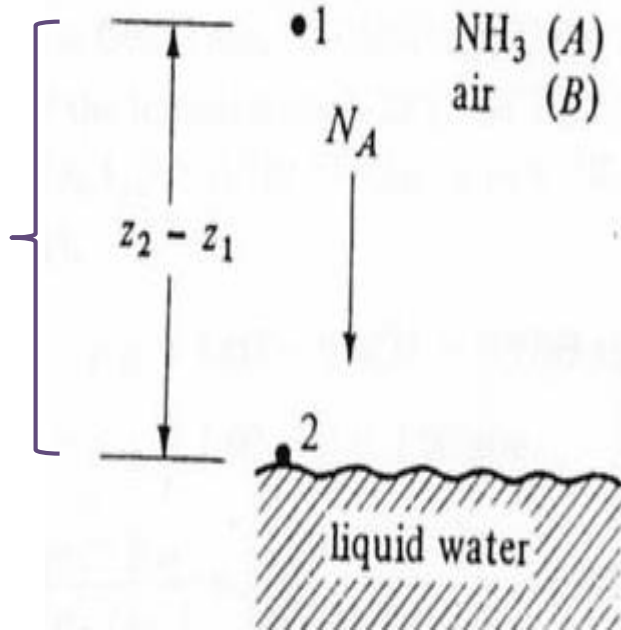


# Film Theory

- **In the previous lectures, diffusion and mass transfer within fluids were considered.**
- **However, in separation processes such as absorption, distillation and extraction) the mass is transferred across an interface between a gas and a liquid or between two liquids.**

Diffusion  
within  
fluids



Diffusion  
between  
fluids

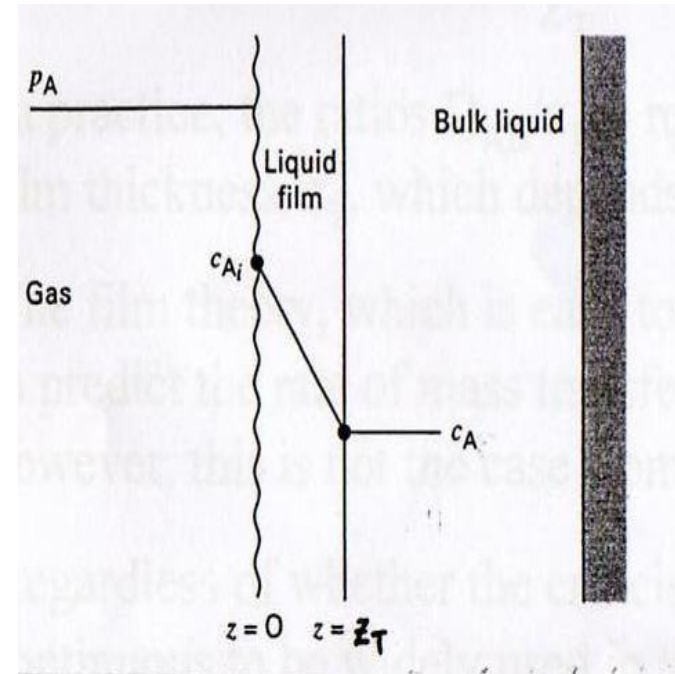
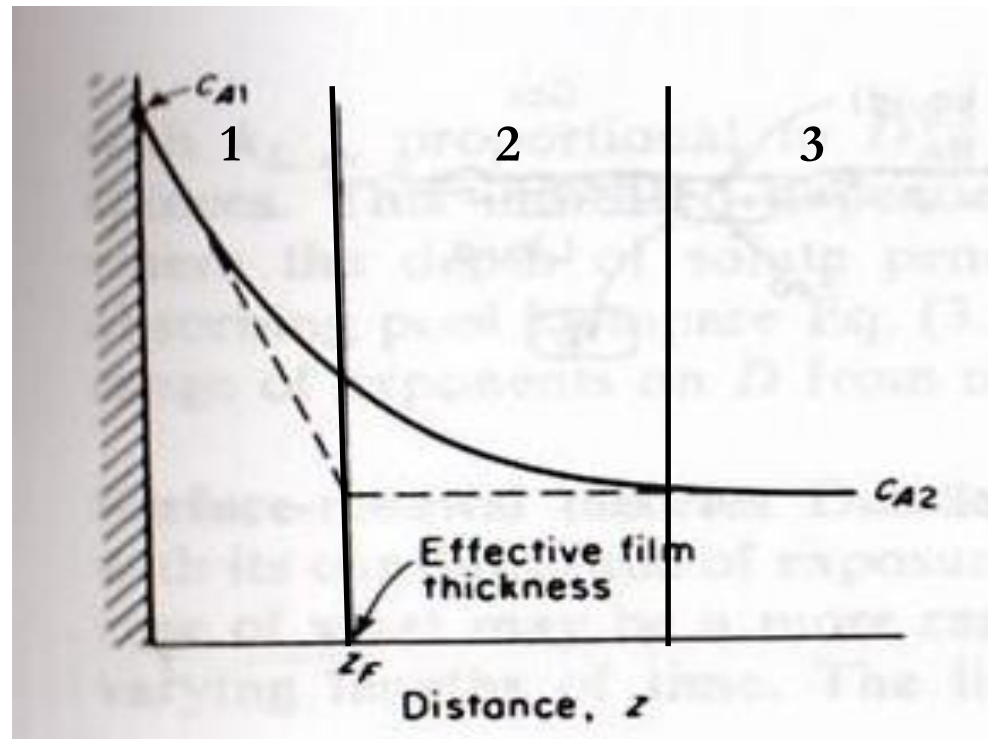


