
- c) In catalytic reaction, the reactants diffuse from the surrounding medium to the catalyst surface, where reaction occur.



Mass transfer is often seen in many situations. Have you ever sprayed perfume in one corner of the room and smelled it a few seconds later in another corner of the room? The perfume moved from the area where it was sprayed (high concentration) to an area where there was less perfume (low concentration)

What would happen to a pot of spaghetti if you left it soaking in water at room temperature for a couple of hours...



- Here's a hint: Mass Transfer is the tendency of a component in a mixture to travel from a region of high concentration into an area of low concentration.
- Applying this to spaghetti. If the mixture is water and spaghetti, the water will want to move into the spaghetti where the concentration is lower.
- If the pasta were left in water at room temperature long enough, it seems the water would diffuse into it until there were equal numbers of water molecules inside and outside the pasta.

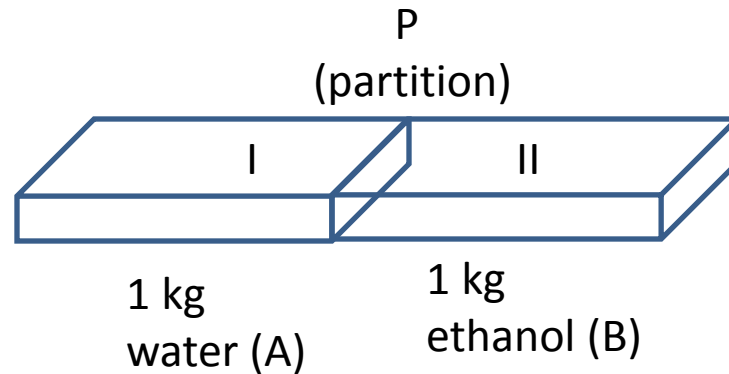
Always the transfer is observed from high concentration to low concentration regions

This phenomenon is called diffusion

In diffusion

Species **A** moves from a region of **high concentration** to the region of **low concentration**





Imagine the partition to be carefully removed, thus allowing diffusing of both liquids to occur. When the **concentration is uniform**, the diffusion will stop.

Mass transfer by ordinary molecular diffusion occurs because of a difference ( $\Delta C$ ) or gradient ( $-dC/dz$ ): that is a species diffuses in the direction of decreasing concentration .

In describing this quantitatively, we need an appropriate measure rate  $\rightarrow$   
Rates will most conveniently described in term **MOLAR FLUX**

$$J_A \text{ (mol/s.m}^2 \text{)}$$

## 1.2 Fick's Law for Molecular Diffusion

Molecular diffusion or molecular transport can be define as the transfer of individual molecules through a fluid by means of the random, individual movements of the molecules.

**Fick's law** applied when the whole bulk fluid is **not moving** and diffusion of the molecules is due to a **concentration gradient**. General Fick's law equation can be written as follows for binary mixture of A and B:

$$J_{AZ} = -cD_{AB} \frac{dx_A}{dz}$$

Where

$J_{AZ}$ = the molar flux of component A in the z direction (kgmolA/s.m<sup>2</sup>)

$c$ = total concentration of A and B (kgmol/m<sup>3</sup>)

$x_A$ = is the mole fraction of A in the mixture A and B

$D_{AB}$ = the molecular diffusivity of the molecule A in B (m<sup>2</sup>/s)

$z$ = distance of diffusion (m)

Diffusion can be represented by a basic equation. Thus rate of diffusion can be expressed as a flux  $J_A$  (gmol/s.m<sup>2</sup>)

$$J_{AZ} = -cD_{AB} \frac{dx_A}{dz}$$

Where

$J_{AZ}$  = the molar flux of component A in the z direction (kgmolA/s.m<sup>2</sup>)

Is the movement of objects from one point to another in a given time. The flux is what we are measuring when studying diffusion.

Units: the units of moles / (time \* area)

$C$  = total concentration of A and B (kgmol/m<sup>3</sup>)

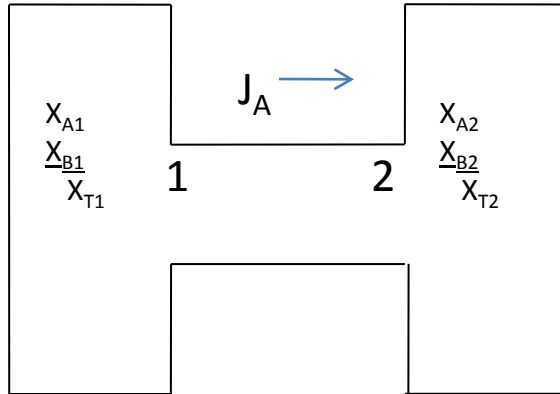
$x_A$  = is the mole fraction of A in the mixture A and B

$D_{AB}$  = the molecular diffusivity of the molecule A in B (m<sup>2</sup>/s)

The diffusivity is the constant that describes how fast or slow an object diffuses.

