

Mass transfer occurs due to difference in chemical potential

2.1.1 Concentration

The concentration of a species in a solution is generally expressed in terms of one of the following:

ρ_i = ‘mass concentration’ of the species i (i.e. mass of i per unit volume of the solution or mixture), in kg/m³ (or lb/ft³)

ρ = ‘total mass concentration’ of all the species in a solution, in kg/m³ (or lb/ft³); the total mass concentration ρ is nothing but the density of the solution

$w_i = \rho_i/\rho$ = mass fraction of the species i in a solution

C_i = molar concentration of the species i in a solution, in kmol/m³ (or lbmol/ft³)

C = total molar concentration of the solution, in kmol/m³ (or lbmol/ft³)

$x_i = C_i/C$ = mole fraction of the species i in a solution.

If there are n species in a solution, we have the following relations.

$$\sum_{i=1}^n \rho_i = \rho; \quad \sum_{i=1}^n C_i = C; \quad \sum_{i=1}^n w_i = 1; \quad \sum_{i=1}^n x_i = 1$$

In a gas mixture, the ‘concentration’ of a species is more commonly expressed in terms of its partial pressure p_i , or the mole fraction, $y_i = p_i/P$, where P is the total pressure. It is customary to denote the mole fraction of a species i by x_i in a solution (liquid) and by y_i in a gas mixture.

By bulk motion we mean the motion in a fluid caused by a pressure difference.

Mass average velocity

In an n -component mixture, the mass average velocity[†] u is defined as

$$u = \frac{\sum_{i=1}^n \rho_i u_i}{\sum_{i=1}^n \rho_i} = \frac{1}{\rho} \sum_{i=1}^n \rho_i u_i \quad (2.1)$$

where u_i is the linear velocity of the i th species in the concerned direction. The quantity u_i does not mean the instantaneous velocity of a molecule of the component. It is rather a statistical mean of the velocities of the molecules of component i in the given direction.

Molar average velocity

Similarly, the molar average velocity of a mixture, U , is defined as

$$U = \frac{\sum_{i=1}^n C_i u_i}{\sum_{i=1}^n C_i} = \frac{1}{C} \sum_{i=1}^n C_i u_i \quad (2.2)$$

If the concentration of a solute in a solution is small, the contribution of the motion of the solute molecules to the average velocity also remains small. So the average velocity becomes virtually equal to the velocity of the medium or the solvent. Again, if the molecular weights of all the species are equal, the mass and the molar average velocities are the same (this is very simple to prove).

Mass flux = mass/area*time not used

Molar flux = moles/area*time used everywhere in mass transfer

Mass flux

$$\text{Relative to a stationary observer} : n_i = \rho_i u_i \quad (2.3)$$

$$\text{Relative to an observer moving with the mass average velocity} : i_i = \rho_i(u_i - U) \quad (2.4)$$

$$\text{Relative to an observer moving with the molar average velocity} : j_i = \rho_i(u_i - U) \quad (2.5)$$

Small u and capital U are already defined previously

Molar flux

$$\text{Relative to a stationary observer} : N_i = C_i u_i \quad (1)$$

$$\text{Relative to an observer moving with the mass average velocity} : I_i = C_i(u_i - U) \quad (1)$$

$$\text{Relative to an observer moving with the molar average velocity} : J_i = C_i(u_i - U) \quad (1)$$

The volume average velocity (= molar average velocity) is

J_i = diffusive flux

$N_i = C_i u_i$ = Total flux

$C_i U$ = convective flux

Total flux = convective flux + diffusive flux

$N_i = C_i U + J_i$

Molecular Diffusion : Single phase homogenous binary system

The basic law of diffusion, called the 'Fick's law', was enunciated by Adolf Eugen Fick, a physiologist, in 1885.[†] The law states that *the molar flux of a species relative to an observer moving with the molar average velocity is proportional to the concentration gradient of the species*. If A diffuses in a binary mixture of A and B, then according to Fick's law, the flux of A is expressed as

$$J_A \propto \frac{dC_A}{dz} \quad \Rightarrow \quad J_A = -D_{AB} \frac{dC_A}{dz} \quad (2.9)$$

Here D_{AB} is the proportionality constant called the 'diffusion coefficient' or the 'diffusivity' of A in a mixture of A and B. The diffusional flux J_A is a positive quantity by convention. Since diffusion occurs spontaneously in the direction of decreasing concentration [$(dC_A/dz) < 0$], the negative sign is incorporated in Eq. (2.9) to make it *consistent* with respect to sign. Equation (2.9) is the mathematical representation of Fick's law for diffusion in a binary mixture.

The Fick's law given by Eq. (2.9) expresses the molar flux J_A with respect to an observer moving with the molar average velocity. In practice, however, the molar flux N_A in a stationary frame of reference is more useful. An expression for N_A can be developed by using Eqs. (2.8) and (2.9).

Molar average velocity [from Eqs. (2.2) and (2.6)] is

$$U = \frac{1}{C} (N_A + N_B)$$

Fluxes of A and B [from Eq. (2.6)] are

$$N_A = C_A u_A \quad \text{and} \quad N_B = C_B u_B$$

Therefore, using Eqs. (2.8) and (2.9),

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

Write similar equation for N_B and use equation of N_A given above and use $C_A + C_B = C = \text{constant}$
You will easily get $D_{AB} = D_{BA}$

(i) The term representing bulk flow, i.e.

$$(N_A + N_B) \frac{C_A}{C}$$

and (ii) the term representing molecular diffusion, i.e.

$$- D_{AB} \frac{dC_A}{dz}$$

If the concentration of A in a mixture is small (dilute solution), the contribution of the bulk flow term given in Eq. (2.15) becomes small too. In such a case, we may write

$$N_A \approx J_A = - D_{AB} \frac{dC_A}{dz} \quad (2.17)$$

Ficks law in terms of chemical potential

$$\mu_A = \mu_A^\circ + RT \ln \alpha_A$$

$$= \mu_A^\circ + RT \ln (\gamma_A c_A)$$

$$\frac{d\mu_A}{dx} = 0 + \frac{RT}{x_A c_A} \cdot x_A \frac{dc_A}{dx} = \frac{RT}{c_A} \frac{dc_A}{dx}$$

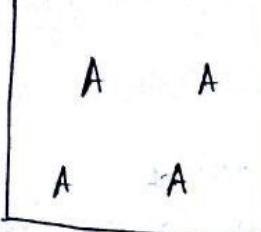
$$\boxed{\frac{dc_A}{dx} = \frac{c_A}{RT} \frac{d\mu_A}{dx}}$$

$$\boxed{J_A = -D_{AB} \frac{dc_A}{dx} = -\frac{D_{AB} c_A}{RT} \frac{d\mu_A}{dx}}$$

Molecular diffusivity correlations for gases

1. For gases Based on Kinetic Theory

gas phase



$D_{AA} = \frac{1}{3} \lambda u$

mean free path, m
average molecular velocity

$\lambda = \frac{K T}{\sqrt{2 \pi \sigma_A^2 P}}$ Boltzmann const.

$u = \sqrt{\frac{8 K N T}{\pi M_A}}$

Diameter of the molecule

$$D_{AA} = \frac{\frac{2}{3} \left(\frac{K}{\pi}\right)^{3/2} N^{1/2} T^{3/2} \left[\frac{1}{M_A}\right]^{1/2}}{P \sigma_A^2}$$

$$D_{AB} = \frac{\frac{2}{3} \left(\frac{K}{\pi}\right)^{3/2} N^{1/2} T^{3/2}}{P \sigma_{AB}^2} \left[\frac{1}{2M_A} + \frac{1}{2M_B}\right]^{1/2}$$

i) Simplest of correlations
ii) ideal binary mixture
→ no intermolecular interaction
iii) Non polar system

2. For gases Heinfelder correlation Here we consider interaction between molecules
 Lennard jones potential sigma is due to interaction between A and B

$$D_{AB} = \frac{\frac{2}{3} \left(\frac{k}{\pi} \right)^{3/2} N^{1/2} T^{3/2}}{R_D P \sigma_{AB}^2} \left[\frac{1}{2M_A} + \frac{1}{2M_B} \right]^{1/2}$$

↑
 Leonard Jones
 parameter

$$D = \frac{1.8 \times 10^{-7} T^{3/2}}{P \sigma_{AB}^2 R_D} \left[\frac{1}{2M_A} + \frac{1}{2M_B} \right]^{1/2}$$

in $\frac{m^2}{s}$

$$f\left(\frac{kT}{\epsilon_{AB}}\right)$$

$$\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}$$

ϵ_{AB} is lennard jones parameter

$$\sigma = 1.18 V_b^{1/3}$$

\nwarrow Molar volume at normal
boiling point.

$$= 0.841 V_c^{1/3}$$

\nwarrow critical volume

$$= 2.44 \left(\frac{T_c}{P_c} \right)^{1/3}$$

$$= 2.44 (T_c/P_c)^{1/3}$$

Please Note in place of 0.841 it should be 0.341

$$\frac{\epsilon_A}{(k)} = 0.77 T_c$$

Boltzmann const.

$$= 1.15 T_b$$

3. Fuller Equation for gases

$$D_{AB} = \frac{10^{-3} \cdot T^{1.75} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \left[\left(\sum V_A \right)_A^{1/3} + \left(\sum V_B \right)_B^{1/3} \right]^2}$$

\downarrow

$\frac{cm^2}{s}$

\downarrow

atm

V_A = Molecular volume if it is not directly given then add volumes of atom to find molecular volume

$$V_A = V_C + 2 \times V_O$$

↓ ↓
for 'C' for 'O' atom

V_{CO_2}

V_A = summation of atomic volume of components

Temp dependence of different correlations

$$D_{AB} \propto T^{3/2} \quad (\text{based on } k_B T)$$

$$D_{AB} \propto T^{3/2} \cdot \frac{1}{\sqrt{M}} \quad (\text{Hirschfelder})$$

$$ND = f \left(\frac{kT}{E_{AC}} \right)$$

$$D_{AB} \propto T^{1.75} \quad (\text{Fuller})$$

$D_{1,n}$ = diffusivity of 1 in a solution mixture of 1,2,3,4,5,6.....n-1,n

Let $y_1, y_2, y_3, \dots, y_{n-1}, y_n$ be the mole fraction of components in mixture

Then,

$$D_{fm} = \frac{1}{y_1' / D_{12} + y_2' / D_{12} + \dots + y_n' / D_{1n}}$$

$$y_n' = \frac{y_n}{1 - y_1}$$

Molecular diffusivity correlations for Liquids

For below equation we have assumed dilute solution

Liquid phase $\xrightarrow{\text{infinite solvent}}$ (very so,

$$D_{AB} = \frac{k \cdot T}{6\pi \cdot r \cdot \mu_B}$$

$$D_{AB} \propto \frac{T}{\mu_B}$$

Stokes Einstein equation based on hydrodynamic equation for perfectly spherical particles

$$\Rightarrow \frac{D_{AB} \cdot \mu_B}{T} = \text{Constant}$$

Inwin equation

$$! - \frac{D_{AB} \cdot \mu_B}{T} = f(v_B)$$

Wilke Chang Equation for Dilute solutions

Wilke' Chang Dilute

$$\frac{D_{AB} \cdot \mu_B}{T} = 7.5 \times 10^{-3} \left(\frac{\phi_B \cdot M_B}{V_A^{0.6}} \right)^{1/2}$$

$\downarrow \text{cm}^2/\text{s}$ $\downarrow \text{cm}^3/\text{g-mole}$

ϕ_B is Association factor of solvent B and viscosity is in g/m-s

Hayduk laudie equation (for conc solutions) Most accurate

→ Hayduk-laudie

$$D_{AB}^\circ = 13.26 \times 10^{-5} \cdot \mu_B^{-1.14} \times V_A^{-0.589}$$

$$\downarrow \text{contipose} \quad \downarrow \text{cm}^3/\text{g-mole}$$

(CP)

$$D_{AB}^\mu = (D_{BA}^\circ \cdot \mu_A)^{x_A} (D_{AB}^\circ \mu_B)^{x_B} \left[1 + \frac{d \ln \gamma_A}{d \ln x_A} \right]^{\text{gamm}}$$

DAB0 (DAB naut) is at infinitely diluted solution

Dab is in cm^2/s

\rightarrow Path length
 when diameter of channel $<$ mean free path

\hookrightarrow Knudsen diffusion

\downarrow λ_{free} is set for any micro channel

\downarrow mean free path λ

$$Kn = \frac{\lambda}{\lambda_{\text{free}}}$$

$Kn \gg 1 \rightarrow$ Knudsen diffusion

$Kn \ll 1 \rightarrow$ no diffusion.

$$J_A = -D_{AB} \frac{dC_A}{dx} \times \begin{matrix} \rightarrow \text{Porosity} \\ \downarrow \end{matrix} \times \frac{1}{t} \rightarrow \begin{matrix} \rightarrow \text{Tortuosity} \\ \text{correction factor} \end{matrix}$$

$\alpha \epsilon \ll 1$

$t \geq 1$

(How much volume really available)

$$\boxed{t=1 \text{ for cylinder}}$$

Dae is effective diffusivity

$$\epsilon \rightarrow \begin{matrix} \text{porosity} \\ \text{correction factor} \end{matrix}, V_{\text{eff}} = \epsilon V_T \Rightarrow \epsilon = \frac{V_{\text{eff}}}{V_T}$$

$$T \rightarrow \text{tortuosity} = \frac{\text{tortuous length}}{\text{actual length}}$$

$$D_{AK} \times \frac{\Sigma}{k} = D_{KA}^{\text{eff}}$$

$$J_A = -D_{KA} \times \frac{dC_A}{dx}$$

$$\text{Ansatz: } D_{KA} = \frac{1}{3} \text{ d.pore} \xrightarrow{U \rightarrow \sqrt{\frac{8kNT}{\pi M_A}}}$$

$$D_{KA} = 4850 \text{ d.pore} \times \sqrt{\frac{T}{M_A}}$$

* when molecular & Knudsen both diffusions are present use replace

D_{KA} by D_{AE}

$$\frac{1}{D_{AE}} = \frac{1 - \alpha y_A}{D_{AB}} + \frac{1}{D_{KA}}$$

$$\alpha = 1 + \frac{N_B \xrightarrow{\text{flux}}}{N_A}$$

In dilute solution $y_A = 0$ or

In counter diffusion $N_B \approx N_A$
hence $\alpha \approx 1$

$$\frac{1}{D_{AE}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

* Surface diffusivity

molecules $\xrightarrow{\text{spares}}$ spares

$$J_A = -D_{AS} \frac{dC_A}{dx}$$

2.8.1 Knudsen Diffusion

The movement of molecules in a mixture is governed by molecular velocity as well as collision with other molecules. Collision of the diffusing molecules with others present in the mixture offers the resistance to diffusion. If gas diffusion occurs in a very fine pore, particularly at a low pressure, the ‘mean free path’ of the molecules may be larger than the diameter of the passage. Then collision with the wall becomes much more frequent than collision with other molecules. The rate of diffusional transport of a species is now governed by its molecular velocity, the diameter of the passage and, of course, the gradient of concentration or partial pressure. This is called ‘Knudsen diffusion’ and becomes important if the pore size is normally below 50 nm. Such a situation commonly occurs for intra-particle transport in a catalyst containing fine pores.