Figure 13

- **Several models have been developed to describe mass transfer at a fluid phase boundary. The earliest and simplest of these is the film theory proposed by Whitman in 1923.**
- **The film theory is based on the assumption that for a fluid flowing turbulently over a solid, the entire resistance to mass transfer resides in a stagnant film in the fluid next to the surface.**
- **Consider the case of a fluid flowing in a cylinder in which a solid dissolves from the walls of the cylinder into the fluid.**
- **When a fluid flows turbulently past a solid surface, with mass transfer occurring from the surface to the fluid, the concentration-distance relation is as shown in **Figure 14.****

- The film theory postulates that the concentration will follow the broken curve of the figure, such that the entire concentration difference  $c_{A1} - c_{A2}$  is attributed to molecular diffusion within an “effective” film of thickness  $z_F$ .



**Figure 14 Film theory**

### 3 regions of mass transfer (MT) can be visualized:

Region	Position	Type of MT
1	Adjacent to the surface, a thin, viscous sublayer film is present.	Molecular diffusion, few or no eddies are present. Large concentration drop occurs across this film, slow rate of diffusion.
2	Transition/buffer region, adjacent to the first region.	Some eddies are present, MT is the sum of turbulent and molecular diffusion.
3	Adjacent to the buffer region (turbulent region).	Most of the transfer is by turbulent diffusion, with small amount by molecular diffusion. The concentration decrease is very small, eddies tend to keep the fluid concentration uniform.

# Mass Transfer Theories

- The equations developed so far can only predicts steady state mass transfer provided the film thickness ( $z_T$ ) is known.
- However, in most cases, the value of  $z_T$  is not known as turbulent flow is desired to increase the rate of transfer per unit area or to create more interfacial area.
- Thus in turbulent flow, a mass transfer coefficient ( $k$ ) is used, which is defined as:

$$k = \frac{\text{Rate of mass transfer}}{\text{Area x concentration difference}} \quad \dots\dots(69)$$

$$\text{Unit} = \frac{\text{mole/s}}{\text{cm}^2 \times \text{mole/cm}^3} = \text{cm/s}$$

**since**

$$\frac{\text{Rate of mass transfer}}{\text{Area}} = \text{molar flux, } J \quad \text{.....(70)}$$