Units: the units of area / time

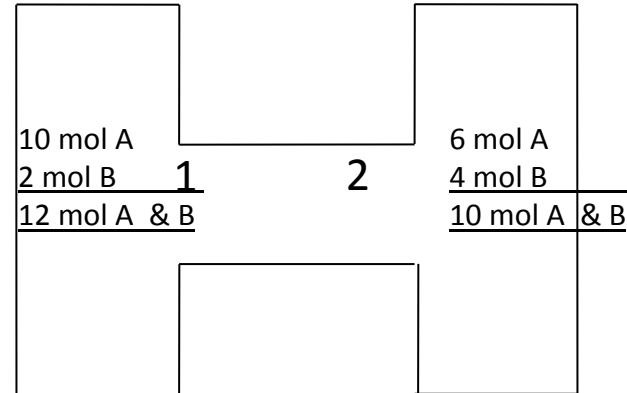
$Z$  = distance of diffusion (m)



$$X_{A1} = 10/12$$

$$X_{B1} = 2/12$$

$$X_{T1} = 10/12 + 2/12 = 1$$



$$X_{A2} = 6/10$$

$$X_{B2} = 4/10$$

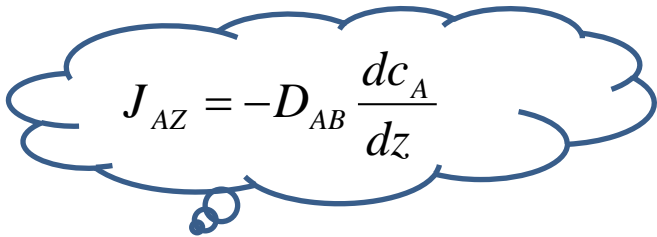
$$X_{T2} = 6/10 + 4/10 = 1$$



Fick's Law for steady state diffusion of a binary mixture of A and B may also be written in many other way such as

$$J_{AZ} = -cD_{AB} \frac{dx_A}{dz}$$

$$J_{AZ} = -D_{AB} \frac{d(C_A)}{dz}$$


$$J_{AZ} = -D_{AB} \frac{dc_A}{dz}$$

$$J_{AZ} = -D_{AB} \frac{\int_{z_{A1}}^{z_{A2}} dc_A}{\int_{z_{A1}}^{z_{A2}} dz}$$



$$J_{AZ} = -D_{AB} \frac{c_{A2} - c_{A1}}{z_2 - z_1}$$



$$J_{AZ} = D_{AB} \frac{c_{A1} - c_{A2}}{z_2 - z_1}$$

In term of partial pressure

$$PV=nRT$$

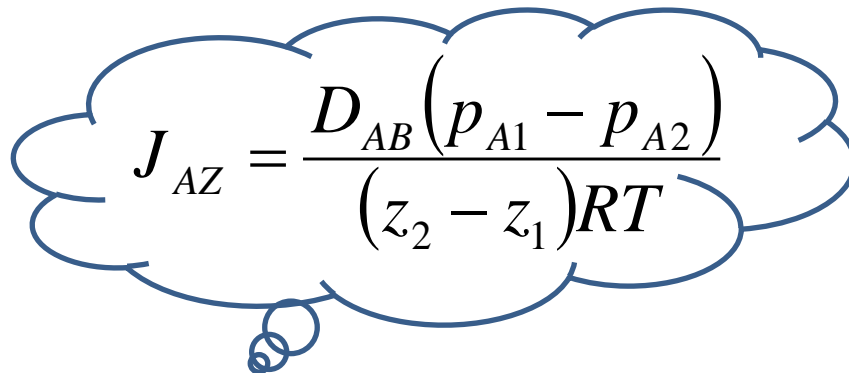
$$P/RT=n/V=C$$

$$p_{A1}/RT = c_{A1}$$

$$J_{AZ} = D_{AB} \frac{c_{A1} - c_{A2}}{z_2 - z_1}$$

$$J_{AZ} = \frac{D_{AB}}{z_2 - z_1} \cdot c_{A1} - c_{A2}$$

$$J_{AZ} = \frac{D_{AB}}{z_2 - z_1} \cdot \frac{p_{A1} - p_{A2}}{RT}$$


$$J_{AZ} = \frac{D_{AB} (p_{A1} - p_{A2})}{(z_2 - z_1) RT}$$



### Example 6.1-1

A mixture of He and N<sub>2</sub> gas is contained in a pipe at 298 K and 1 atm total pressure which constant throughout. At the end of the pipe at point 1 the partial pressure  $p_{A1}$  of He is 0.6 atm and at the other end 0.2 m,  $p_{A2}=0.2$  atm. Calculate the flux of He at steady state if  $D_{AB}$  of He-N<sub>2</sub> mixture is  $0.687 \times 10^{-4} \text{m}^2/\text{s}$ . Used  $R = 82.057 \times 10^{-3} \text{m}^3 \cdot \text{atm}/(\text{kgmol} \cdot \text{K})$

## 1.3 MOLECULAR DIFFUSION IN GASES

### 1.3A EQUIMOLAR COUNTERDIFFUSION IN GASES

Figure 1 is given of 2 gases A and B at constant total pressure in 2 large chambers connected by a tube where molecular diffusion at steady state is occurring.

$p_{A1} > p_{A2}$  and  $p_{B2} > p_{B1}$  ← **different in concentration gradient...**

Molecules of A diffuse to the right and B to the left.

The net moles of A diffusing to right must equal the net moles of B to the left.

$$J_{AZ} = -J_{BZ}$$

$$J_{AZ} = -D_{AB} \frac{dc_A}{dz} = -J_{BZ} = -(-D_{BA} \frac{dc_B}{dz})$$

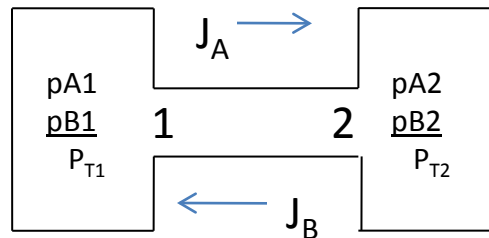


Figure 1

### Example 6.2-1

Ammonia gas (A) is diffusing through a uniform tube 0.1 m long containing  $N_2$  gas (B) at  $1.0132 \times 10^5$  Pa pressure and 298 K. At point 1,  $p_{A1} = 1.013 \times 10^4$  Pa and point 2  $p_{A2} = 0.507 \times 10^4$  Pa. The diffusivity  $D_{AB} = 0.230 \times 10^{-4} \text{ m}^2/\text{s}$ . Calculate the flux  $J_A$ . Used  $R = 82.057 \times 10^{-3} \text{ m}^3 \cdot \text{atm}/(\text{kgmol} \cdot \text{K})$