2.8.2 Surface Diffusion

Surface diffusion is the transport of adsorbed molecules on a surface in the presence of a concentration gradient. Molecules adsorbed on a surface remain anchored to the active sites. If the fractional surface coverage (it is the ratio of the actual amount adsorbed to that required to form a monolayer) is less than unity, some of the active sites remain vacant. An adsorbed molecule tends to migrate to an adjacent empty site if it has sufficient energy to jump the energy barrier. Since the active sites are discrete, the migration or surface diffusion is visualized to occur by a ‘hopping’ or ‘leap-frog’ mechanism [Figure 2.19(c)]. Several models of surface diffusion have been proposed in the literature. The flux due to surface diffusion is given by a Fick’s law-type equation, i.e.

$$J_s = - D_s \frac{dC_s}{dz} \quad (2.83)$$

where

D_s = surface diffusion coefficient, in m^2/s

C_s = surface concentration of the adsorbed molecules, in kmol/m^2 .

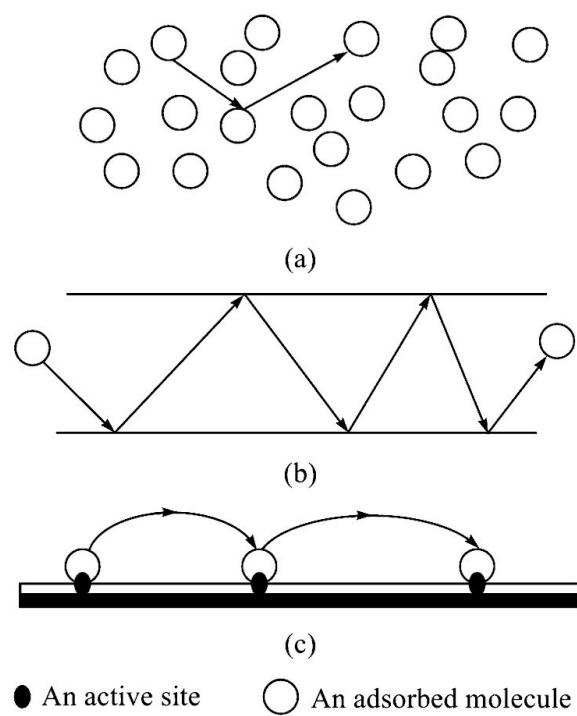
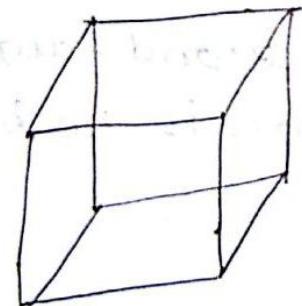


Figure 2.19 Illustration of (a) diffusion in a continuum, (b) Knudsen diffusion, and (c) surface diffusion.

Mass Balance



Rate of
(moles in - moles out + moles
generated)

= Rate of mole accumulation

(0, 0, 0)

($\sigma^x, \sigma^y, \sigma^z$)

$$[N_A|_x - N_A|_{x+\sigma^x}] \sigma^y \sigma^z + [N_A|_y - N_A|_{y+\sigma^y}] \sigma^x \sigma^z$$

$$+ [N_A|_z - N_A|_{z+\sigma^z}] \sigma^x \sigma^y + R_A = \frac{d}{dt} (\sigma^x \sigma^y \sigma^z)$$

$$-\left(\frac{\partial N_A|_x}{\partial x} + \frac{\partial N_A|_y}{\partial y} + \frac{\partial N_A|_z}{\partial z}\right) + R_A = -\frac{dS_A}{dt} = \frac{1}{M_A} \frac{dp_A}{dt}$$

Considering only one dimensional flow (along X only), Steady state, Constant area, Binary mixture, single phase and No chemical reaction(moles generated = 0)

for steady state, binary, non reacting system
and constant area

$$-\frac{dN_A}{dx} + \cancel{R_A}^0 = \cancel{\frac{dc_A}{dt}}^0$$

$$\frac{dN_A}{dx} = 0$$

$$J_A = c_A(u_A - v)$$

for $v=0$, there is no bulk convective transfer

$$J_A = N_A - (\cancel{\frac{c_A}{c}(N_A + N_B)})^0$$

$$\frac{dJ_A}{dx} = 0 \Rightarrow \frac{d}{dx} (-D_{AB} \frac{dc_A}{dx}) = 0$$

$$\Rightarrow \boxed{\frac{d^2c_A}{dx^2} = 0} \quad \leftarrow \text{Ficks second law}$$

when there is no bulk flow

Dimensional analysis to show

No convective mass flux \Rightarrow No bulk convective mass transfer

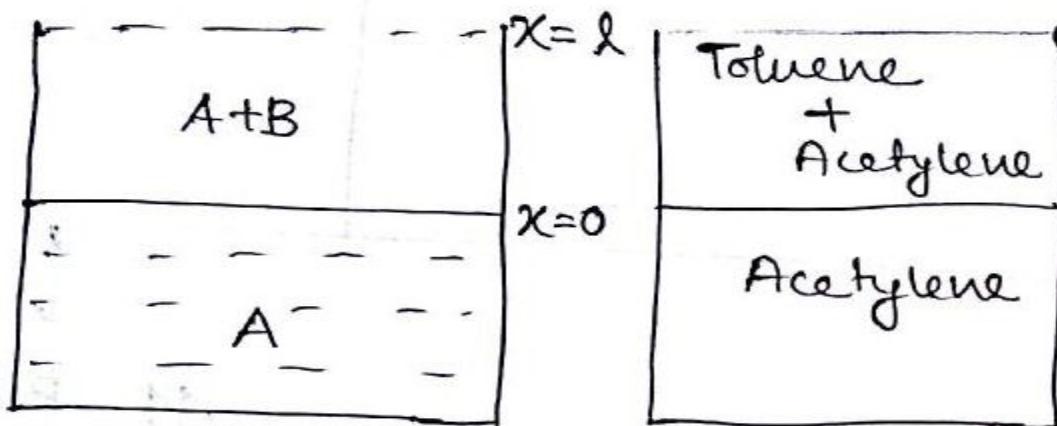
2.3.1 Diffusion of A Through Non-diffusing B

This situation can be illustrated using an example. Dry air is required for burning of sulphur in a sulphuric acid plant. Air is dried in contact with concentrated sulphuric acid in a ‘packed tower’(see Chapter 5). Moisture(A) diffuses through a *film* or layer of air(B), reaches the acid surface and gets absorbed in it. But air (we consider air a single substance or component) being virtually insoluble in sulphuric acid, will not diffuse. In other words, the moisture has a ‘source’ (the bulk of air is the source) and a ‘sink’ (the acid), but ‘dry’ air has a ‘source’ but no ‘sink’. So air is ‘non-diffusing’. There are numerous other real-life examples of this limiting situation.

The component B being non-diffusing, its flux $N_B = 0$. So, Eq. (2.19) reduces to

Case 1

$A \uparrow, B \neq$



$$N_A = -D_{AB} \frac{dc_A}{dx} + \frac{c_A}{c} (N_A + N_B)$$

$$\frac{d(N_A)}{dx} = 0 \Rightarrow N_A = f(x)$$

$$\text{at } x=0 \quad c_A = c_{A_1}$$

$$x=l \quad c_A = c_{A_2}$$

$$N_B = 0$$

$$N_A = -D_{AB} \frac{dc_A}{dx} + \frac{c_{A_1}}{c} N_A$$

$$N_A \left(\frac{c_A}{c} - 1 \right) = D_{AB} \frac{dc_A}{dx}$$

$$\frac{N_A \cancel{D_{AB}} dx}{D_{AB} C} = \frac{dC_A}{C_A - C}$$

$$N_A \int_0^l dz = - D_{AB} \cdot C \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{C - C_A}$$

$$N_A = \frac{D_{AB} \cdot C}{l} \ln \left(\frac{C - C_{A2}}{C - C_{A1}} \right)$$

$$= \frac{\bar{D}_{AB} \cdot \bar{C}}{l(C_B)_{em}} (C_{A1} - C_{A2})$$

----- Mass transfer coefficient

$$C = C_{B1} + C_{A1} = C_{B2} + C_{A2}$$

$$(C_B)_{em} = \frac{C_{B2} - C_{B1}}{\ln \left(\frac{C_{B2}}{C_{B1}} \right)}$$

Mass flux = Mass transfer coefficient
 x Δ (driving force)

In reality

$$N_A \rightarrow \text{const}$$

$$l \rightarrow l \gg \Delta x$$

$$N_A = \frac{D_A \cdot C}{(C - C_A)} \frac{dC_A}{dx} \quad \frac{d(N_A)}{dx} = 0$$

$$\frac{d}{dx} \left(\frac{D_A \cdot C}{(C - C_A)} \frac{dC_A}{dx} \right) = 0$$

$$C_A|_0 = C_{A1}, \quad C_A|_L = C_{A2}$$

$$\frac{dC_A}{dx} \frac{c - C_A}{(c - C_A)} = C_1$$

$$\ln(c - C_A) = C_1 x + C_2$$

$$\frac{c - C_A}{c - C_{A1}} = \left[\frac{c - C_{A2}}{c - C_{A1}} \right]^{x/L}$$

$$N_A = \frac{D_{AB} \cdot c}{l(Y_B)_{em}}$$

$$Y_A = \frac{C_{A1}}{c}$$

$$Y_B = \frac{C_{A2}}{c}$$

For gas

$$\textcircled{1} \quad N_A = \frac{D_{AB} c}{l} \left[\frac{Y_{A1} - Y_{A2}}{(Y_B)_{em}} \right], (Y_B)_{em} = \frac{Y_{B2} - Y_{BL}}{\ln \left(\frac{Y_{B2}}{Y_{BL}} \right)}$$

$$\textcircled{2} \quad N_A = \frac{D_{AB} P}{RT l} \left[\frac{P_{A1} - P_{A2}}{(P_B)_{em}} \right], (P_B)_{em} = \frac{P_{B2} - P_{BL}}{\ln \left(\frac{P_{B2}}{P_{BL}} \right)}$$

For liquid

$$N_A = \frac{D_{AB} c}{l} \left[\frac{\chi_{A1} - \chi_{A2}}{(\chi_B)_{em}} \right], (\chi_B)_{em} = \frac{\chi_{B2} - \chi_{BL}}{\ln \left(\frac{\chi_{B2}}{\chi_{BL}} \right)}$$

$$c = \frac{P}{RT} = \frac{P}{\frac{M}{\text{Average}}}$$

For gas

For liquid

Gas-phase

Conc $\rightarrow P, P_A$

$$C_A = \frac{P_A}{RT}$$

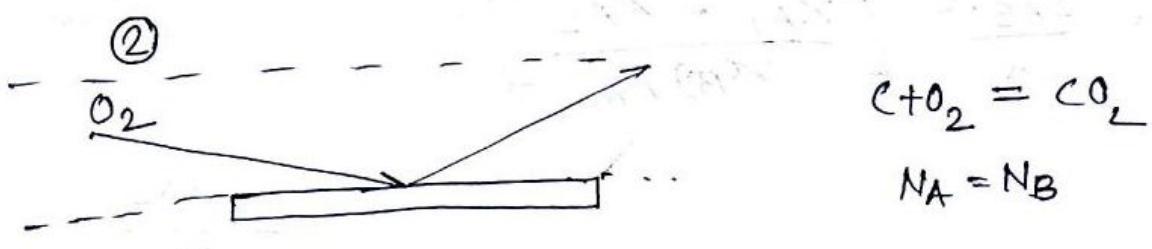
$$\gamma_A = \frac{C_A}{C} \text{ (gas-phase)}$$

Liquid-phase

$$\gamma_X A = \frac{C_A}{C}$$

2.3.2 Equimolar Counterdiffusion of A and B

This is a situation in which the components A and B both diffuse at equal rates but in opposite directions. Like the previous case, there are many real-life examples of this limiting case as well. Take the example of a particle of carbon burning in air. We visualize that 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 a molecule of O_2 diffuses to the surface, a molecule of CO_2 is formed which diffuses out through the 'air-film' (provided that CO_2 is the only product of combustion) at steady state. So oxygen and carbon dioxide undergo 'equimolar counterdiffusion'. Separation of a liquid mixture containing the components A and B by distillation may be cited as another practical example. In distillation (see Chapter 7), the vapour rising through the distillation column remains in intimate contact with the down-flowing liquid. Exchange of mass occurs between the phases—the more volatile component moves from the liquid to the vapour phase and the less volatile one gets transported from the vapour to the liquid phase (see Example 2.7). If the column is perfectly insulated against heat loss and the molar heats of vaporization of the components are equal, the mass exchange between the phases will occur in equimolar counterdiffusion mode. For equimolar counterdiffusion of A and B, we may write $N_A = -N_B^\dagger$, i.e. $N_A + N_B = 0$. Substituting this relation in Eq. (2.19),



①

$$N_A = - D_{AB} \frac{dc_A}{dx} + \frac{c_A}{C} \xrightarrow{0} (N_A + N_B)$$

$$N_A = - D_{AB} \frac{dc_A}{dx}$$

$$\frac{d(N_A)}{dx} = 0 \Rightarrow N_A \neq f(x)$$

$$c_A = c_{A1}, \quad c_A = c_{A2}$$

$$N_A = - D_{AB} \frac{(c_{A1} - c_{A2})}{l}$$

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

$$\frac{d}{dx} \left(- D_{AB} \frac{dc_A}{dx} \right) = 0$$

$$- D_{AB} \frac{dc_A}{dx} = c_1$$

$$c_A = - \frac{c_1}{D_{AB}} x + c_2$$

$$N_A = \frac{D_{AB} \cdot c}{l} \left[\frac{x_{A_1} - x_{A_2}}{(x_B)_{em}} \right]$$

2.7 DIFFUSION THROUGH A VARIABLE AREA

So far we have analyzed problems in which the cross-sectional area of diffusion remains constant. This is true for a flat geometry. However, there are many situations where the area of diffusion changes along the direction of diffusion, or changes with time even. Two common geometries that involve diffusion through a variable area are the cylindrical and the spherical

2.7.1 Diffusion in Spherical Geometry

Evaporation of a drop of water in stagnant air will be analyzed here as a model case. Let us consider an evaporating drop that has radius r_s at any instant t . Imagine a thin spherical shell of inner radius r and thickness Δr around the drop as shown in Figure 2.15. This is a binary system involving diffusion of water vapour(A) through air(B). Then

$$\begin{aligned} \text{Rate of input of } A \text{ into the thin shell (at } r = r) &: (4\pi r^2)N_A|_r \\ \text{Rate of output of } A \text{ from the thin shell (at } r = r + \Delta r) &: (4\pi r^2)N_A|_{r+\Delta r} \end{aligned}$$

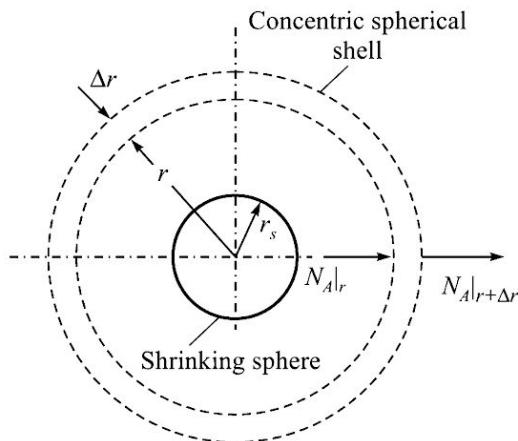


Figure 2.15 A sketch indicating shell balance for mass transfer from a sphere.

The notation $|_r$ means that the quantity is evaluated at the position r .