**Therefore:**

$$k_c = \frac{J_A}{C_{Ai} - C_A} \quad \text{in terms of concentration} \quad \text{.....(71)}$$

$$k_y = \frac{J_A}{y_{Ai} - y_A} \quad \text{in terms of molar fraction in vapor phase} \quad \text{.....(72)}$$

$$k_x = \frac{J_A}{x_{Ai} - x_A} \quad \text{in terms of molar fraction in liquid phase} \quad \text{.....(73)}$$



- Note that only the unit of  $k_c$  is in cm/s, while the unit of  $k_x$  and  $k_y$  is similar to  $J_A$  as molar fraction is dimensionless.
- However,  $k_c$  can be correlated with  $k_x$  and  $k_y$  by the molar density:

$$k_y = k_c \rho_M = \frac{k_c P}{RT} \quad \dots\dots(74)$$

$$k_x = k_c \rho_M = \frac{k_c \rho_x}{\bar{M}} \quad \dots\dots(75)$$

where:

$\rho_M$  = molar density of fluid (mole/m<sup>3</sup>)

$\rho_x$  = normal density of fluid (kg/m<sup>3</sup>)

$\bar{M}$  = average molecular weight of fluid (kg/mole)

- The significance of  $k_c$  is brought out by combining Eq. (71) with Eq. (31) for steady state equimolar counterdiffusion in a stagnant film. Combination of both equations give:

$$k_c = \frac{J_A}{c_{Ai} - c_A} = \frac{D_{AB}(c_{Ai} - c_A)}{z_T} \frac{l}{(c_{Ai} - c_A)} \quad \text{.....(76)}$$

$$k_c = \frac{D_{AB}}{z_T} \quad \text{.....(77)}$$

- Thus, the mass transfer coefficient is the molecular diffusivity divided by the thickness of the diffusion path.
- When dealing with unsteady state diffusion (with changing in concentration gradients and mass transfer rates) or diffusion in flowing streams, Eq. (77) still can be used to give an effective film thickness from known value of  $k_c$  and  $D_{AB}$ .

## EXERCISE:

SO<sub>2</sub> (A) is absorbed into water (B) from air in an absorption tower. At a specific location, SO<sub>2</sub> is transferred at the rate of 0.0270 kmol SO<sub>2</sub>/m<sup>2</sup>.h and the liquid phase mole fraction are 0.0025 and 0.0003 respectively, at the two-phase interphase and in the bulk liquid. If the diffusivity of SO<sub>2</sub> in water is 1.7x10<sup>-5</sup> cm<sup>2</sup>/s, determine the mass-transfer coefficient,  $k_c$  and the film thickness,  $z_T$  neglecting the bulk flow effect.

Ans:  $z_T = 0.0028$  cm

# Solution

Given:

$$x_{Ai} = 0.0025$$

$$x_{Ab} = 0.0003$$

$$N_A = 0.027 \text{ kmol SO}_2/\text{m}^2\cdot\text{h}$$

$$D_{AB} = 1.7 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$N_{SO_2} = \frac{0.027 \frac{\text{kmol SO}_2}{\text{m}^2 \cdot \text{h}} \times 1000 \frac{\text{mol}}{\text{kmol}}}{3600 \frac{\text{s}}{\text{h}} \times \left(100 \frac{\text{cm}}{\text{m}}\right)^2} = 7.5 \times 10^{-7} \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}}$$

For dilute conditions, the concentration of water is:

$$c = \frac{1 \frac{\text{g}}{\text{cm}^3}}{18.02 \frac{\text{g}}{\text{mol}}} = 5.55 \times 10^{-2} \frac{\text{mol}}{\text{cm}^3}$$