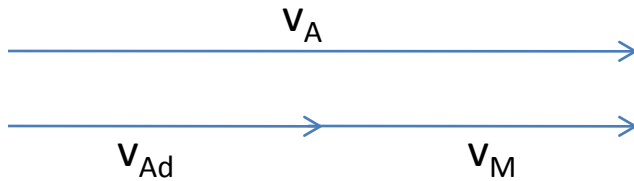
### 1.3B DIFFUSION PROCESS TOGETHER WITH CONVECTION

Up to now we consider Fick's Law for a diffusion in a **stationary fluid**; that is there has no net **movement or convective** flow of the entire phase of the binary mixture A and B

Diffusion flux  $J_A$  occurred because of the **concentration gradient**

$$J_A \text{ (kg mol A/s.m}^2\text{)} = v_{Ad} C_A \left( \frac{m}{s} \frac{\text{kgmolA}}{m^3} \right)$$

Now let us consider what happens when the whole fluid is moving in bulk or convective flow to the right. **Component A still diffusing to the right, together with the moving fluid.**



$v_m$  = velocity of the bulk  
 $v_{Ad}$  = diffusion velocity of A  
 $v_A$  = actual velocity of A

Then  $v_A = v_{Ad} + v_m$  .....Eq. 1

Multiplying with  $C_A$       $C_A v_A = C_A v_{Ad} + C_A v_m$  .....Eq.2

.....Eq.3

**total flux of A**  
 relative to the  
 stationary point

$$N_A = J_A + C_A v_m$$

Blue arrows point from the text labels to the terms in the equation: one from 'total flux of A' to  $N_A$ , one from 'diffusion flux of A' to  $J_A$ , and one from 'convective flux of A' to  $C_A v_m$ .

**diffusion flux of A**  
 relative to the moving fluid

**convective flux of A**  
 relative to the stationary  
 point

Let  $N$  be the total convective flux

$$N = c v_M = N_A + N_B \quad \text{.....Eq.4}$$

$$v_M = N_A + N_B / c \quad \text{.....Eq.5}$$

Substituting equation..5 into equation ..3

$$N_A = J_A + C_A (N_A + N_B / c)$$

$$N_A = J_A + c_A / c (N_A + N_B)$$

$$N_A = J_A + \frac{c_A}{c} (N_A + N_B)$$

$$N_A = -c D_{BA} \frac{dx_A}{dz} + \frac{c_A}{c} (N_A + N_B)$$

Final equation for **diffusion plus convection** to use when the flux  $N_A$  is used, which is **relative to a stationary point**

.....Eq.6



### 1.3C DIFFUSION THROUGH STAGNANT, NONDIFFUSING B

**Diffusion of A through stagnant or nondiffusing B at steady state.**

One boundary at the end of diffusion path is **impermeable to component B**

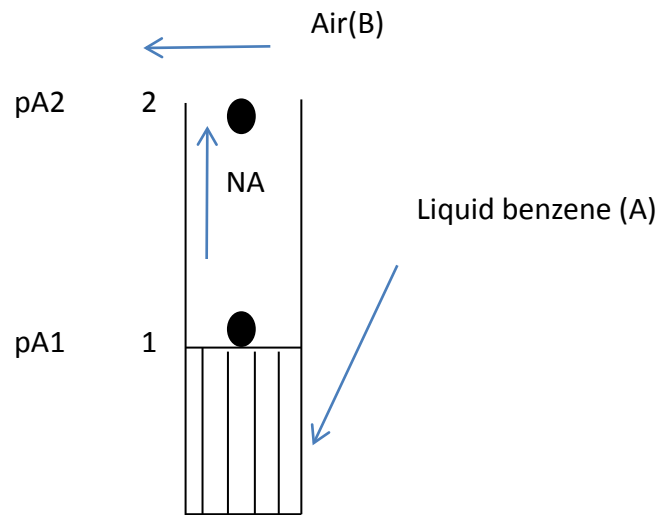
Example **evaporation of benzene (A)**, at the bottom of a narrow tube, where a large amount of inert/nondiffusing air, B passed over the top.

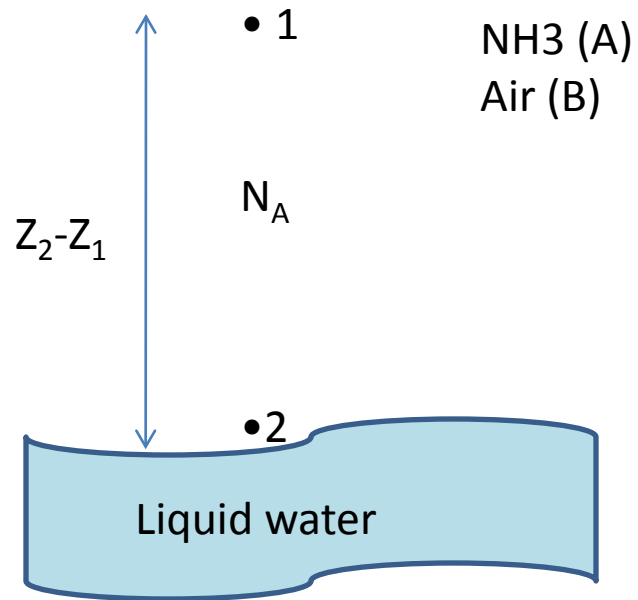
**Benzene (A) diffuses through the air (B) in the tube**

The boundary at liquid surface point 1, impermeable to air (air insoluble in benzene liquid)

Hence, **air (B) cannot diffuse into the surface**. Thus  $N_B=0$

At point 2, partial pressure  $p_{A2}=0$ , since a large volume of air is passing by.