By a steady-state mass balance (note that the rate of accumulation = 0),

$$(4\pi r^2)N_A|_r - (4\pi r^2)N_A|_{r+\Delta r} = 0$$

Input	Output	Accumulation
-------	--------	--------------

Dividing both sides by Δr and taking the limit $\Delta r \rightarrow 0$,

$$\lim_{\Delta r \rightarrow 0} \frac{(4\pi r^2)N_A|_r - (4\pi r^2)N_A|_{r+\Delta r}}{\Delta r} = 0 \Rightarrow -\frac{d}{dr}(4\pi r^2 N_A) = 0$$

$$\Rightarrow 4\pi r^2 N_A = \text{constant} = W \text{ (say)} \quad (2.70)$$

Equation (2.70) is a very important result for *steady state* diffusion through a variable area and can be generalized as

$$(\text{Area})(\text{Flux}) = \text{Constant} \quad (2.71)$$

In this case water vapour diffuses out, but air does not diffuse because it is not soluble in water. So the case corresponds to diffusion of A through non-diffusing B . Since diffusion occurs in the radial direction, we replace z by r in Eq. (2.19) to get

$$N_A = - \frac{D_{AB} \cdot C}{(C - C_A)} \frac{dC_A}{dr}$$

$$N_B = 0$$

$C \equiv$ conc. in gas phase

$$\int N_A dr = - D_{AB} \cdot C \int \frac{dC_A}{C - C_A}$$

~~$C_{A\infty}$~~ ~~C_{AS}~~

$$\int_{\infty}^{\infty} \frac{w}{4\pi r^2} dr = - D_{AB} C \int_{\infty}^{\infty} \frac{dC_A}{C - C_A}$$

~~r_1~~

w = area \times mole flux

$$\left[- \frac{w}{4\pi r} \right]_{r_1}^{\infty} = + D_{AB} \cdot C \left[\ln \left(\frac{C}{C_A} \right) \right]_{C_{AS}}^{C_{A\infty}}$$

$$\frac{w}{4\pi r} = + D_{AB} \cdot C \ln \left[\frac{C - C_{A\infty}}{C - C_{AS}} \right]$$

$$\frac{w}{4\pi D_{AB} C \cdot r} = \ln \left(\frac{C}{C - C_{AS}} \right)$$

$$C - C_{AS} = C \cdot e^{-4\pi D_{AB} C \cdot r}$$

$$C_{AS} = C \left(1 - e^{-4\pi D_{AB} C \cdot r} \right)$$

$$w = 4\pi D_{AB} C \left[\ln \left(\frac{C - C_{A\infty}}{C - C_{AS}} \right) \right] \cdot r$$

Since W is the constant molar rate of mass transfer [see Eq. (2.70)], it is equal to the rate of vaporization of the drop at any instant. This rate can be related to the change in the drop radius by the following equation.

$$\frac{d}{dt} \left[\frac{4}{3} \pi r^3 \left(\frac{P_A}{M_A} \right) \right] = -W$$

The negative sign is incorporated because the size of the drop decreases with time. Equating Eqs. (2.74) and (2.75),

$$= -4\pi D_{AB} \text{C}_r \ln \left(\frac{C - C_{A,\infty}}{C - C_{A,S}} \right) = 4\pi \left(\frac{P_A}{M_A} \right)_\infty$$

Gas phase const.

$$4\pi \left(\frac{P_A}{M_A} \right)_\infty \int_{r_{so}}^{r_{sf}} dr = -4\pi D_{AB} \cdot C \ln \left(\frac{C - C_{A,\infty}}{C - C_{A,S}} \right) \int_0^{t_f} dt$$

$$r_{so}^2 - r_{sf}^2 = 2 D_{AB} \cdot C \left(\frac{M_A}{P_A} \right) \ln \left(\frac{C - C_{A,\infty}}{C - C_{A,S}} \right) \cdot t_f$$

for 2(a) counter

Equimolar Diffusion

$$N_A = -D_{AB} \frac{dc_A}{dt}$$

$$r_{so}^2 - r_{sf}^2 = 2 D_{AB} \left(\frac{M_A}{P} \right) (C_{A,\infty} - C_{A,S}) t_f$$

Ex:-2 Spherical particle



$$NA = -NB$$

$$\frac{d(NA + 4\pi r_s^2)}{dt} = 0, NA + 4\pi r_s^2 \overset{!}{=} W$$



$$\frac{d(NA + 4\pi r_s^2)}{dt} = 0$$

$$NA - \frac{CA(NA + NB)}{C} = -D_{AB} \cdot \frac{dCA}{dr}$$

$$\Rightarrow NA = -D_{AB} \cdot \frac{dCA}{dr}$$

$$\Rightarrow \frac{W}{4\pi r_s^2} = -D_{AB} \cdot \frac{dCA}{dr}$$

$$\Rightarrow -\frac{1}{r_s^2} \cdot dr_s = D_{AB} \cdot \frac{4\pi}{W} \cdot dCA$$

$$\Rightarrow \frac{1}{r_{s0}} \left|_{r_{s1}}^{r_{s0}} \right. = D_{AB} \cdot \frac{4\pi}{W} \cdot CA \left|_{CA_1}^{CA_0} \right.$$

$$\Rightarrow \frac{1}{r_{s0}} - \frac{1}{r_{s1}} = D_{AB} \cdot \frac{4\pi}{W} \cdot (CA_0 - CA_1)$$

$$\Rightarrow W = D_{AB} \cdot 4\pi (CA_0 - CA_1) \cdot \left[\frac{1}{r_{s1}} - \frac{1}{r_{s0}} \right]$$

$$W = \frac{dNA}{dt} = -d \left[\frac{4\pi r_s^2 \cdot g}{3 \cdot MA} \right] / dt$$

$$\Rightarrow D_{AB} \cdot 4\pi \cdot (CA_0 - CA_1) \left[\frac{1}{r_{s1}} - \frac{1}{r_{s0}} \right] = -4\pi r_s^2 \cdot \frac{g}{MA} \cdot \frac{d r_s}{dt}$$

$$\Rightarrow W = -4\pi r_s^2 \cdot \frac{g}{MA} \cdot \frac{d r_s}{dt}$$

$$\Rightarrow D_{AB} \cdot 4\pi \cdot (CA_0 - CA_1) \cdot \frac{1}{r_s} = -4\pi \cdot r_s^2 \cdot \frac{g}{MA} \cdot \frac{d r_s}{dt}$$

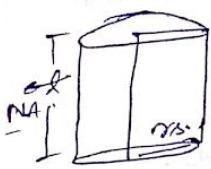
$$\Rightarrow D_{AB} \cdot (CA_0 - CA_1) \cdot \frac{MA}{g} = -r_s^3 \cdot \frac{d r_s}{dt}$$

$$\Rightarrow D_{AB} \cdot (CA_0 - CA_1) \cdot \frac{MA}{g} \cdot t \Big|_{t=0}^{t} = -\frac{r_s^4}{4} \Big|_{-t}^0$$

$$\Rightarrow D_{AB} \cdot (CA_0 - CA_1) \cdot \frac{MA}{g} \cdot t = \frac{r_s^4}{4}$$

$$\Rightarrow t = \frac{r_s^4 \cdot g}{4 \cdot MA \cdot (D_{AB} \cdot CA_0 - CA_1)}$$

Cylindrical-body-



$$\frac{d}{dt} NA \cdot (2\pi \cdot r_s \cdot l) = 0 \\ W = NA \cdot 2\pi r_s \cdot l$$

$$NA - \frac{c}{C} (NA + NB) = -DAB \cdot \frac{dc_A}{dr}$$

$$\Rightarrow \frac{NA}{C} (C - CA) = -DAB \cdot \frac{dc_A}{dr}$$

$$\Rightarrow \frac{1}{C} \cdot \frac{W}{2\pi \cdot r_s \cdot l} \cdot (C - CA) = -DAB \cdot \frac{dc_A}{dr}$$

$$\Rightarrow \frac{W}{C \cdot 2\pi \cdot l \cdot DAB} + \frac{dc_A}{dr} = -\frac{dc_A}{C - CA}$$

$$\Rightarrow \frac{W}{C \cdot 2\pi \cdot l \cdot DAB}, m_{rs} \Big|_{r_s}^{r_A} = m_{CA} \Big|_{CA}^{CA_A}$$

$$\Rightarrow \frac{W}{C \cdot 2\pi \cdot l \cdot DAB}, m_{rs} \Big|_{r_s} = \cancel{m_{CA}} \frac{m_{CA_A}}{C - CA_A}$$

$$\Rightarrow W = \frac{m_{CA_A} \cdot C \cdot 2\pi \cdot l \cdot DAB}{C - CA_A} \Big|_{r_s}$$

$$W = \frac{dA_A}{dt} = - \frac{d}{dt} \left(\pi \cdot r_s^2 \cdot l \cdot \frac{g}{MA} \right)$$

$$\Rightarrow \frac{m_{CA_A}}{C - CA_A} \cdot \frac{C \cdot 2\pi \cdot l \cdot DAB}{m_{rs} \Big|_{r_s}} = - \frac{\pi \cdot 2\pi \cdot l \cdot g}{MA} \cdot \frac{d}{dt}$$

$$\Rightarrow \frac{m_{CA_A}}{C - CA_A} \cdot C \cdot DAB \cdot dt = - \frac{g}{MA} \cdot (m_{rs} - m_{rs}) dr$$

$$\Rightarrow \frac{m_{CA_A}}{C - CA_A} \cdot C \cdot DAB \cdot t \cdot \frac{MA}{g} = - \int_{r_s}^0 r_s \cdot (m_{rs} - m_{rs}) dr$$

$$= \frac{r_s^2}{2} \cdot m_{rs} + \int_0^{r_s} r_s \cdot m_{rs} dr$$

$$I = \int_0^{r_s} r_s \cdot m_{rs} \cdot dr$$

$$= \frac{r_s^2}{2} \cdot m_{rs} \Big|_0^{r_s} - \int_0^{r_s} \frac{r_s^2}{2} \cdot \frac{1}{r_s} \cdot dr$$

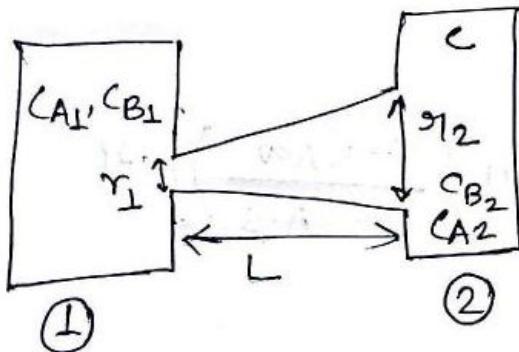
$$= \frac{r_s^2}{2} \cdot m_{rs} - \frac{r_s^2}{4}$$

$$t = \frac{g}{MA \cdot DAB \cdot C} \cdot \frac{m_{CA_A}}{C - CA_A} \cdot \left(\frac{r_s^2}{2} \cdot m_{rs} + \frac{r_s^2}{2} \cdot m_{rs} - \frac{r_s^2}{4} \right)$$

2.7.2 Diffusion Through a Tapered Tube

Let us consider two 'large' vessels connected by a tapered tube of length L . The end radii of the tubes are r_1 (at vessel 1) and r_2 (at vessel 2). The vessels contain mixtures of the gases A and B at the same total pressure P and temperature T . The partial pressures of A in the vessels are p_{A1} and p_{A2} , respectively. Since the vessels are 'large', the compositions of the gases in the two vessels are assumed to remain fairly constant in spite of the diffusional transport occurring through the connecting tube. It is required to determine the rate of diffusion through the tube at steady state.

2(b) Tapered pipe



$c_{A1} > c_{A2} \Rightarrow$ A diffuse from ① to ②
maintained at same
temp. & pressure

$$N_A \pi r^2 = W$$

$$N_A = - D_{AB} \frac{dc_A}{dx}$$

↖ important

$$\frac{W}{\pi} \frac{dx}{r^2} = - D_{AB} dc_A$$

$$c_1 = c_{1\perp} + \frac{x}{L} (c_{12} - c_{11})$$

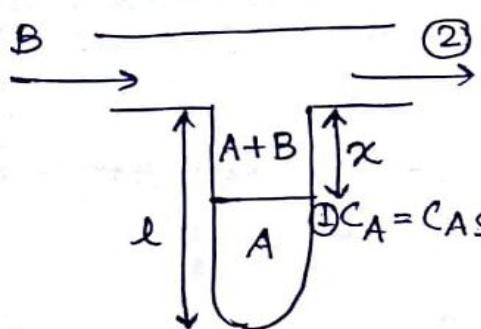
$$\frac{W}{\pi} \int_0^L \frac{dx}{[c_{1\perp} + \frac{x}{L} (c_{12} - c_{11})]^2} = - D_{AB} \int_{c_{A\perp}}^{c_{A2}} dc_A$$

$$W = \pi D_{AB} \frac{r_1 r_2}{c} (c_{A\perp} - c_{A2})$$

2.5.2 Use of the Stefan Tube

This method is suitable if, under the given set of experimental conditions, one of the components (say A) is available as a volatile liquid and the other component (B) is a gas which is *not soluble* in A. The apparatus is very simple. A vertical glass tube, sealed at the bottom, is joined to a larger diameter horizontal tube to form a tee (T) as shown in Figure 2.12. The liquid A is taken in the narrow vertical tube and the gas B is forced through the horizontal tube. Evaporated A diffuses through the mixture of A and B in the vertical tube, reaches the top and is swept away by the flowing stream of B. As B is insoluble in A, it will not diffuse and the situation will conform to *diffusion of A through non-diffusing B*. The liquid level in the vertical tube will drop very slowly and *pseudo-steady state assumption* (i.e. A diffuses through the tube virtually at steady-state at all time) is reasonable. This means that as the liquid level falls by a small amount, a new steady-state rate of diffusion is established simultaneously. The drop in the liquid level over a period of time is noted.

Stefan tube



B is not soluble in A

Flow rate of B is large

A↑, B≠

$$N_B = 0$$

$$t=0, x=x_1 \quad | \quad C_{A1} = C_{AS} = C_{A1}$$

$$t=t_f, x=x_f \quad | \quad C_{A2} = 0 = C_{A2}$$

$$N_A = \frac{D_{ABC}}{C_{B\text{em}} x} (C_{A1} - C_{A2})$$

a ≡ cross sectional area of vertical tube

$$\frac{d}{dt} (a(l-x) \frac{P_A}{M_A}) = -N_A \cdot a$$

$$\frac{P_A}{M_A} \int_{x_1}^{x_f} dx = \frac{D_{ABC}}{C_{B\text{em}}} (C_{A1} - C_{A2}) \int_0^{t_f} dt$$

~~$$\frac{P_A}{2M_A} (x_f^2 - x_1^2) = \frac{D_{ABC}}{C_{B\text{em}}} (C_{A1} - C_{A2}) t_f$$~~

$$\frac{P_A}{2M_A} (x_f^2 - x_1^2) = \frac{D_{ABC}}{C_{B\text{em}}} (C_{A1} - C_{A2}) t_f$$

2.5.1 Twin-bulb Method

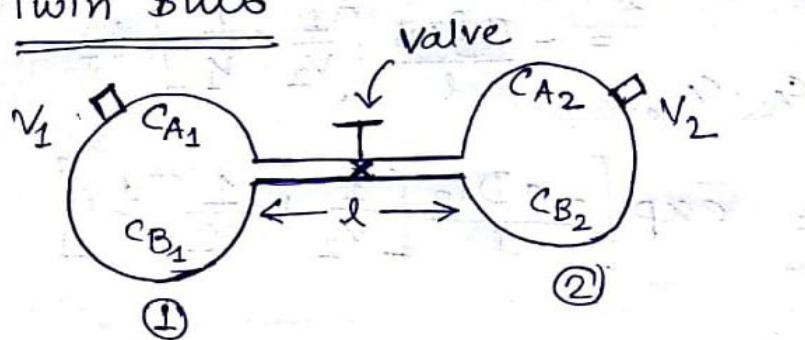
The apparatus used in this method consists of two reasonably large bulbs or chambers of volumes V_1 and V_2 , connected by a narrow tube fitted with a plug-type valve or a stopcock. There should be a suitable arrangement for stirring the contents of the bulbs in order to keep the concentrations in them uniform (the bulbs are said to be ‘well-mixed’). The entire assembly should be maintained at a constant temperature. A schematic sketch of the apparatus is shown in Figure 2.11.