From equations:

$$k_c = \frac{D_{AB}}{z_T} \quad N_A = \frac{cD_{AB}}{z_T} (x_{Ai} - x_{Ab})$$

$$k_c = \frac{D_{AB}}{z_T} = \frac{N_A}{c(x_{Ai} - x_{Ab})}$$

$$\therefore = \frac{7.5 \times 10^{-7} \left( \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \right)}{5.55 \times 10^{-2} \left( \frac{\text{mol}}{\text{cm}^3} \right) (0.0025 - 0.0003)}$$

$$= 6.14 \times 10^{-3} \text{ cm/s}$$

Therefore:

$$z_T = \frac{D_{AB}}{k_c} = \frac{1.7 \times 10^{-5} \left( \frac{\text{cm}^2}{\text{s}} \right)}{6.14 \times 10^{-3} \left( \frac{\text{cm}}{\text{s}} \right)} = 0.0028 \text{ cm}$$

Effective film thickness,  $z_T$  is very small and this is typical for turbulent flow mass transfer processes.

# Type of MT Coefficients

## A) Definition of MT coefficients:

For turbulent MT with constant  $c$  :

$$J_A = -\left(D_{AB} + \varepsilon_M\right) \frac{dc_A}{dz} \quad \dots\dots(78)$$

where:

$D_{AB}$  = molecular diffusivity ( $m^2/s$ )

$\varepsilon_M$  = mass eddy diffusivity ( $m^2/s$ )

$\varepsilon_M$  is variable, near to zero at the interface or surface and increases as the distance from the wall increases.

Since the variation of  $\varepsilon_M$  is not generally known, use the average value of  $\overline{\varepsilon_M}$ . Integrating Eq. (78) between points 1 and 2 gives:

$$J_{A1} = \frac{D_{AB} + \overline{\varepsilon_M}}{z_2 - z_1} (c_{A1} - c_{A2}) \quad \text{.....(79)}$$

The flux  $J_{A1}$  is based on the surface area  $A_1$  since the cross sectional area may vary. The value of  $z_2 - z_1$ , the distance of the path is often not known. Hence, Eq. (79) is simplified and is written using a convective mass-transfer coefficient  $k'_c$  :

$$J_{A1} = k'_c (c_{A1} - c_{A2}) \quad \text{.....(80)}$$

where

$$k'_c = \frac{D_{AB} + \overline{\varepsilon_M}}{z_2 - z_1} \quad \text{.....(81)}$$

## B) MT coefficient for equimolar counterdiffusion

**Similar to the total molar flux,  $N_A$  in molecular diffusion with the term  $\varepsilon_M$  added:**

$$N_A = -c(D_{AB} + \varepsilon_M) \frac{dx_A}{dz} + x_A(N_A + N_B) \quad \dots\dots(82)$$

**For the case of equimolar counterdiffusion, where**

**$N_A = -N_B$ , and integrating at steady state, calling**

$$k'_c = \frac{D_{AB} + \overline{\varepsilon_M}}{z_2 - z_1}$$

**gives**

$$N_A = k'_c (c_{A1} - c_{A2}) \quad \dots\dots(83)$$



**MT coefficients can also be defined in several ways.**

**Consider:**

**$y_A$  = mole fraction in vapor phase**

**$x_A$  = mole fraction in liquid phase**

**Therefore, Eq. (83) can be written as follows for equimolar counterdiffusion:**

**Gases:**

$$N_A = k'_c(c_{A1} - c_{A2}) = k'_G(p_{A1} - p_{A2}) = k'_y(y_{A1} - y_{A2}) \quad \text{.....(84)}$$

**Liquids:**

$$N_A = k'_c(c_{A1} - c_{A2}) = k'_L(c_{A1} - c_{A2}) = k'_x(x_{A1} - x_{A2}) \quad \text{.....(85)}$$

All of these MT coefficients can be related to each other. For example, using Eq. (84) and substituting  $y_{A1} = c_{A1}/c$  and  $y_{A2} = c_{A2}/c$  into the equation:

$$N_A = k'_c(c_{A1} - c_{A2}) = k'_y(y_{A1} - y_{A2}) = k'_y\left(\frac{c_{A1}}{c} - \frac{c_{A2}}{c}\right) = \frac{k'_y}{c}(c_{A1} - c_{A2}) \quad \text{.....(86)}$$