**Absorption of NH3 (A) vapor** which is in air (B) **by water**

**Water is impermeable** to the **air (B)**  $\rightarrow N_B=0$

Neglected the evaporation of water

$$N_A = J_A + \frac{c_A}{c}(N_A + N_B) \quad \text{.....Eq.7}$$

$$N_A = -cD_{BA} \frac{dx_A}{dz} + \frac{c_A}{c}(N_A + 0) \quad \text{.....Eq.8}$$

Substituting  $c=P/RT$ ,  $p_A=x_AP$  and  $c_A/c=p_A/P$  into Eq. 8

$$N_A = -\frac{D_{AB}}{RT} \frac{dp_A}{dz} + \frac{p_A}{P} N_A \quad \text{.....Eq.9}$$

Rearranging and integrating



$$N_A = \frac{D_{AB}P}{RT(z_2 - z_1)} \ln \frac{P - p_{A2}}{P - p_{A1}} \quad \text{.....Eq.10}$$

Eq .7 is the final equation to calculated the flux of A. It is often written in another form

$$N_A = \frac{D_{AB}P}{RT(z_2 - z_1)p_{BM}} (p_{A1} - p_{A2}) \quad \text{.....Eq.11}$$

$$P = p_{A1} + p_{B1}$$

$$P = p_{A2} + p_{B2}$$

Where

$$p_{BM} = \frac{p_{B2} - p_{B1}}{\ln(p_{B2} / p_{B1})} = \frac{p_{A1} - p_{A2}}{\ln\left[\frac{(P - p_{A2})}{(P - p_{A1})}\right]} \quad \text{.....Eq.12}$$

### Example 6.2-2

Water in the bottom of narrow metal tube is held at a constant temp of 293 K. The total press of air is  $1.01325 \times 10^5$  pa and the temperature is 293 K. Water evaporates and diffuses through the air in the tube and the diffusion path  $z_2 - z_1$  is 0.1524m long. Diffusivity is  $0.25 \times 10^{-4}$  m<sup>2</sup>/s. Vapor pressure of water at 293 K is  $2.341 \times 10^3$  Pa. Calculate the rate of evaporation.