Initially, the valve in the connecting tube is kept closed. The two bulbs are evacuated. One of the bulbs is repeatedly flushed with pure A and the other with pure B and then filled with the gases at the same pressure, P . The valve is then opened to allow diffusion to start and continue undisturbed for some time, at the end of which the valve is closed. Samples of the gases from the bulbs are taken and analyzed for their composition.

Because the total pressures in the bulbs remain constant and equal, equimolar counter-diffusion through the connecting tube occurs. The bulbs being large, the concentrations or partial pressures of the components in the bulbs will change rather slowly. A theoretical analysis of

diffusion in the system can be made with the pseudo-steady state[†] approximation. This means that, at any instant, diffusion through the connecting tube occurs at steady state. As the concentrations in the bulbs change a little, a new steady state of diffusion is attained *simultaneously*.

Twin Bulb



Equimolar counts
diffusion as
both of the bulb
are maintained
at same pressure

t, C_{A1}, C_{A2}

$$t=0, C_{A1} = C_{A10}, \quad \boxed{C_{A2} = C_{A20}}$$

$$t=t_f, C_{A1} = C_{Af1}, \quad C_{A2} = C_{Af2}$$

$$N_A = \frac{D_{AB}}{l_1} (C_{A1} - C_{A2}) = -N_B$$

$$\frac{d}{dt} (V_1 C_{A1}) = - N_A \cdot a$$

$$\frac{dC_{A1}}{dt} = - \frac{a}{V_1} \frac{D_{AB}}{l} (C_{A1} - C_{A2}) \quad \dots \textcircled{1}$$

$$\frac{d}{dt} (V_2 C_{A2}) = N_A \cdot a ; [N_A = -N_B]$$

$$\frac{dC_{A2}}{dt} = \frac{a}{V_2} \frac{D_{AB}}{l} (C_{A1} - C_{A2}) \quad \dots \textcircled{2}$$

$$\frac{dC_{A1}}{dt} - \frac{dC_{A2}}{dt} = - \frac{a D_{AB}}{l} (C_{A1} - C_{A2}) \left[\frac{1}{V_2} + \frac{1}{V_1} \right]$$

$$\int \frac{d(C_{A1} - C_{A2})}{d(C_{A1} - C_{A2})} = - \frac{a D_{AB}}{l} \left[\frac{1}{V_2} + \frac{1}{V_1} \right] \int dt$$

$$\left[\ln \left(\frac{C_{A1} - C_{A2}}{C_{A1_0} - C_{A2_0}} \right) \right]_{C_{A1}, C_{A2}} = - \frac{\alpha D_{AB}}{l} \left[\frac{1}{V_2} + \frac{1}{V_1} \right] t_f$$

$$\frac{C_{A1} - C_{A2}}{C_{A1_0} - C_{A2_0}} = \exp \left[- \frac{\alpha D_{AB}}{l} \left[\frac{1}{V_2} + \frac{1}{V_1} \right] t_f \right]$$

Diaphragm cell

2.6.2 Experimental Determination of Liquid-phase Diffusion Coefficient

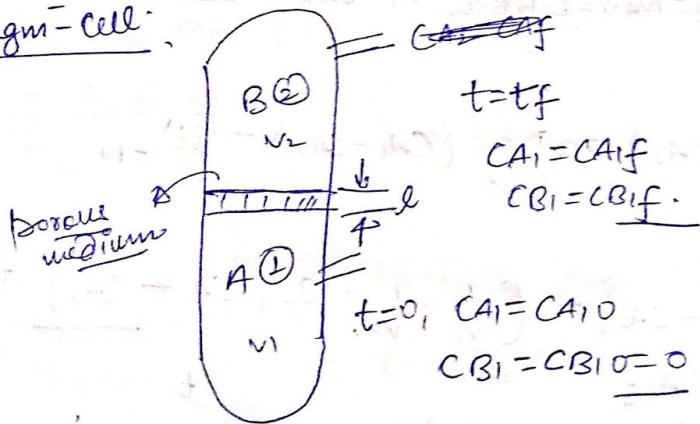
There are a number of methods for the determination of the liquid-phase diffusion coefficient. Here we describe a common method that uses a ‘diaphragm cell’ (Dullien and Shemilt, 1961).

The diaphragm cell is a two-compartment cell, as shown in Figure 2.14, separated by a porous diaphragm usually of sintered glass. Solutions of the species *A* in the solvent *B* at two different concentrations are taken in the two compartments. Diffusion is allowed to occur through the narrow passageways of the pores from the higher concentration cell to the lower concentration

cell for some time. At the end of a run, samples of the solutions are taken from the cells and analyzed for the concentrations of A . The contents of the compartments are always kept well-stirred. If the area of cross-section of the diaphragm is a and ε is its porosity, then the effective area available for diffusion is $a\varepsilon$. However, the length of the diffusion path is not equal to the thickness of the diaphragm since the pores are not straight. Many of the pores are interconnected and some may even have dead ends. A simple method to take into account this characteristic of the pores is to introduce an empirical parameter called ‘tortuosity factor’, τ . It is the ratio of the average length of the diffusion path (through the diaphragm) to the thickness of the diaphragm.

The working equation for the calculation of the diffusion coefficient from the data collected with a diaphragm cell can be derived following the procedure adopted in the case of the twin-bulb method (Section 2.5.1). For diffusion in the liquid phase, particularly at low concentrations [see Eq. (2.17)], it is reasonable to neglect the bulk flow term in Eq. (2.14). The approximate form of Fick’s law is

Diaphragm-Cell



$$\frac{-d}{dt}(CA_1) = \frac{1}{V_1} \cdot D_{AB} \times \alpha \times \frac{\epsilon}{I} \cdot (CA_1 - CA_2)$$

$$\frac{d}{dt}(CA_2) = \frac{1}{V_2} \cdot D_{AB} \times \alpha \times \frac{\epsilon}{I} \cdot (CA_1 - CA_2)$$

$$\Rightarrow \frac{d(CA_1 - CA_2)}{CA_1 - CA_2} = D_{AB} \frac{\alpha \times \epsilon}{I} \cdot \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \cdot dt$$

$$\Rightarrow \ln \frac{CA_{1,0}}{CA_{1,f} - CA_{2,f}} = D_{AB} \frac{\alpha \times \epsilon}{I} \cdot \left(\frac{1}{V_1} + \frac{1}{V_2} \right) t \\ \text{all-constant}$$

$$\Rightarrow \ln \frac{CA_{1,0}}{CA_{1,f} - CA_{2,f}} = D_{AB} \times k_{cell} \underline{st}$$

$$k_{cell} = \frac{\epsilon \cdot \alpha}{I} \left[\frac{1}{V_1} + \frac{1}{V_2} \right]$$

other words, the rate of mass transfer increases dramatically if there is motion in the medium. This occurs because of convection. Mass transfer occurring under the influence of motion in a fluid medium is called ‘convective mass transfer’. We may try to *visualize* a simple *mechanism* of dissolution of the sugar crystals in a stirred cup of water. The water just in contact with a crystal (or, in other words, the liquid at the ‘solid–liquid interface’) gets saturated with sugar almost instantly. Here ‘interface’ means the contact surface between the two phases. The dissolved sugar diffuses from the interface to the bulk liquid through a thin layer or ‘film’ of the solution adhering to the crystal. More sugar dissolves in the liquid simultaneously at the interface. The ‘thickness’ of the film that we visualize decreases if the stirring rate is more rapid. The more brisk the motion of the liquid is, the thinner is the film and the quicker is the rate of dissolution or the rate of mass transfer. The picture we visualize is schematically represented in Figure 3.1.

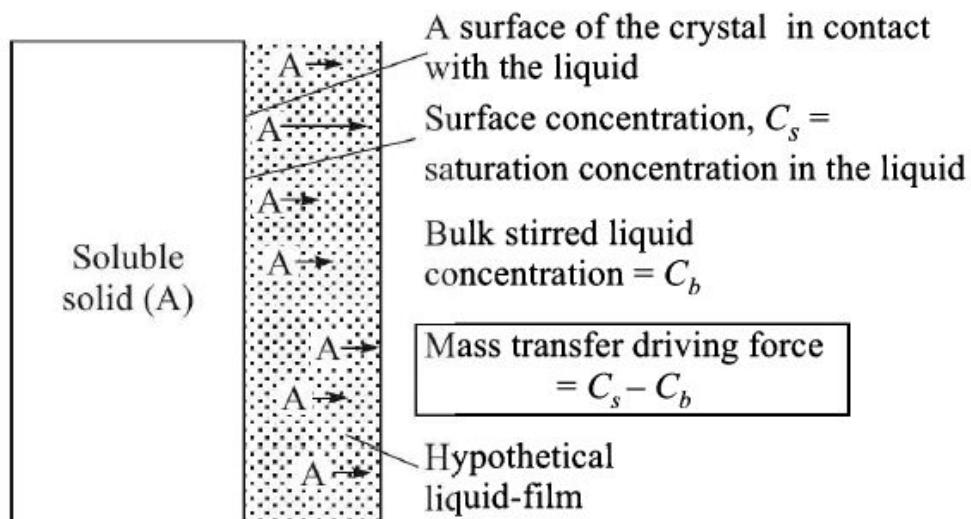


Figure 3.1 Visualization of the dissolution process of a solid.

properly understood. The concept of *mass transfer coefficient* has been introduced with a view to developing a simple and practically useful approach to the solution of such problems. The idea is similar to defining ‘heat transfer coefficient’ for expressing the rate of convective heat transfer between a surface and a fluid in motion.

The inverse of mass transfer coefficient is a measure of the 'mass transfer resistance'. If the driving force is expressed as the difference in concentration (kmol/m^3 , say), the unit of mass transfer coefficient is m/s (or cm/s , ft/s , etc. which is the same as the unit of velocity).

If the mass transfer coefficient is expressed as the ratio of the local flux and the local driving force, it is called the 'local mass transfer coefficient'. When it is expressed as the ratio of the average flux (over a surface) and the average driving force, it is known as the 'average mass transfer coefficient'.

$$\text{Mass flux} \propto \Delta \nabla (\text{driving force})$$

$$\text{Mass flux} = (\text{constant}) (\nabla \Delta (\text{driving force}))$$

↑
M.T.C

$$N_A = k_c (\nabla C_A)$$

$$= k_y (\nabla y_A)$$

$$= k_o (\nabla P_A)$$

$\left. \begin{array}{c} \\ \\ \end{array} \right\} \text{gases}$

$$N_A = k_L (\nabla C_A)$$

$$= k_x (\nabla x_A)$$

$\left. \begin{array}{c} \\ \\ \end{array} \right\} \text{liquid}$

$$\boxed{k_c \cdot C = k_y}$$

$$\frac{k_c}{RT} = k_g$$

$$\underline{\underline{k_c = k_L}}$$

\downarrow k_{eff} in way of calculating C .

$$k_y = Pk_G; \quad k_x = (\rho/M)_{av}k_L$$

3.7.1 The Film Theory (also called ‘Film Model’)

Let us describe this theory (Whitman, 1923) through an illustration. We consider mass transfer from a solid surface to a flowing liquid. Even though the bulk liquid is in turbulent motion, the flow near the wall may be considered to be laminar. The concentration of the dissolved solid (A) will decrease from C_{Ai} at the solid–liquid interface[#] to C_{Ab} at the bulk of the liquid. In reality the concentration profile will be very steep near the solid surface where the effect of turbulence is practically absent (Figure 3.6). Molecular diffusion is responsible for mass transfer near the wall while convection dominates a little away from it. The film theory, however, visualizes a simpler picture. It is based on the following assumptions.

- (a) Mass transfer occurs by purely molecular diffusion through a stagnant fluid layer at the phase boundary (here the wall is the phase boundary). Beyond this film, the fluid is well-mixed having a concentration which is the same as that of the bulk fluid (i.e. C_{Ab}).
- (b) Mass transfer through the film occurs at steady state.
- (c) The bulk flow term [i.e. $(N_A + N_B)C_A/C$, see Eq. (2.15)] in the expression for the Fick’s law is small. So the flux can be written as $N_A = -D_{AB}(dC_A/dz)$. As stated before, this is valid when: (i) the flux is low and (ii) the mass transfer occurs at low concentrations [or the mass transfer occurs by equimolar counterdiffusion]. For many practical situations this assumption is satisfactory.

This assumption is causatively.

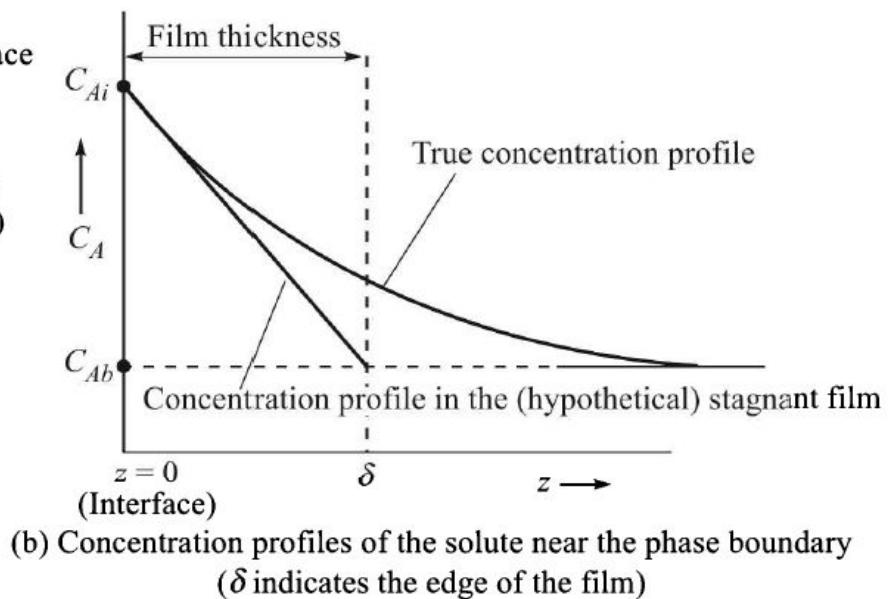
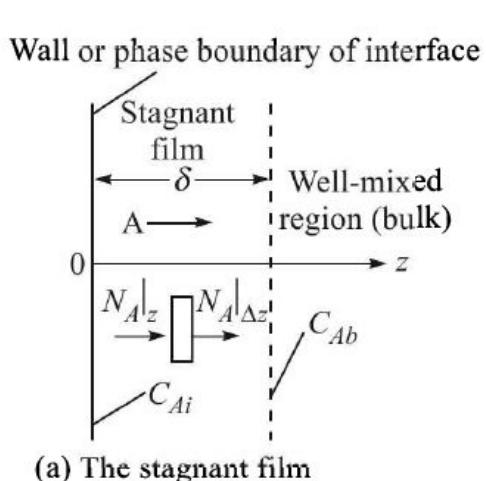


Figure 3.6 The stagnant film and the concentration profiles.

the stagnant film. We consider an elementary volume of thickness Δz and of unit area normal to the z -direction (i.e. the direction of mass transfer). We make a steady state mass balance over this element located at position z .