Hence

$$k'_c = \frac{k'_y}{c} \quad \text{.....(87)}$$

### **C) MT coefficient for A diffusing through stagnant, nondiffusing B**

For A diffusing through stagnant, nondiffusing B where  $N_B = 0$ , Eq. (82) gives for steady state:

$$\begin{aligned} N_A &= \frac{k'_c}{x_{BM}} (c_{A1} - c_{A2}) = k_c (c_{A1} - c_{A2}) \\ &= \frac{k'_x}{x_{BM}} (x_{A1} - x_{A2}) = k_x (x_{A1} - x_{A2}) \end{aligned} \quad \dots(88)$$

where:

$k_c$  = MT coefficient for A diffusing through stagnant B.  
 $x_{BM}$  and  $y_{BM}$  are similar to the equations defined in the previous lectures.

## Rewriting Eq. (88) using other units:

### Gases:

$$N_A = k_c (c_{A1} - c_{A2}) = k_G (p_{A1} - p_{A2}) = k_y (y_{A1} - y_{A2}) \quad \dots\dots(89)$$

### Liquids:

$$N_A = k_c (c_{A1} - c_{A2}) = k_L (c_{A1} - c_{A2}) = k_x (x_{A1} - x_{A2}) \quad \dots\dots(90)$$

All of these MT coefficients can be related to each other. For example, setting Eq. (88) equal to Eq. (90) gives:

$$N_A = \frac{k'_c}{x_{BM}} (c_{A1} - c_{A2}) = k_x (x_{A1} - x_{A2}) = k_x \left( \frac{c_{A1}}{c} - \frac{c_{A2}}{c} \right) \quad \dots\dots(91)$$

Hence

$$\frac{k'_c}{x_{BM}} = \frac{k_x}{c} \quad \dots\dots(92)$$

# Summary

TABLE 7.2-1. Flux Equations and Mass-Transfer Coefficients

*Flux equations for equimolar counterdiffusion*

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

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

*Flux equations for A diffusing through stagnant, nondiffusing B*

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

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

*Conversions between mass-transfer coefficients*

Gases:

$$k'_c c = k'_c \frac{P}{RT} = k_c \frac{P_{BM}}{RT} = k'_G P = k_G p_{BM} = k_y y_{BM} = k'_y = k_c y_{BM} c = k_G y_{BM} P$$

Liquids:

$$k'_c c = k'_L c = k_L x_{BM} c = k'_L \rho / M = k'_x = k_x x_{BM}$$

(where  $\rho$  is density of liquid and  $M$  is molecular weight)

*Units of mass-transfer coefficients*

	<i>SI Units</i>	<i>Cgs Units</i>	<i>English Units</i>
$k_c, k_L, k'_c, k'_L$	$\frac{\text{m}}{\text{s}}$	$\frac{\text{cm}}{\text{s}}$	$\frac{\text{ft}}{\text{h}}$
$k_x, k_y, k'_x, k'_y$	$\frac{\text{kg mol}}{\text{s} \cdot \text{m}^2 \cdot \text{mol frac}}$	$\frac{\text{g mol}}{\text{s} \cdot \text{cm}^2 \cdot \text{mol frac}}$	$\frac{\text{lb mol}}{\text{h} \cdot \text{ft}^2 \cdot \text{mol frac}}$
$k_G, k'_G$	$\frac{\text{kg mol}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$ $\frac{\text{kg mol}}{\text{s} \cdot \text{m}^2 \cdot \text{atm}}$ (preferred)	$\frac{\text{g mol}}{\text{s} \cdot \text{cm}^2 \cdot \text{atm}}$	$\frac{\text{lb mol}}{\text{h} \cdot \text{ft}^2 \cdot \text{atm}}$

### Example :

A large volume of pure gas  $B$  at 2 atm pressure is flowing over a surface from which pure  $A$  is vaporizing. The liquid  $A$  completely wets the surface, which is the blotting paper. Hence, the partial pressure of  $A$  at the surface is the vapor pressure of  $A$  at 298 K, which is 0.20 atm. The  $k'_y$  has been estimated to be  $6.78 \times 10^{-5}$  kg mole/m<sup>2</sup>·s·mole frac. Calculate  $N_A$ , the vaporization rate, and also the value of  $k_y$  and  $k_G$ .