## 1.4 MOLECULAR DIFFUSION IN LIQUIDS

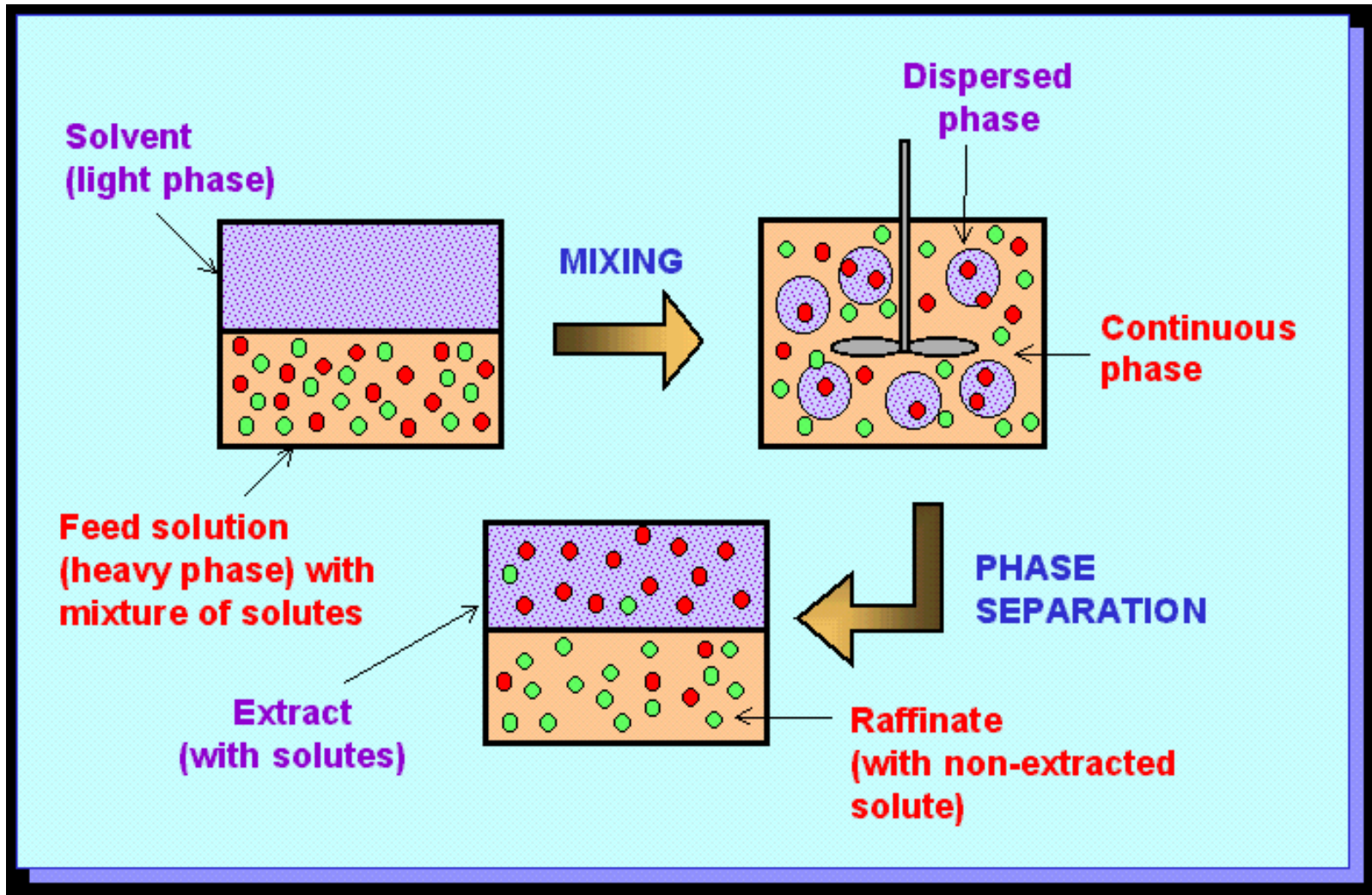
Example diffusion of solutes in liquid

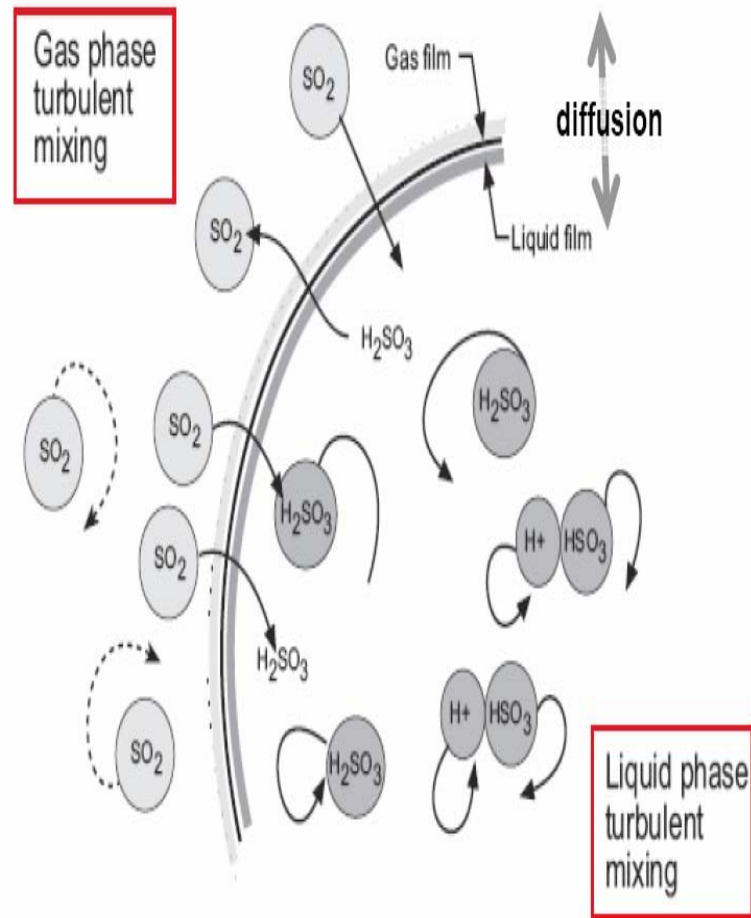
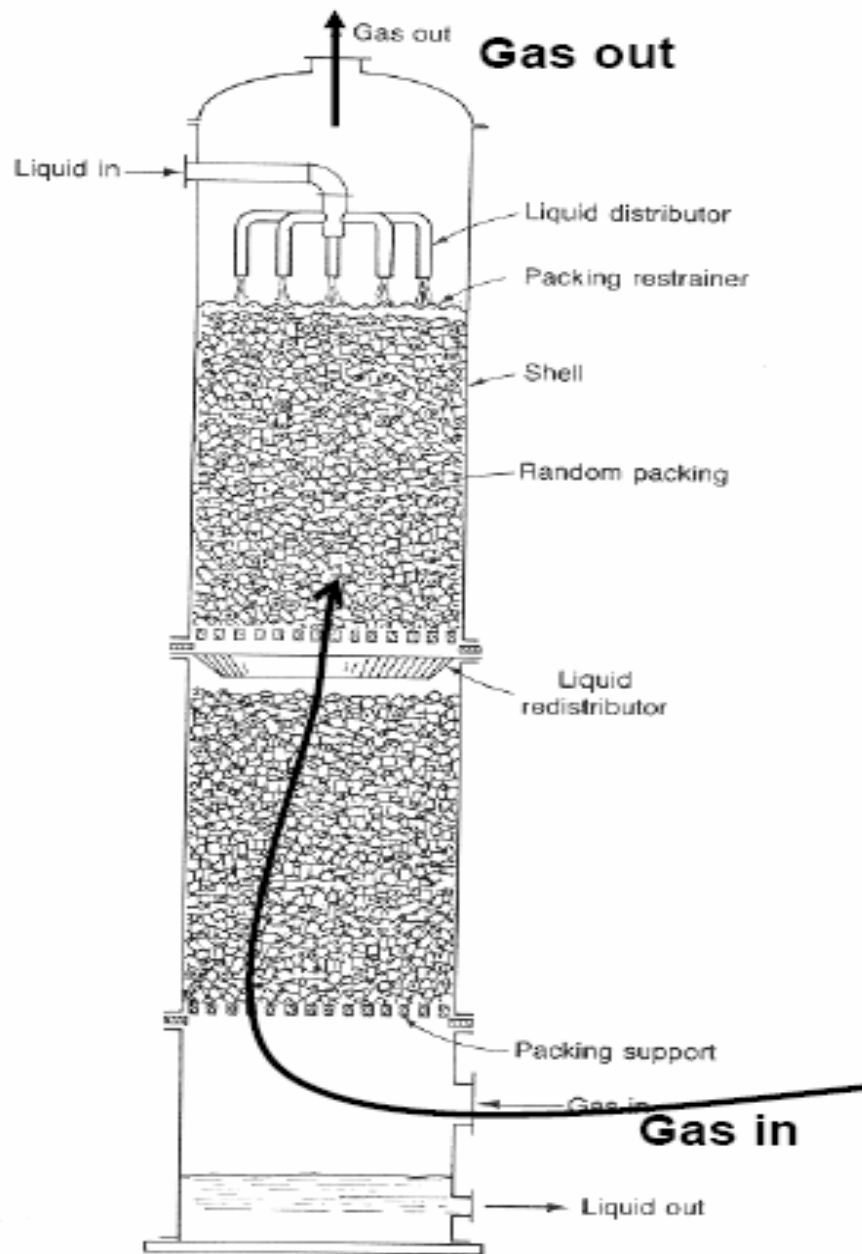
Liquid-liquid extraction  
Gas absorption  
Oxygenation of rivers by the air