Rate of input[†] of the solute at $z = N_A|_z$

Rate of output of the solute at $z + \Delta z = N_A|_{z+\Delta z}$

Rate of accumulation = 0 (at steady state)

$$\Rightarrow N_A|_z - N_A|_{z+\Delta z} = 0$$

Dividing by Δz throughout and taking the limit $\Delta z \rightarrow 0$, we get

$$-dN_A/dz = 0$$

Putting $N_A = -D_{AB} \frac{dC_A}{dz}$ in the preceding equation, we have

$$D_{AB} \frac{d^2 C_A}{dz^2} = 0 \quad \text{i.e.} \quad \frac{d^2 C_A}{dz^2} = 0 \quad (3.28)$$

Integrating Eq. (3.28) and using the following boundary conditions (i) and (ii),

- (i) $z = 0$ (i.e. the wall or the phase boundary or the interface), $C_A = C_{Ai}$
- (ii) $z = \delta$ (i.e. the other end of the film of thickness, δ), $C_A = C_{Ab}$,

we get

$$C_A = C_{Ai} - (C_{Ai} - C_{Ab}) \frac{z}{\delta} \quad (3.29)$$

The above equation indicates that the theoretical concentration profile, according to the film theory, is linear as shown in Figure 3.6(b) (where the ‘true’ concentration profile is also shown). The mass transfer flux through the film is constant at steady state and is given as

$$N_A = -D_{AB} \left[\frac{dC_A}{dz} \right]_{z=0} = \frac{D_{AB}}{\delta} (C_{Ai} - C_{Ab}) \quad (3.30)$$

Comparing with Eq. (3.3), the mass transfer coefficient is

$$k_L = \frac{D_{AB}}{\delta} \quad (3.31)$$

Thus the mass transfer coefficient can be calculated from the film theory if the diffusivity and the film thickness are known. Whereas the former can possibly be obtained from the literature or may be estimated by using a suitable correlation, the latter (i.e. the film thickness δ) is unknown. So this theory does not help us in reality to predict the mass transfer coefficient. However, the film theory, like two other theories described below, has been extremely useful in the analysis of mass transfer accompanied by a chemical reaction (as we shall see in Chapter 16).

Before going into the details of this theory, let us have a close look at the phenomenon of mass transfer from a rising gas bubble—for example, absorption of oxygen from an air bubble in a fermenter. As the bubble rises, the liquid elements from the bulk reach the top of the bubble, move along its spherical surface, reach its bottom and then get detached from it. The detached liquid elements eventually get mixed up with the bulk liquid (Figure 3.7). Absorption of oxygen in a small liquid element occurs as long as the element remains at the gas–liquid interface (i.e. in contact with the gas). Similar phenomena occur in a large number of other situations involving mass transfer at a phase boundary. Thus, we may generalize the

picture by arguing that in the case of mass transfer at a phase boundary, an element of liquid reaches the interface (by any mechanism whatsoever) and stays there for a short while when it receives some solute from the other phase. At the end of its stay at the interface, the liquid element moves back into the bulk liquid carrying with it the solute it picked up during its brief stay at the interface. In the process, the liquid element makes room for another liquid element, fresh from the bulk, on the surface of the bubble. The above visualization (or ‘model’) of the process of mass transfer at a phase boundary forms the basis of the ‘Penetration Theory’ proposed by Higbie (1935). The following are the basic assumptions of the penetration theory.

- (a) Unsteady state mass transfer occurs to a liquid element so long as it is in contact with the bubble (or the other phase).
- (b) Equilibrium exists at the gas–liquid interface.
- (c) Each of the liquid elements stays in contact with the gas (or the other phase) for the same period of time.

If we confine our attention to mass transfer to a gas bubble of diameter d_b rising at a velocity u_b , the contact time of a liquid element with the gas is $t_c = d_b/u_b$. Unsteady state mass transfer to a liquid element during this period of time can be described by a partial differential equation given below (this equation can be derived by using an approach very similar to that used in the case of unsteady heat conduction to a semi-infinite medium, as discussed Chapter 15). The equation is

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2} \quad (3.32)$$

The appropriate initial and boundary conditions are:

Initial condition	$: t = 0,$	$z \geq 0;$	$C_A = C_{Ab}$
Boundary condition 1	$: t > 0,$	$z = 0;$	$C_A = C_{Ai}$
Boundary condition 2	$: t > 0,$	$z = \infty;$	$C_A = C_{Ab}$

$$\frac{C_A - C_{Ab}}{C_{Ai} - C_{Ab}} = 1 - \operatorname{erf}\eta; \quad \text{where } \eta = \frac{z}{2\sqrt{D_{AB}t}} \quad (3.34)$$

The mass flux to the element at any time t can be derived from the equation

$$N_A(t) = -D_{AB} \left[\frac{\partial C_A}{\partial z} \right]_{z=0} = \sqrt{\frac{D_{AB}}{\pi t}} (C_{Ai} - C_{Ab}) \quad (3.35)$$

The flux decreases with time because of a gradual build-up of the solute concentration within the element and the resulting decrease in the driving force. At a large time, the element becomes nearly saturated and the flux becomes vanishingly small.

The average mass flux over the contact time t_c is given by

$$N_{A,av} = \frac{1}{t_c} \int_0^{t_c} N_A(t) dt = 2 \sqrt{\frac{D_{AB}}{\pi t_c}} (C_{Ai} - C_{Ab}) \quad (3.36)$$

Comparing Eqs. (3.35) and (3.36) with Eq. (3.3),

$$\text{Instantaneous mass transfer coefficient, } k_L = \sqrt{\frac{D_{AB}}{\pi t}} \quad (3.37)$$

$$\text{Average mass transfer coefficient, } k_{L,av} = 2 \sqrt{\frac{D_{AB}}{\pi t_c}} \quad (3.38)$$

The above equations show that the mass transfer coefficient is proportional to the square root of diffusivity. Although this is again not in conformity with experimental observations in general, this is definitely an improvement over the film theory for a more realistic visualization. Here the contact time t_c is the model parameter like the film thickness δ in the film theory.

3.7.3 The Surface Renewal Theory

One of the major drawbacks of the penetration theory is the assumption that the contact time or the ‘age’ of the liquid elements is the same for all. In a turbulent medium it is much more probable that some of the liquid elements are swept away, while still young, from the interface

by eddies while some others, unaffected by the eddies for the time being, may continue to be in contact with the gas for longer times. As a result, there will be a ‘distribution of age’ of the liquid elements present at the interface at any moment. This is how Danckwert (1951) visualized the phenomenon. He assumed that (i) the liquid elements at the interface are being randomly replaced by fresh elements from the bulk, (ii) at any moment each of the liquid elements at the surface has the same probability of being replaced by a fresh element, (iii) unsteady state mass transfer occurs to an element during its stay at the interface. The Danckwert’s theory is thus called the *surface renewal theory*. The model parameter is the fractional rate of surface renewal (s , the fraction of the surface area renewed in unit time). The equation for the mass transfer coefficient according to the Danckwert’s theory is as follows (the derivation is shown in Chapter 16).

$$k_L = \sqrt{D_{AB}s} \quad (3.39)$$

Similarity between Mass, Heat and Energy transfer

3.8 MOMENTUM, HEAT AND MASS TRANSFER ANALOGIES

Transport of momentum, heat and mass in a medium in laminar motion are all diffusional processes and occur by similar mechanisms. The three basic laws in this connection—Newton’s law of viscosity that governs the rate of transport of momentum, Fourier’s law of heat conduction and Fick’s law of diffusion—can all be expressed in similar forms.

$$\text{Newton's Law: Momentum flux, } \tau = -\mu \frac{du_x}{dz} \Rightarrow \tau = -v \frac{d}{dz}(\rho u_x) \quad (3.42)$$

$$\text{Fourier's Law: Heat flux, } q_z = -k \frac{dT}{dz} \Rightarrow q_z = -\alpha \frac{d}{dz}(\rho c_p T) \quad (3.43)$$

$$\text{Fick's Law: Mass flux (at a low concentration), } N_A = -D_{AB} \frac{dC_A}{dz} \quad (3.44)$$

In Eq. (3.42), τ is the shear stress which is the same as momentum flux, ρu_x is the ‘volumetric concentration of momentum’ in the x -direction (i.e. momentum per unit volume of the liquid), and $v = \mu/\rho$, is the ‘momentum diffusivity’. In Eq. (3.43), $\rho c_p T$ is the ‘volumetric concentration of thermal energy’ and $\alpha (= k/\rho c_p)$ is the ‘thermal diffusivity’. Thus, all the above three equations state that the flux is proportional to the gradient of the quantity transported (momentum, heat energy, or mass), and the proportionality constant is the corresponding ‘diffusivity’ (that has the same unit, m^2/s , in all the cases). A negative sign is included in each equation to indicate that transport occurs in the direction of decreasing concentration (of momentum, heat, or mass).

Boundary Layer Theory

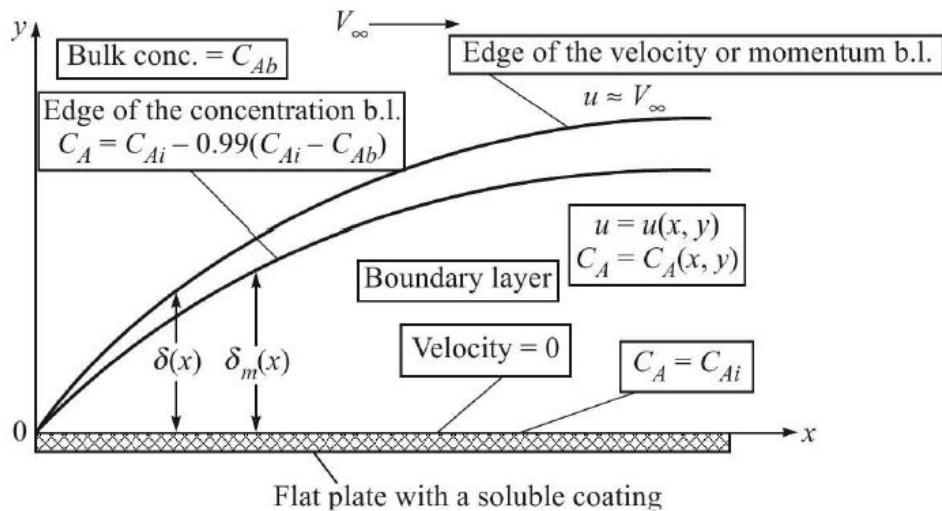


Figure 3.8 Momentum and concentration boundary layers on a flat plate for $Sc > 1$. V_∞ = free stream velocity; C_{Ab} = bulk concentration; C_{Ai} = surface concentration or the solubility of the coated solid in the liquid. Since $Sc > 1$, the momentum diffusivity is larger than the molecular diffusivity ($v_\infty > D_{AB}$), and the momentum boundary layer is thicker than the concentration boundary layer as a result.

Mass transfer in boundary layer flow occurs in a way similar to that of heat transfer. If the plate is coated with a soluble substance and the liquid (or gas) flows over it, two boundary layers are formed—the ‘velocity boundary layer’ and the ‘concentration’ or ‘mass boundary layer’ (Figure 3.8). It may be recalled that in boundary layer flow over a heated plate, a thermal boundary

layer is formed along with the velocity or momentum boundary layer (thickness = δ). The concentration distribution in the boundary layer is a function of position, $C_A = C_A(x, y)$, and its thickness is a function of the distance from the leading edge, $\delta = \delta_m(x)$. The thickness of the concentration boundary layer δ_m is defined as the distance over which the solute concentration drops by 99% of the concentration difference between the wall and the bulk liquid. The relative thicknesses of the velocity and the concentration boundary layers depend upon the value of the Schmidt number, Sc (which is the ratio of the momentum diffusivity to the molecular diffusivity). If the Schmidt number is greater than unity, the thickness of the momentum boundary layer at any location on the plate is more than the concentration boundary layer. It can be shown that $\delta/\delta_m = Sc^{1/3}$ (Deen, 1998; Bird et al., 2002).

Schmidt number, Sc (which is the ratio of the momentum diffusivity to the molecular diffusivity).

Theoretical analysis of mass transfer in a laminar boundary can be done following the same approach as adopted in the case of heat transfer, and the following equation for the local Sherwood number, Sh_x , can be developed.

$$Sh_x = \frac{k_{L,x} x}{D_{AB}} = 0.332(Re_x)^{1/2}(Sc)^{1/3} \quad (3.40)$$

Here x is the distance of a point from the leading edge of the plate, $k_{L,x}$ is the local mass transfer coefficient, and Re_x is the 'local Reynolds number'. If l is the length of the plate, the 'average Sherwood number', Sh_{av} , can be obtained from the above equation as follows:

$$Sh_{av} = \frac{k_{L,av} l}{D_{AB}} = 0.664(Re_l)^{1/2}(Sc)^{1/3} \quad (3.41)$$

In the above equation, $k_{L,av}$ is the mass transfer coefficient averaged over the length of the plate, and $Re_l = \rho V_\infty l / \mu$ is the 'plate Reynolds number' based on the length of the plate, l .

It is to be noted that the boundary layer theory predicts that the mass transfer coefficient k_L varies as $(D_{AB})^{2/3}$ which reasonably matches the experimental findings in many cases.

$$\begin{aligned} Sh &= \frac{\text{Convection flux}}{\text{Diffusion flux}} \\ &= \frac{k_c \cdot (\Delta CA)}{D_{AB} \cdot (\Delta CA)} \\ &= \frac{k_c \cdot l}{D_{AB}} \\ \text{Sc no. - } &\quad \frac{Sc}{(Schmidt)} \\ \text{Sc} &= \frac{D_{AB}}{D_{AB}} = \frac{\gamma}{D_{AB}} \end{aligned}$$

$$Sc = \frac{\nu}{D_{AB}} \approx P_n$$

Film, Penet, S.R \rightarrow implicit.