### Solution:

This is the case of  $A$  diffusing through  $B$ , where the flux of  $B$  normal to the surface is zero, since  $B$  is in large volume and assuming that  $B$  is not soluble in liquid  $A$ .

$$p_{A1} = 0.20 \text{ atm}$$

$$p_{A2} = 0 \text{ (pure gas } B)$$

$$\begin{aligned} y_{A1} &= p_{A1}/P & y_{A2} &= 0 \\ &= 0.20/2.0 \\ &= 0.10 \end{aligned}$$

From the Eq. (89) :  $N_A = k_y (y_{A1} - y_{A2})$

From Table 7.2-1, we have a value of  $k'_y$  which is related to  $k_y$  by:

$$\boxed{k_y y_{BM} = k'_y}$$

Find  $k_y$  by first calculating  $y_{BM}$ :

$$y_{B1} = 1.0 - 0.10 = 0.90 \qquad y_{B2} = 1.0 - 0 = 1.0$$

$$y_{BM} = \frac{y_{B2} - y_{B1}}{\ln(y_{B2} / y_{B1})} = \frac{1.0 - 0.90}{\ln(1.0 / 0.90)} = 0.95$$

Then, from the previous Eq.,

$$k_y = \frac{k'_y}{y_{BM}} = \frac{6.78 \times 10^{-5}}{0.95} = 7.137 \times 10^{-5} \text{ kgmole/m}^2 \cdot \text{s} \cdot \text{mole frac.}$$

Similarly, from Table 7.2-1, calculate  $k_G$ :

$$k_G y_{BM} P = k_y y_{BM}$$

$$k_G = \frac{k_y}{P} = \frac{7.137 \times 10^{-5} \text{ kgmol/m}^2 \cdot \text{s}}{2 \times 1.01325 \times 10^5 \text{ Pa}} = 3.522 \times 10^{-10} \text{ kgmole/m}^2 \cdot \text{s} \cdot \text{Pa}$$

$$k_G = \frac{k_y}{P} = \frac{7.137 \times 10^{-5} \text{ kgmole/m}^2 \cdot \text{s}}{2.0 \text{ atm}} = 3.569 \times 10^{-5} \text{ kgmole/m}^2 \cdot \text{s} \cdot \text{atm}$$



Using Eq. (89) to calculate the flux  $N_A$ :

$$\begin{aligned} N_A &= k_y(y_{A1} - y_{A2}) \\ &= 7.137 \times 10^{-5} (0.10 - 0) \\ &= 7.137 \times 10^{-6} \text{ kgmole/m}^2 \cdot \text{s} \end{aligned}$$

Also:

$$p_{A1} = 0.20 \text{ atm} = 0.20(1.01325 \times 10^5) = 2.0265 \times 10^4 \text{ Pa}$$

Using Eq. (89) again to calculate the flux  $N_A$ :

$$\begin{aligned} N_A &= k_G(p_{A1} - p_{A2}) \\ &= 3.522 \times 10^{-10} \text{ kgmol/m}^2 \cdot \text{s} \cdot \text{Pa} (2.0265 \times 10^4 - 0) \text{ Pa} \\ &= 7.137 \times 10^{-6} \text{ kgmole/m}^2 \cdot \text{s} \end{aligned}$$

$$\begin{aligned}N_A &= k_G(p_{A1} - p_{A2}) \\&= 3.569 \times 10^{-5} \text{ kgmol/m}^2 \cdot \text{s} \cdot \text{atm} (0.20 - 0) \text{ atm} \\&= 7.138 \times 10^{-6} \text{ kgmole/m}^2 \cdot \text{s}\end{aligned}$$

Note that in this case, since the concentration were diluted,  $y_{BM}$  is close to 1.0 and  $k_y$  and  $k'_y$  differ very little.