Since the molecules in a liquid are packed together much more closely than in gases, the density and the resistance to **diffusion in liquid much greater** → flux in liquid is lower than flux in a gas

Difference of **diffusion in gases** than **diffusion in liquid** →

Diffusion in liquid **often quite dependent on concentration** of the diffusing components









## Equimolar counterdiffusion

Starting from general equation  $N_A = -cD_{BA} \frac{dx_A}{dz} + \frac{c_A}{c}(N_A + N_B)$

For equimolar counter diffusion  $N_A = -N_B$  than the equation become

$$N_A = -cD_{BA} \frac{dx_A}{dz} \quad \longrightarrow \quad N_A = D_{AB} \frac{c_{A1} - c_{A2}}{z_2 - z_1}$$

$$N_A = D_{AB} \frac{c_{A1} - c_{A2}}{z_2 - z_1} = \frac{D_{AB} c_{av} (x_{A1} - x_{A2})}{z_2 - z_1}$$

where

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

## Diffusion of A through nondiffusing B

### Example

Dilute solution of propionic acid (A) in water (B) solution being contact with toluene

Only propionic acid (A) diffuses through water phase,

to the boundary

and then into toluene phase.

The toluene – water is a barrier to diffusion of B and  $N_B = 0$

$$N_A = \frac{D_{AB}P}{RT(z_2 - z_1)p_{BM}}(p_{A1} - p_{A2}) \quad \longrightarrow \quad N_A = \frac{D_{AB}c_{av}}{(z_2 - z_1)x_{BM}}(x_{A1} - x_{A2})$$

where

$$x_{BM} = \frac{x_{B2} - x_{B1}}{\ln(x_{B2}/x_{B1})}$$

### Example 6.3-1

An ethanol (A)-water (B) solution in the form of a stagnant film 2.0 mm thick at 293 K is in contact at one surface with an organic solvent in which ethanol is soluble and water insoluble. At point 1 the concentration of ethanol is 16.8 wt% and the solution density is  $\rho_1 = 972.8 \text{ kg/m}^3$ . At point 2 the concentration of ethanol is 6.8 wt% and the solution density is  $\rho_2 = 988.1 \text{ kg/m}^3$ . The diffusivity of ethanol is  $0.74 \times 10^{-9} \text{ m}^2/\text{s}$ . Calculate the flux of ethanol  $N_A$ .

## MOLECULAR DIFFUSION IN SOLIDS

Diffusion of gases, liquid and solid → in solids are generally slower than rates in liquids and gases.

Example

The diffusion of phosphorus and boron into silicon

Diffusion of nitrogen or hydrogen in to the rubber

Diffusion of water into foodstuffs

Reaction process, diffusion of solution into the catalyst

There are two types of diffusion in solid :

- Diffusion in solid following Ficks law
  - Diffusion in solids does not depend on the actual structure of the solid
- Diffusion in porous solid where the actual structure and void channels are important.

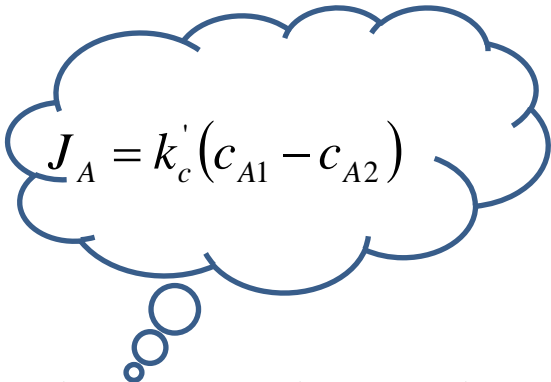
## 1.6 MASS TRANSFER COEFFICIENT

Fick's Law for steady state diffusion of a binary mixture A and B, written as:

Also be written in

$$J_A = -cD_{AB} \frac{dx_A}{dz}$$

$$J_A = \frac{D_{AB}}{z_2 - z_1} (c_{A1} - c_{A2})$$


$$J_A = k'_c (c_{A1} - c_{A2})$$

$k'_c = \text{constant}$ ,  $k'_c = D_{AB}/dz$

Known as mass transfer coefficient

### 1.6.1 Mass transfer coefficient for equimolar counterdiffusion

Equation for mass transfer :

$$N_A = k'_c (c_{A1} - c_{A2})$$

If  $y_A$  is mole fraction in a gas phase and  $x_A$  in a liquid phase, then the equation can be written as follows

$$\text{Gases : } N_A = k'_c (c_{A1} - c_{A2}) = k'_G (p_{A1} - p_{A2}) = k'_y (y_{A1} - y_{A2})$$

$$\text{Liquid : } N_A = k'_c (c_{A1} - c_{A2}) = k'_L (c_{A1} - c_{A2}) = k'_x (x_{A1} - x_{A2})$$