B.L \rightarrow explicit.

$$\rightarrow \underline{Sh = f(Re, Sc)}$$

$$Sh = \frac{Conv. N.T.}{\text{Diffusional M.T.}}$$

$$= \frac{k_c \cdot L}{D_{AB}} \approx Nu$$

$$Re = \frac{\rho \cdot V \cdot L}{\mu}$$

$$Sc = \frac{\nu}{D_{AB}} \approx Pr$$

$$Pe_H = Re \cdot Pr$$

$$Pe_M = Re \cdot Sc$$

$$St_H = \frac{Nu}{Re \cdot Pr}$$

$$St_M = \frac{Sh}{Re \cdot Sc}$$

$$Nu = \frac{\text{Heat transfer due to convection}}{\text{Heat transfer due to conduction}}$$

$$= \frac{hA\Delta T}{K \cdot A \frac{\Delta T}{L}} = \frac{hL}{K}$$

$Sh \equiv$ Sherwood Number

$$= \frac{\text{Mass transfer due to convective mass transfer}}{\text{molecular diffusion}}$$

Ignoring bulk flow $N_A + N_B = 0$

$$Sh = \frac{\frac{K_c A \Delta C_A}{D_{AB} \frac{l}{l} A \Delta C_A}}{D_{AB}} = \frac{K_c l}{D_{AB}} = \frac{K_L l}{D_{AB}}$$

For $N_A + N_B \neq 0$

$$Sh = \frac{K_c l}{D_{AB}} \left[\frac{C}{(C_B)_{em}} \right]$$

$$Re = \frac{\rho v D}{\mu} = \frac{G_D}{\mu}$$

$$Pr = \frac{\gamma}{\alpha} \Leftrightarrow Sc \equiv \text{Schmidt Number} \\ = \frac{\gamma}{D_{AB}}$$

$$Pe_H = Re \cdot Pr$$

$$St_H = \frac{Nu}{Pe}$$

$$\left. \begin{array}{l} Pe_M = Re \cdot Sc \\ St_M = \frac{Sh}{Pe_M} \end{array} \right\} \text{For mass transfer}$$

Boundary layer thickness depends on Schmidt & Prandtl number.

$$\frac{k_L \cdot x}{D_{AB}} = 0.332 \left(\frac{x \nu_{AB} P}{\mu} \right)^{1/2} \left(\frac{\gamma}{D_{AB}} \right)^{1/3}$$

$$Sh_x = 0.332 (Re_x)^{1/2} \left(\frac{Sc}{Pe} \right)^{1/3}$$

$$Sh_x \propto Re^n$$

$$\propto Sc^m$$

$$\frac{\int_0^L Sh_x dx}{\int_0^L x dx} = \overline{Sh}_L = 0.664 (Re_L)^{1/2} (Sc)^{1/3} = \frac{k_L \cdot L}{D_{AB}}$$

Average Sherwood number

$k_L \propto D_{AB}$	film theory
$\propto D_{AB}^{1/2}$	Penetration theory
$\propto D_{AB}^{1/2}$	Surface Renewal u
$\propto D_{AB}^{2/3}$	Boundary Layer theory

Reynolds analogy

The similarity of the three transport laws has been extended to relate the appropriate dimensionless groups involving the heat transfer coefficient and the mass transfer coefficient to the friction factor. Such relations or ‘analogies’ (Skelland, 1974) can be used to estimate the heat transfer coefficient (h), or the mass transfer coefficients (k_G , k_L , etc.) if the friction factor of the flowing medium is known. Here we mention a few simple analogies without going into the theoretical formalism (see Skelland, 1974; Hines and Maddox, 1985; Dutta, 2001). The oldest such analogy in the case of heat transfer was proposed by Reynolds applicable to *transport in pipe flow*. Extending the analogy to the case of mass transfer, we may write

$$St_H = \frac{Nu}{Re Pr} = \frac{f}{2} \quad \text{and} \quad St_M = \frac{Sh}{Re Sc} = \frac{f}{2} \quad (3.48)$$

Here St_H is the Stanton number for heat transfer and St_M is that for mass transfer, Nu is the Nusselt number involving the heat transfer coefficient, and f is the friction factor for the fluid flowing through a pipe.

Prandtl analogy

The Prandtl analogy, also applicable to transport in pipe flow, is given by

$$St_H = \frac{f/2}{1 + 5\sqrt{f/2} (Pr - 1)} \quad \text{and} \quad St_M = \frac{f/2}{1 + 5\sqrt{f/2} (Sc - 1)}$$

The Prandtl analogy reduces to the Reynolds analogy if $Pr = 1$ or $Sc = 1$.

Colburn related the mass transfer coefficient to the friction factor by proposing the well-known ‘Colburn analogy’. He introduced the Colburn j -factor and suggested the following analogies for transport in pipe flow.

$$j_H = St_H \Pr^{2/3} = \frac{Nu}{Re \Pr^{1/3}} = 0.023 Re^{-0.2} \quad (3.50)$$

and $j_D = St_M Sc^{2/3} = \frac{Sh}{Re Sc^{1/3}} = 0.023 Re^{-0.2} \quad (3.51)$

Here the subscripts ‘ H ’ and ‘ M ’ refer to heat and mass transfer respectively [the subscript ‘ D ’ in j_D means diffusion and is synonymous to the subscript M in Eq. (3.49)]. The importance of the analogies lies in the fact that if the heat transfer coefficient is known at a particular hydrodynamic condition characterized by the Reynolds number, the mass transfer coefficient in

a system having similar geometry and at similar hydrodynamic condition (i.e. the same Reynolds number) can be determined just by putting $j_H = j_D$.

If the two phases are at *equilibrium*, there is no net transfer of the solute from one phase to the other. However, this does not mean that there is no transfer of solute molecules from one phase to the other at all. It rather means that if a few molecules go from phase-I to phase-II, the same number of molecules move from phase-II to phase-I in order to maintain the concentrations in the phases constant. This equilibrium is sometimes called ‘dynamic equilibrium’.

4.2.1 Raoult’s Law

For an *ideal* gas–liquid or vapour–liquid system, the equilibrium relationship obeys the Raoult’s law. The law is mathematically expressed as

$$p_A^* = x_A P_A \quad (4.1)$$

where

P_A = vapour pressure of A at the given temperature

x_A = mole fraction of the solute A in the liquid

p_A^* = equilibrium partial pressure exerted by the solute.

A solution behaves ideally when

- (a) the solute and the solvent molecules have similar sizes and similar intermolecular forces,
- (b) the excess volume of mixing is zero, and
- (c) the heat of mixing is zero when both the solute and the solvent are liquids.

When the solute is a gas, the heat of mixing is equal to the heat of condensation.

Most solutions are, however, non-ideal. There are some solutions which are nearly ideal in their behaviour.

4.2.2 Henry's Law

Equilibrium data for many non-ideal gas–liquid systems at low concentrations can be expressed by the Henry's law (for more details about Henry's law, see Carroll, 1999)

$$p_A^* = Hx_A \quad (4.2)$$

where H is the Henry's law constant, and p_A^* and x_A have significances as stated above. The constant H for a given solute–solvent pair is a strong function of temperature (it increases with

4.3.1 Concentration Profiles Near the Interface

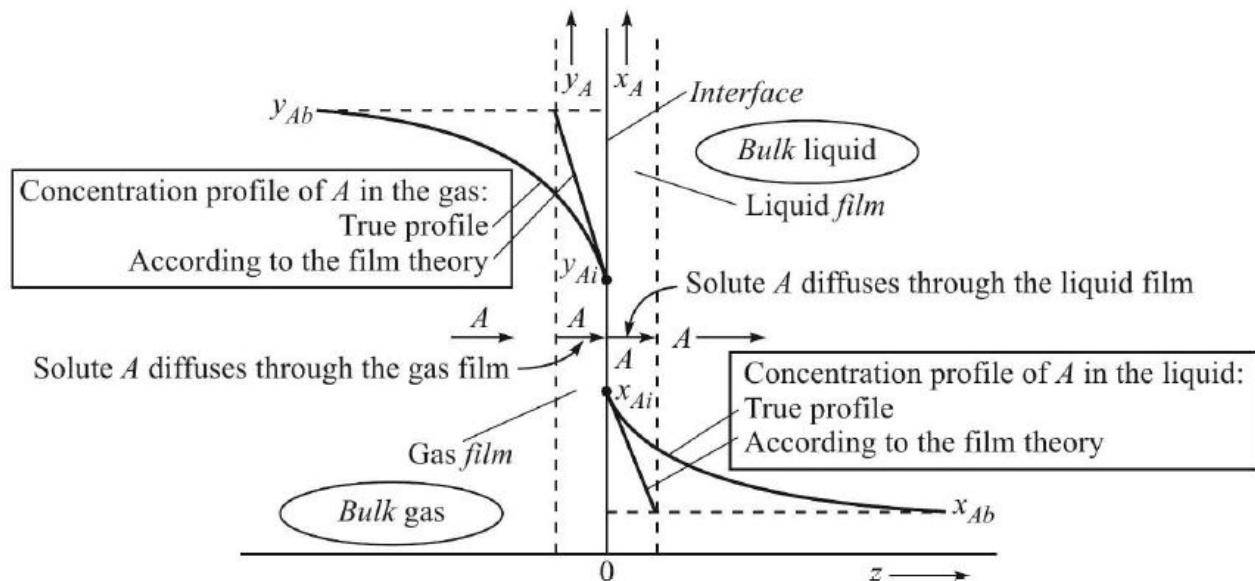


Figure 4.3 Concentration profile of the solute A on the two sides of the interface in a dilute solution.

... on the liquid side of the interface. Commonly, these are called the interfacial concentrations.

In most situations involving mass transfer, we assume that equilibrium exists at the interface, i.e. y_{Ai} and x_{Ai} are at equilibrium. This is sometimes written as

$$y_{Ai} = \varphi(x_{Ai}) \quad (4.7)$$

4.3.3 Determination of the Interfacial Concentrations

The determination of the interfacial concentrations is very often necessary in mass transfer calculations. We can do it algebraically or graphically. If mass transfer occurs from a gas phase to a liquid phase at *steady state*, the mass flux of the solute A from the bulk gas to the interface must be equal to that from the interface to the bulk liquid. This is because, at steady state, there cannot be any accumulation of the solute anywhere. In terms of the gas- and the liquid-phase coefficients (see Table 3.1), we can write

$$N_A = k_y(y_{Ab} - y_{Ai}) = k_x(x_{Ai} - x_{Ab}) \quad (4.9)$$

Gas-phase flux to the interface Liquid-phase flux from the interface

Assuming interfacial equilibrium, x_{Ai} and y_{Ai} are related by Eq. (4.7).

$$y_{Ai} = \varphi(x_{Ai}) \quad (4.7)$$

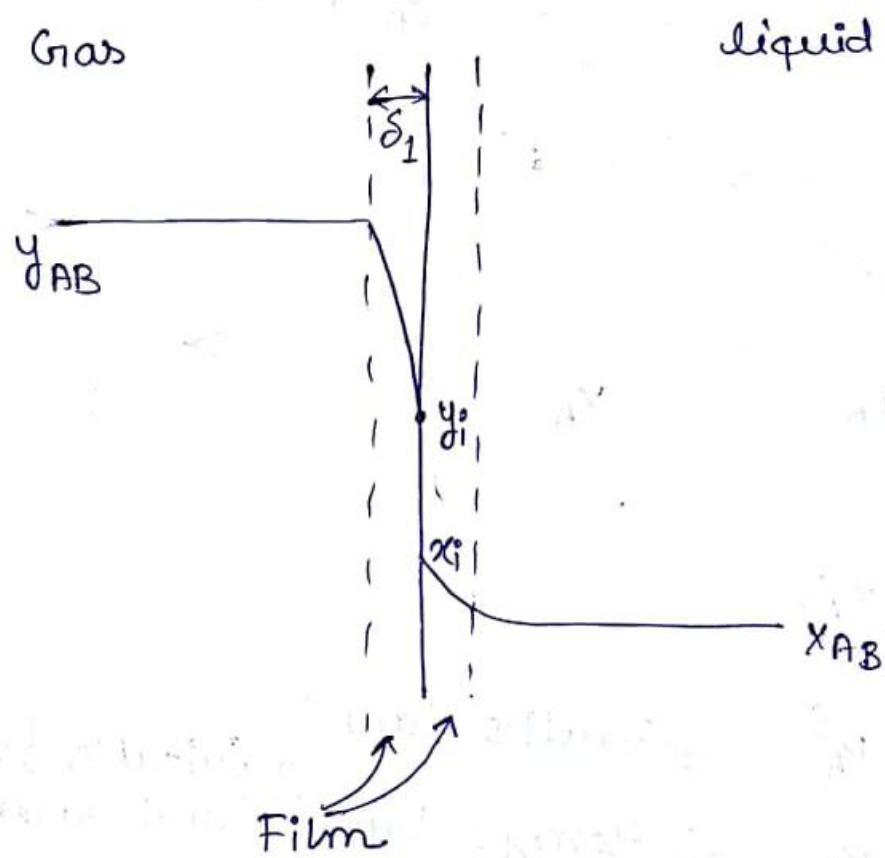
If the bulk concentrations (x_{Ab} and y_{Ab}) and the mass transfer coefficients (k_x and k_y) are known, the algebraic Eqs. (4.9) and (4.7) can be solved for the two unknowns x_{Ai} and y_{Ai} , which are the interfacial concentrations. This is the algebraic procedure. However, the equilibrium data are mostly available in the tabular form rather than in the functional form such as Eq. (4.7). So a graphical procedure described below is of wider use.

Refer to Figure 4.4. Equilibrium data are plotted on the x - y plane to obtain the equilibrium curve. The point M , representing the bulk concentrations of the phases (x_{Ab} , y_{Ab}), is located on the same plane. From Eq. (4.9), we may write

$$\frac{y_{Ab} - y_{Ai}}{x_{Ab} - x_{Ai}} = -\frac{k_x}{k_y} \quad (4.10)$$

It is now obvious that if a line of slope $-k_x/k_y$ is drawn through the point M and extended to the equilibrium line, the point N will be reached. The point N , lying on the equilibrium line, gives the interfacial concentrations.

- 1) Transport of A from bulk to interface
- 2) At interface equilibrium will be established
- 3) A will be transported from interface to bulk



All mass transfer resistance exists in a thin film at the interface. There are two such films at interface on both sides.

$$\begin{aligned}
 N_A &= \frac{1}{R_y} \Delta y_A \quad \text{Local mass transfer coefficient} \\
 &= \frac{1}{R_x} \Delta x_A
 \end{aligned}$$

4.4 THE OVERALL MASS TRANSFER COEFFICIENT

The calculation of the flux of interphase mass transfer by using Eq. (4.9) becomes an easy job if the interfacial and bulk concentrations of the solute in either of the phases are known. But, as a matter of fact, interfacial concentrations are not directly measurable quantities and cannot be specified as such in a practical problem. Even in an experimental set-up on mass transfer study, it is only the bulk concentrations that can be measured by taking samples of the phases and analyzing for the solute contents. In reality, the interfacial concentrations cannot be accurately measured since it is not possible to collect a sample of any phase from the interface, which is just a geometrical surface. Thus, Eq. (4.9) does not help us much for practical mass transfer

At this point, we also need to consider how the ‘overall driving force’ should be expressed in relation to the overall mass transfer coefficient. In the case of heat transfer, the difference in the bulk temperatures of the two phases is taken as the driving force. In mass transfer, the driving force can be expressed in terms of the gas-phase concentration difference or the liquid-phase concentration difference (unlike in the case of heat transfer where the difference of the bulk temperature of the two phases is the driving force irrespective of the nature of the phases). So, depending upon how we express the overall driving force, we define two overall mass transfer coefficients as shown below (here the concentrations are expressed in the mole fraction unit).

$$N_A = K_y (y_{Ab} - y_{Ab}^*) \quad (4.11)$$

$$= K_x (x_{Ab}^* - x_{Ab}) \quad (4.12)$$

In Eq. (4.11), K_y is the ‘overall gas-phase mass transfer coefficient’ in which the suffix ‘y’ means that the corresponding driving force should be expressed in terms of gas-phase mole fraction difference. But what is y_{Ab}^* ? It is the mole fraction of the solute in the gas phase *that can remain in equilibrium* with a solution having a mole fraction x_{Ab} of the solute A. By virtue of the equilibrium relation (4.7), we can write

$$y_{Ab}^* = \varphi(x_{Ab}) \quad (4.13)$$

because x_{Ab} and y_{Ab}^* are in equilibrium (as stated before, we often use an * to denote the equilibrium concentration).

The quantity $(y_{Ab} - y_{Ab}^*)$ is the overall driving force on the ‘gas-phase basis’. We have assumed here that mass transfer occurs from the gas to the liquid phase. If it is so, the system must be away from equilibrium, and $(y_{Ab} - y_{Ab}^*)$ gives a measure of how far the system is away from equilibrium.

Similarly, in Eq. (4.12), K_x is the ‘overall liquid-phase mass transfer coefficient’, and $(x_{Ab}^* - x_{Ab})$ is the overall driving force on liquid-phase basis. Here x_{Ab}^* is the mole fraction of A in the solution that can remain in equilibrium with a gas-phase containing solute A at a mole fraction y_{Ab} . Invoking Eq. (4.7), we can now write

$$y_{Ab} = \varphi(x_{Ab}^*) \quad (4.14)$$

The next important question is: How to relate the overall coefficients, K_y and K_x , with the ‘individual coefficients’, k_x and k_y ?[†] We will do this by taking the help of a geometrical

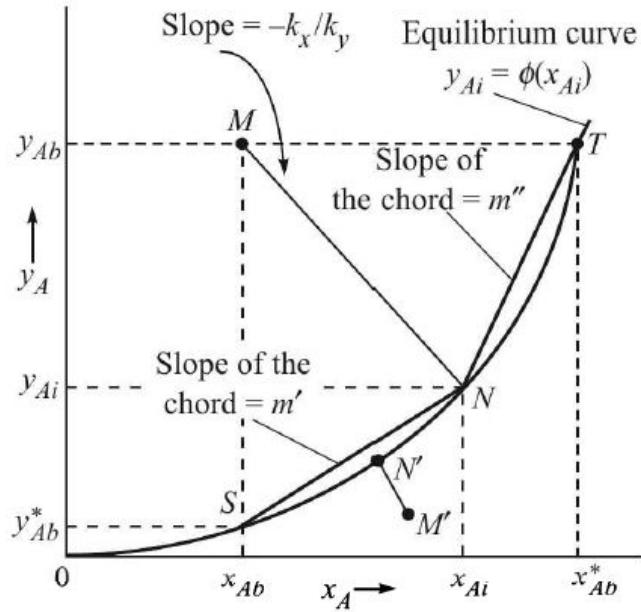


Figure 4.5 Geometrical representation of the overall driving force.

Now, at steady state, the flux is the same irrespective of whether the gas- or the liquid-phase mass transfer coefficient is used, i.e.

$$N_A = k_y(y_{Ab} - y_{Ai}) = k_x(x_{Ai} - x_{Ab}) = K_y(y_{Ab} - y_{Ab}^*) \quad (4.15)$$

or $(y_{Ab} - y_{Ai}) = \frac{N_A}{k_y}$ (4.16a)

$$(x_{Ai} - x_{Ab}) = \frac{N_A}{k_x} \quad (4.16b)$$

and $(y_{Ab} - y_{Ab}^*) = \frac{N_A}{K_y}$ (4.16c)

From Figure 4.5,

$$\begin{aligned} (y_{Ab} - y_{Ab}^*) &= (y_{Ab} - y_{Ai}) + (y_{Ai} - y_{Ab}^*) = (y_{Ab} - y_{Ai}) + \frac{(y_{Ai} - y_{Ab}^*)}{(x_{Ai} - x_{Ab})}(x_{Ai} - x_{Ab}) \\ &= (y_{Ab} - y_{Ai}) + m'(x_{Ai} - x_{Ab}) \end{aligned} \quad (4.17)$$

From Eqs. (4.16) and (4.17),

$$\frac{N_A}{K_y} = \frac{N_A}{k_y} + \frac{m' N_A}{k_x} \quad \Rightarrow \quad \frac{1}{K_y} = \frac{1}{k_y} + \frac{m'}{k_x} \quad (4.18)$$

Proceeding in a similar fashion, we can express the overall liquid-phase mass transfer coefficient in terms of the individual coefficients.

$$N_A = k_y(y_{Ab} - y_{Ai}) = k_x(x_{Ai} - x_{Ab}) = K_x(x_{Ab}^* - x_{Ab})$$

i.e. $(x_{Ab}^* - x_{Ab}) = \frac{N_A}{K_x}$ (4.19)

and $\begin{aligned} (x_{Ab}^* - x_{Ab}) &= \frac{(x_{Ab}^* - x_{Ai})}{(y_{Ab} - y_{Ai})}(y_{Ab} - y_{Ai}) + (x_{Ai} - x_{Ab}) \\ &= \frac{1}{m''}(y_{Ab} - y_{Ai}) + (x_{Ai} - x_{Ab}) \end{aligned}$ (4.20)

From Eqs. (4.20), (4.19) and [4.16(a),(b)],

$$\frac{N_A}{K_x} = \frac{N_A}{m'' k_y} + \frac{N_A}{k_x} \quad \Rightarrow \quad \frac{1}{K_x} = \frac{1}{m'' k_y} + \frac{1}{k_x} \quad (4.21)$$

$$\frac{1}{K_x} = \frac{1}{m'' k_y} + \frac{1}{k_x}$$

Since K_y is the overall mass transfer coefficient, its inverse, $1/K_y$, can be considered to be the ‘overall mass transfer resistance’ *on the gas-phase basis* [see Eq. (4.18)]. It is the sum of the individual mass transfer resistances of the two phases described below.

$$\frac{1}{k_y} = \text{individual gas-phase mass transfer resistance}$$

$$\frac{m'}{k_x} = \text{individual liquid-phase mass transfer resistance (on gas phase basis)}$$

Similar is the message of Eq. (4.21).

$$\frac{1}{k_x} = \text{individual liquid-phase mass transfer resistance}$$

$$\frac{1}{m'' k_x} = \text{individual gas-phase mass transfer resistance (on liquid-phase basis)}$$

Also,

The fractional resistance offered by the gas-phase

$$= \frac{\text{resistance offered by the gas-phase}}{\text{total resistance of the two phases}} = \frac{1/k_y}{1/K_y} \quad (4.22)$$

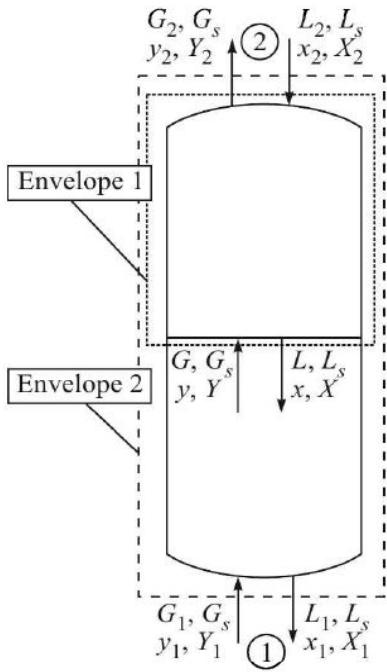
The fractional mass transfer offered by the liquid-phase

$$= \frac{\text{resistance offered by the liquid-phase}}{\text{total resistance of the two phases}} = \frac{m'/k_x}{1/K_y} \quad (4.23)$$

If the Henry’s law ($y = mx$) is applicable for any system, the equilibrium line in Figure 4.5 becomes straight and the slopes of the chords in Eqs. (4.18) and (4.21) become equal, i.e. $m' = m'' = m$.

4.5.1 The Steady-state Countercurrent Mass Transfer

A countercurrent contacting apparatus is shown in Figure 4.7. The meanings of the various notations are also shown in the figure. The phase L is heavier and flows down the apparatus and



Notations

G_1 = Rate of input of phase G at section 1, mol/time

G_2 = Rate of output of phase G at section 2, mol/time

G_s = Rate of flow of phase G on *solute-free basis*, mol/time

G = Rate of flow of phase G at any section, mol/time

y_1, y_2, y = Mole fractions of the solute in phase G at respective sections

Y_1, Y_2, Y = Mole ratios of the solute in phase G at respective sections

L_1 = Rate of output of phase L at section 1, mol/time

L_2 = Rate of output of phase L at section 2, mol/time

L_s = Rate of flow of phase L on *solute-free basis*, mol/time

L = Rate of flow of phase L at any section, mol/time

x_1, x_2, x = Mole fractions of the solute in phase L at respective sections

X_1, X_2, X = Mole ratios of the solute in phase L at respective sections

$$G_s = \frac{G}{1+Y} \quad Y = \frac{y}{1-y} \quad L_s = \frac{L}{1+X} \quad X = \frac{x}{1-x}$$

Figure 4.7 Mass balance for steady state countercurrent contact.

$$L_s X_2 + G_s Y_1 = L_s X_1 + G_s Y_2 \Rightarrow G_s(Y_1 - Y_2) = L_s(X_1 - X_2)$$

...,

$$L_s X_2 + G_s Y_1 = L_s X_1 + G_s Y_2 \Rightarrow G_s(Y_1 - Y_2) = L_s(X_1 - X_2)$$

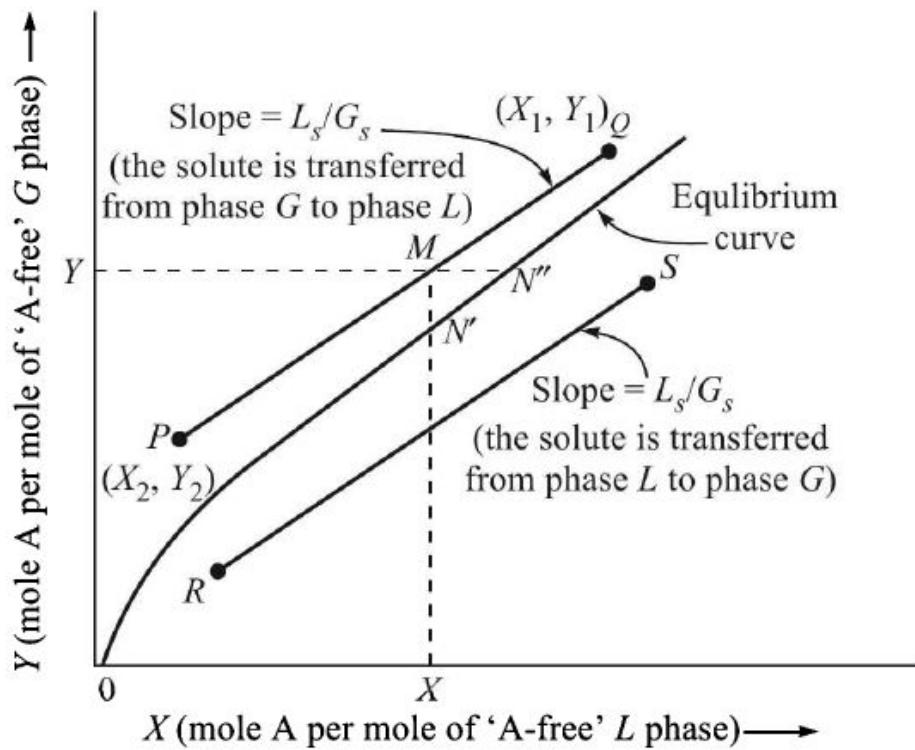


Figure 4.8 The operating line for a countercurrent contact (concentrations are in mole ratio unit).

$$Gy + L_2x_2 = G_2y_2 + Lx$$

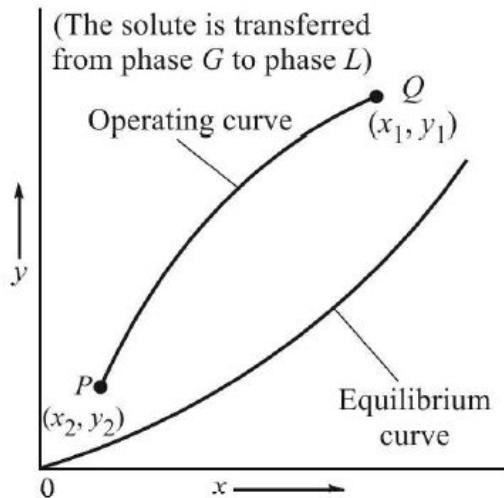


Figure 4.9 The operating curve for a counter-current process (the concentrations expressed in mole fraction).

In this case note that g and I are not constant and varies because of mass transfer

$x-y$ plane, such as that shown in Figure 4.9. However, if the concentrations of the phases are *low*, the variations in the flow rates of L and G will be rather small. In such a case, the operating line will be *nearly straight*.

4.5.2 The Steady-state Cocurrent Process

$$G_s(Y_1 - Y_2) = L_s(X_2 - X_1) \quad G_s(Y_1 - Y_2) = L_s(X_2 - X_1)$$

together with the operating line, PQ . If the bulk concentrations of the phases at any section are (X, Y) , represented by the point M on the operating line, then MN' gives the overall gas-phase driving force and MN'' gives the overall liquid-phase driving force at this section. If a line of slope $-k_x/k_y$ is drawn through M and meets the equilibrium curve at the point M' , it gives the interfacial concentrations at the particular section. If the phases are allowed to be in contact for a sufficiently long time, the outgoing streams will reach equilibrium, and the equilibrium concentrations will be given by the point F . Thus the equilibrium curve, in effect,

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phases.
 $X-Y$ plane

Figure 4.10 Mass balance in a steady state cocurrent process (notations as in Figure 4.7).

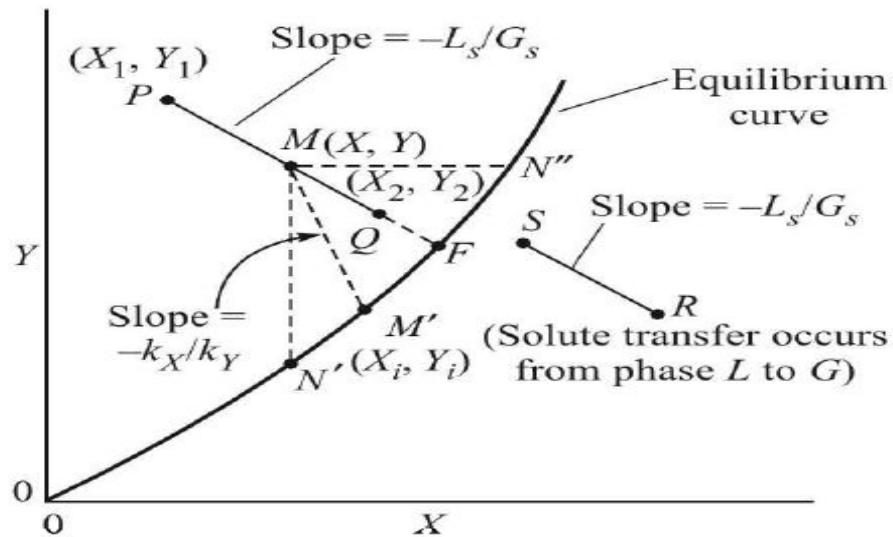


Figure 4.11 Operating lines for cocurrent contact (concentration in the mole ratio unit).