Substituting  $y_{A1} = c_{A1}/c$  and  $y_{A2} = c_{A2}/c$  into the equation

$$N_A = k'_c (c_{A1} - c_{A2}) = k'_y (y_{A1} - y_{A2}) = k'_y \left( \frac{c_{A2}}{c} - \frac{c_{A1}}{c} \right) = \frac{k'_y}{c} (c_{A1} - c_{A2})$$

Hence

$$k'_c = \frac{k'_y}{c}$$

### 1.6.2 Mass transfer coefficient for A diffusing through stagnant, nondiffusing B.

$$N_A = \frac{k'_c}{x_{BM}} (c_{A1} - c_{A2}) = k_c (c_{A1} - c_{A2})$$

where

$$= \frac{k'_x}{x_{BM}} (x_{A1} - x_{A2}) = k_x (x_{A1} - x_{A2})$$

$$x_{BM} = \frac{x_{B2} - x_{B1}}{\ln(x_{B2} / x_{B1})}$$

Gases:  $N_A = k_c (c_{A1} - c_{A2}) = k_G (p_{A1} - p_{A2}) = k_y (y_{A1} - y_{A2})$

Liquids:  $N_A = k_c (c_{A1} - c_{A2}) = k_L (c_{A1} - c_{A2}) = k_x (x_{A1} - x_{A2})$

$$N_A = \frac{k'_c}{x_{BM}} (c_{A1} - c_{A2}) = k_x (x_{A1} - x_{A2}) = k_x \left( \frac{c_{A1}}{c} - \frac{c_{A2}}{c} \right)$$

Hence  $\frac{k'_c}{x_{BM}} = \frac{k_x}{c}$

### Example 7.2-1

A large volume of pure B at 2 atm pressure is flowing over a surface from which pure A is vaporizing. The liquid A completely wets the surface, which is a blotting paper. Hence the partial pressure of A at the surface is the vapor pressure at 298 K, which is 0.2 atm. The  $k'_y$  has been estimated to be  $6.78 \times 10^{-5}$  kgmol/s.m<sup>2</sup>.mol frac. Calculate  $N_A$  the vaporization rate,  $k_y$  and  $k_G$ .



## 1.7 INTERPHASE MASS TRANSFER

Figure 10.41

- Assuming solute A is diffusing from the bulk phase G to the liquid phase L, it must pass through phase G → through the interface → through phase L in series
- **Concentration gradient** must exist to cause this mass transfer through the resistances in each phase as shown in Fig 10.41

The concentration in the bulk **gas phase  $y_{AG}$**

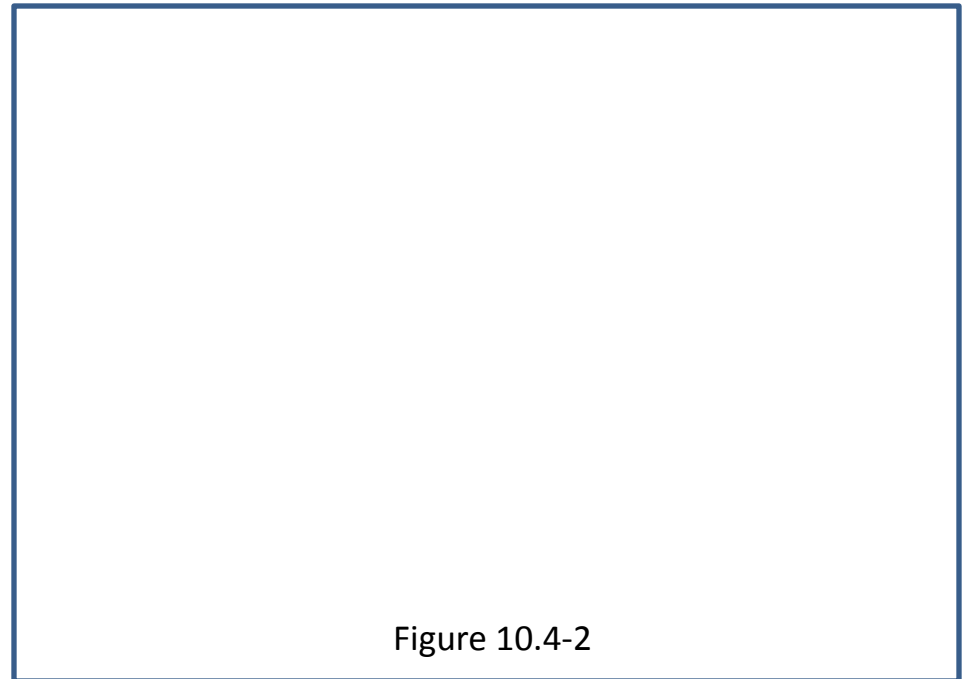
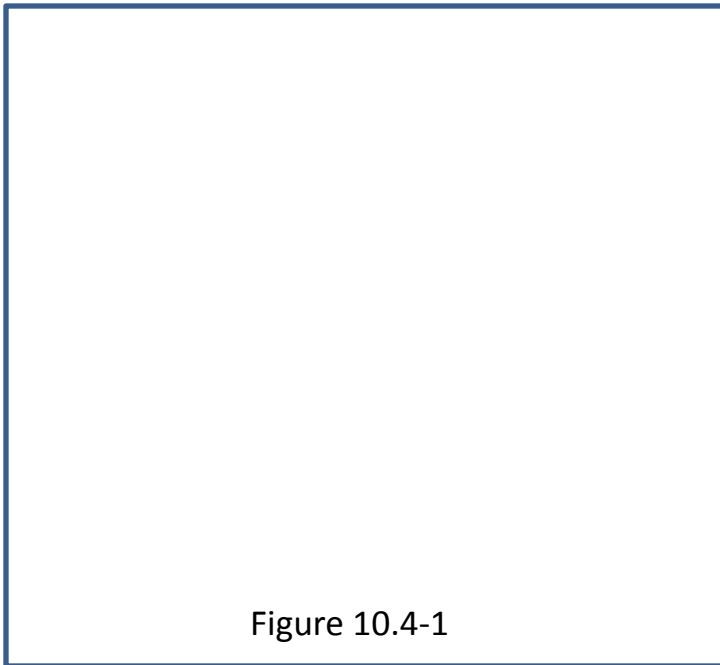
decreased to  **$y_{Ai}$  at the interface**

liquid concentration  **$x_{Ai}$  at interface**

falls to  **$x_{AL}$**

## 1.7.1 Interphase mass transfer-equimolar counter diffusion

For equimolar counterdiffusion, the concentration of Fig 10.4-1 can be plotted on x-y diagram as in Fig 10.4.2



Point P bulk phase composition  $y_{AG}, x_{AL}$

Point M, interphase concentration  $y_{Ai}$  and  $x_{Ai}$

## Equimolar counterdiffusion

For A diffusing from the gas to liquid and B in equimolar counterdiffusion from liquid to gas,

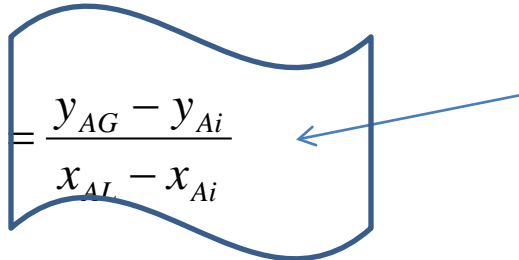
$$N_A = k'_y (y_{AG} - y_{Ai}) = k'_x (x_{Ai} - x_{AL})$$

Where:

$k'_y$  gas-phase mass transfer coefficient in kg mol/s.m<sup>2</sup>.mol frac.

$k'_x$  liquid-phase mass transfer coefficient in kg mol/s.m<sup>2</sup>.mol frac.

Rearranging above Eq.


$$\frac{k'_x}{k'_y} = \frac{y_{AG} - y_{Ai}}{x_{AL} - x_{Ai}}$$

Slope of PM

## Diffusion of A through stagnant or nondiffusing B



.....Figure 10.4.3

$$N_A = k_y (y_{AG} - y_{Ai}) = k_x (x_{Ai} - x_{AL})$$

$$\text{Where } (1 - y_A)_{iM} = \frac{(1 - y_{Ai}) - (1 - y_{AG})}{\ln[(1 - y_{Ai}) / (1 - y_{AG})]}$$

$$k_y = \frac{k'_y}{(1 - y_A)_{iM}} \quad k_x = \frac{k'_x}{(1 - x_A)_{iM}}$$

$$(1 - x_A)_{iM} = \frac{(1 - x_{AL}) - (1 - x_{Ai})}{\ln[(1 - x_{AL}) / (1 - x_{Ai})]}$$

Then

$$N_A = \frac{k'_y}{(1 - y_A)_{iM}} (y_{AG} - y_{Ai}) = \frac{k'_x}{(1 - x_A)_{iM}} (x_{Ai} - x_{AL})$$

$$\frac{-k'_x / (1 - x_A)_{iM}}{k'_y / (1 - y_A)_{iM}} = \frac{(y_{AG} - y_{Ai})}{(x_{AL} - x_{Ai})}$$

Slope of PM

### 17.3 Overall Mass-Transfer Coefficient

The overall mass transfer  $K'_y$  is defined as

$$N_A = K'_y (y_{AG} - y_A^*) \quad \text{Eq.17.1.}$$

$$N_A = k'_y (y_{AG} - y_{Ai}) = k'_x (x_{Ai} - x_{AL}) \quad \text{Eq.17.2}$$

From Fig. 10.4.2

$$y_{AG} - y_A^* = (y_{AG} - y_{Ai}) + (y_{Ai} - y_A^*) \quad \text{Eq.17.3}$$

Between point E and M the slope  $m'$

$$m' = \frac{y_{Ai} - y_A^*}{x_{Ai} - x_{AL}} \quad \text{Eq.17.4}$$

Solving Eq.17.a for  $(y_{Ai} - y_A^*)$  and substituting into Eq. 17.3

$$y_{AG} - y_A^* = (y_{AG} - y_{Ai}) + m' (x_{Ai} - x_{AL}) \quad \text{Eq.17.5}$$

Then, on substituting Eq.17.1 and 17.2 into Eq17.5 and canceling out  $N_A$

$$\frac{1}{K'_y} = \frac{1}{k'_y} + \frac{m'}{k'_x}$$

For **diffusion of A through stagnant of nondiffusing B**,  
the overall mass transfer coefficient as follows

$$\frac{1}{K'_y / (1 - y_A)_{*M}} = \frac{1}{k'_y / (1 - y_A)_{iM}} + \frac{m'}{k'_x / (1 - x_A)_{iM}}$$

Where...

$$(1 - y_A)_{*M} = \frac{(1 - y_A^*) - (1 - y_{AG})}{\ln \left[ \frac{(1 - y_A^*)}{(1 - y_{AG})} \right]}$$