4.6 MASS TRANSFER IN STAGE-WISE CONTACT OF TWO PHASES

Counter current

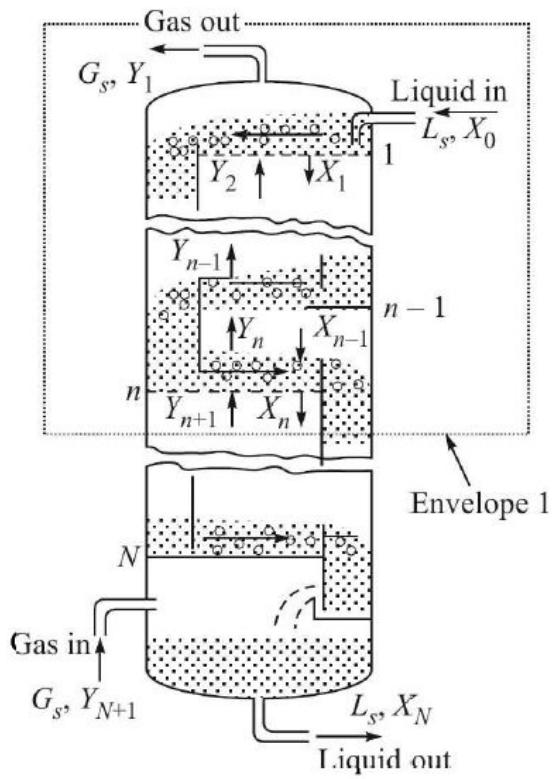


Figure 4.12 Countercurrent contact in a tray tower.

4.6.1 Stage

Any device or combination of devices in which two immiscible phases are brought into intimate contact in order to achieve mass transfer (of one or more solutes) from one phase to the other is called a *stage*. An efficient contact of the phases in a stage *tends* to bring them to equilibrium. If the contacting is so efficient that the phases reach equilibrium when they leave, the stage is called an *ideal stage*. This leads to the definition of ‘stage efficiency’. The stage efficiency gives a measure of how close to the equilibrium the phases may reach in a stage. An ideal stage has 100% efficiency. A group of interconnected stages in which the phases flow from one stage to other, in sequence, is called a *cascade*.

$$G_s(Y_{n+1} - Y_1) = L_s(X_n - X_0) \quad G_s(Y_{N+1} - Y_1) = L_s(X_N - X_0)$$

There is an obvious question in this connection. What should we do if the construction does not end up exactly at the point P ? We get *fraction of a plate* in the last step of construction. This is explained in Figure 4.13(b). The idea behind expressing the number of ideal plates as a mixed fraction is that if we divide this number by the *overall plate efficiency*, we get a better estimate of the number of real trays required for the separation^{††}.

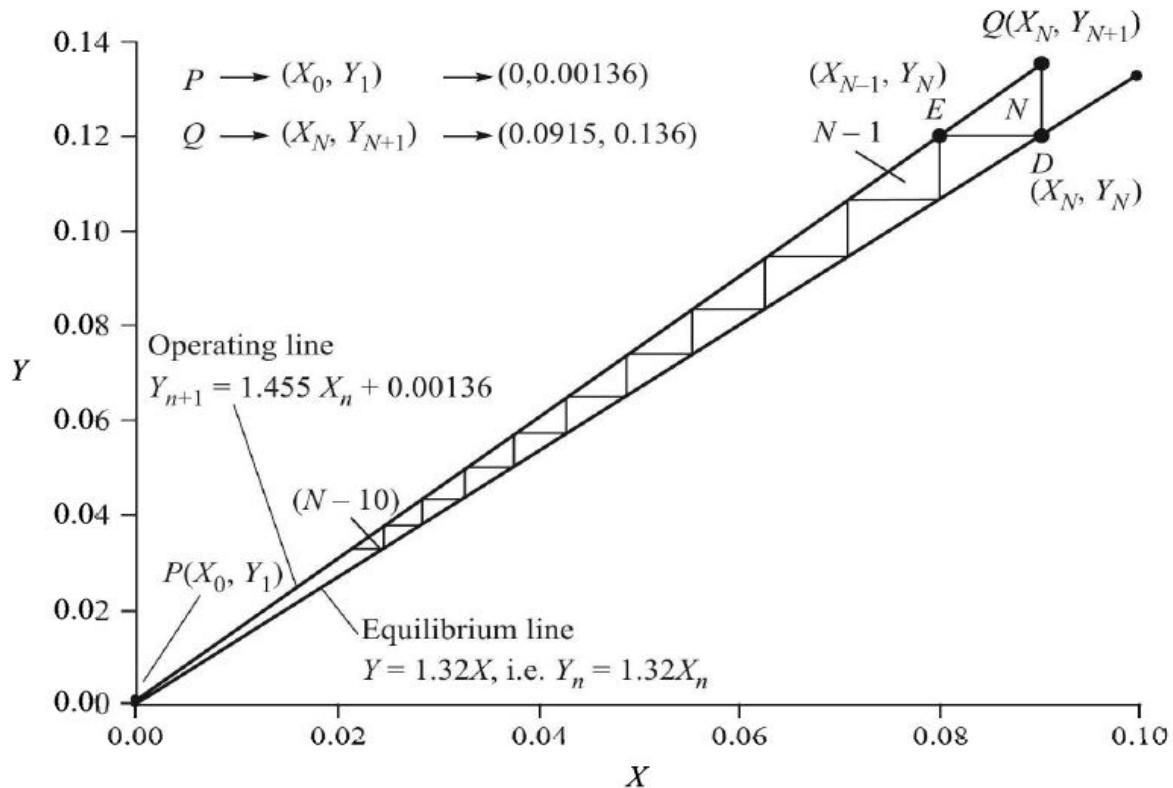


Figure 4.13 (a) Graphical construction of stages for countercurrent mass transfer (data from Example 4.5).

4.6.3 Algebraic Determination of the Number of Ideal Stages

the phase flow rates are on solute-free basis, the operating line is always linear. If the equilibrium line is also straight, say, given by $Y = \alpha X$, the point (X_n, Y_n) lies on this line, i.e.

$$Y_n = \alpha X_n \quad (4.33)$$

Substituting for X_n in the operating line Eq. (4.31) and rearranging,

$$\begin{aligned} Y_{n+1} - Y_1 &= \frac{L_s}{G_s}(X_n - X_0) = \bar{A} Y_n - \bar{A} \alpha X_0; \quad \bar{A} = \frac{L_s}{\alpha G_s} \\ \Rightarrow Y_{n+1} - \bar{A} Y_n &= Y_1 - \bar{A} \alpha X_0 \end{aligned} \quad (4.34)$$

In the case of gas absorption, the quantity $\bar{A} = L_s/\alpha G_s$ is called the *absorption factor*. This quantity has a direct mathematical significance—it is the ratio of the slope of the operating line to that of the equilibrium line, $(L_s/G_s)/\alpha$. Equation (4.34) is a first-order non-homogeneous linear ‘difference equation’ that can be solved by using the standard technique. The corresponding

$$N = \frac{\log \left[\left(\frac{Y_{N+1} - \alpha X_0}{Y_1 - \alpha X_0} \right) \left(1 - \frac{1}{\bar{A}} \right) + \frac{1}{\bar{A}} \right]}{\log \bar{A}}$$

The solution given by Eq. (4.40), does not apply when $\bar{A} = 1$. In this case Eq. (4.34) becomes

$$Y_{n+1} - Y_n = Y_1 - \bar{A} \alpha X_0 \quad (4.42)$$

If we write this equation for $n = N, N - 1, N - 2, \dots, 1$, and add, we get

$$\begin{aligned} Y_{N+1} - Y_1 &= N(Y_1 - \bar{A} \alpha X_0) \\ \Rightarrow N &= \frac{Y_{N+1} - Y_1}{Y_1 - \bar{A} \alpha X_0} \end{aligned}$$

4.6.4 The Number of Ideal Stages for Steady State Crosscurrent Contact

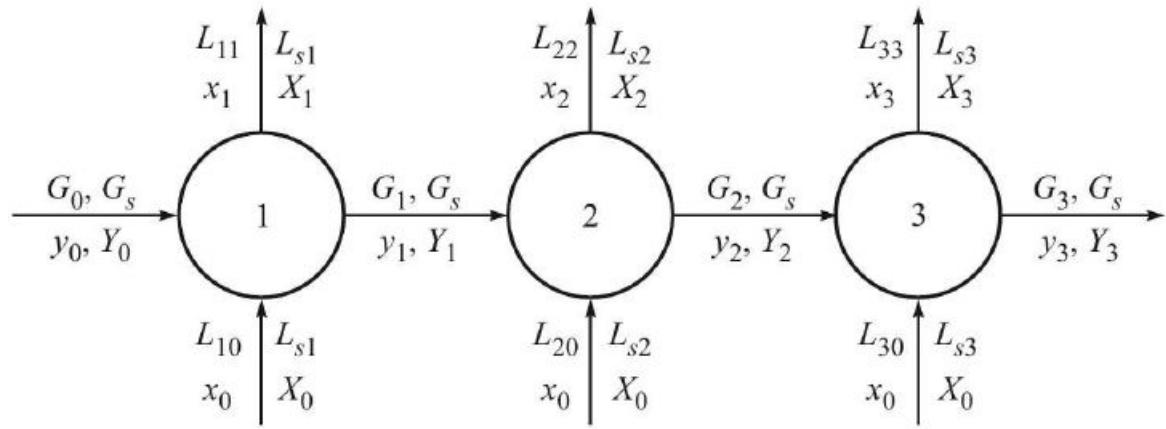


Figure 4.16 Flow arrangement in a cross-flow cascade.

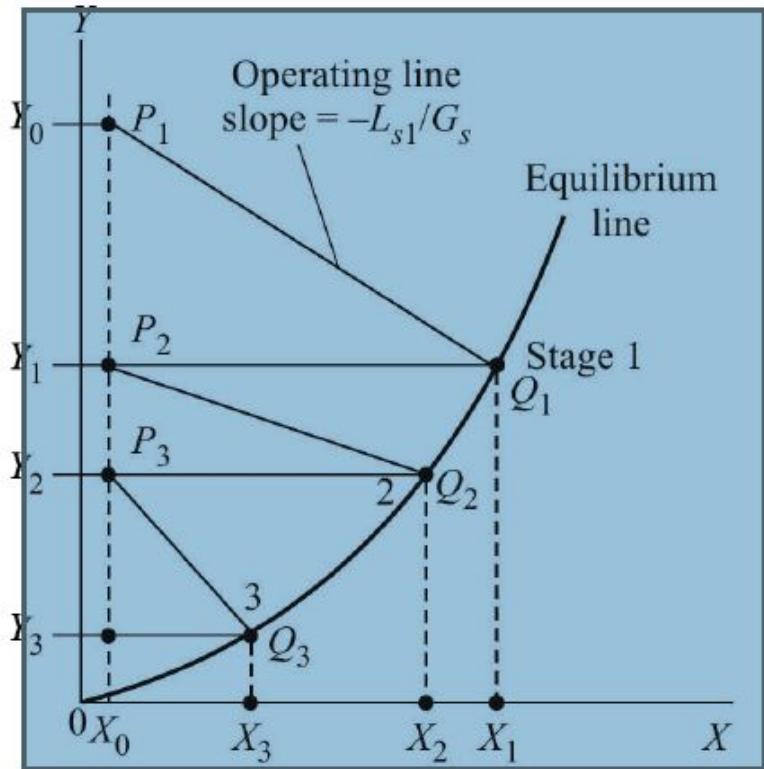
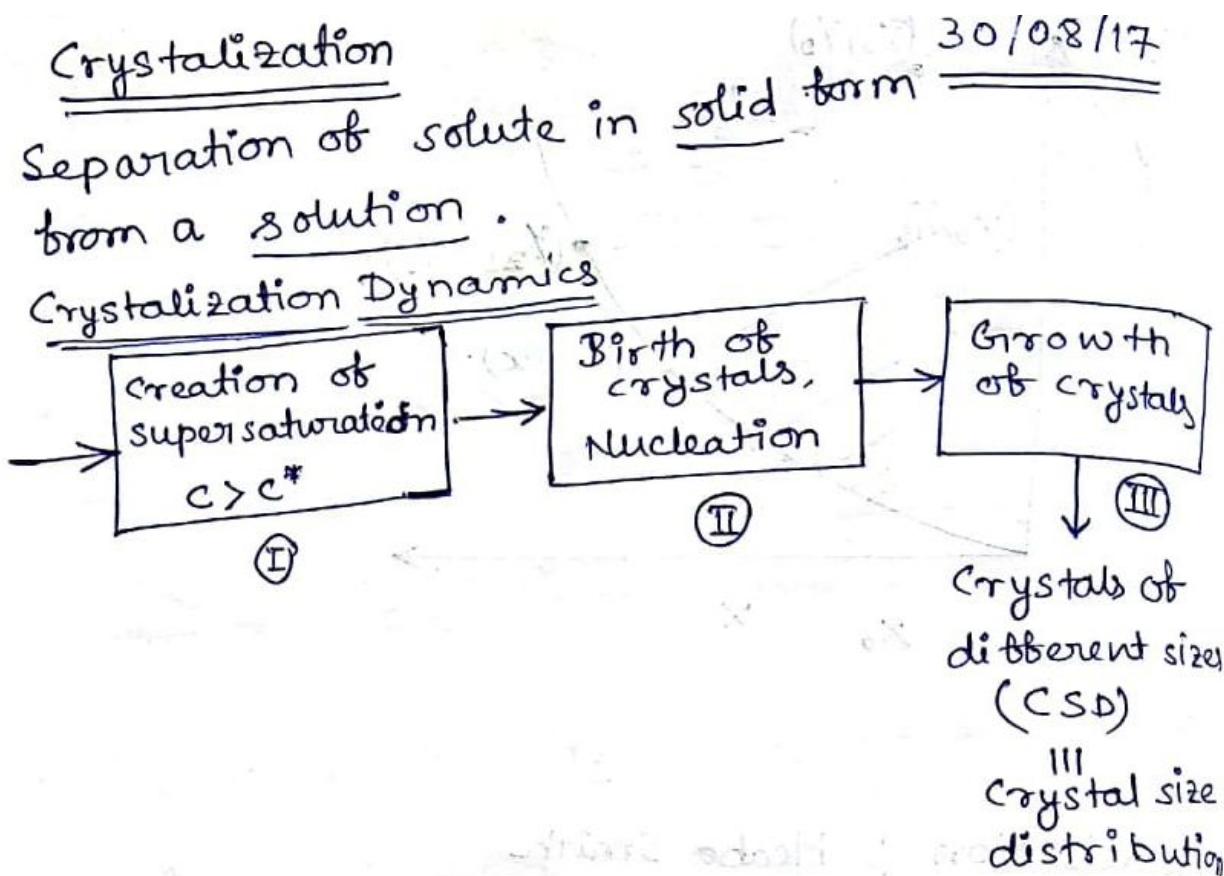


Figure 4.17 Graphical construction of a cross-current cascade (Mass transfer from phase G to phase L).

Figure 4.17. The equilibrium curve is drawn on the $X-Y$ plane. The operating line for stage 1 is drawn through the point $P_1(X_0, Y_0)$ with a slope $-L_{s1}/G_s$. The operating line is extended to meet the equilibrium curve at the point Q_1 if the stage is ideal. The operating line for stage 2 starts from P_2 (which has an ordinate $Y = Y_0$, and abscissa corresponding to the point Q_1) and will have a slope $-L_{s2}/G_s$. The operating lines for the three stages are P_1Q_1 (slope = $-L_{s1}/G_s$), P_2Q_2 (slope = $-L_{s2}/G_s$), and P_3Q_3 (slope = $-L_{s3}/G_s$). If equal amounts of phase L are supplied to the stages, the operating lines will be parallel. If all the stages are *ideal*, the construction procedure can be continued to find out the number of stages required to reduce the concentration of G phase to a specified level.



at the given temperature. Conversely, if we have a supersaturated solution, and a few seed crystals are dropped into it, a driving force for transportation of the solute from the bulk of the solution to the crystal surface will come into play. Thus, the extent of supersaturation in a solution is the driving force for crystallization. It may be mentioned that the solubility of very small

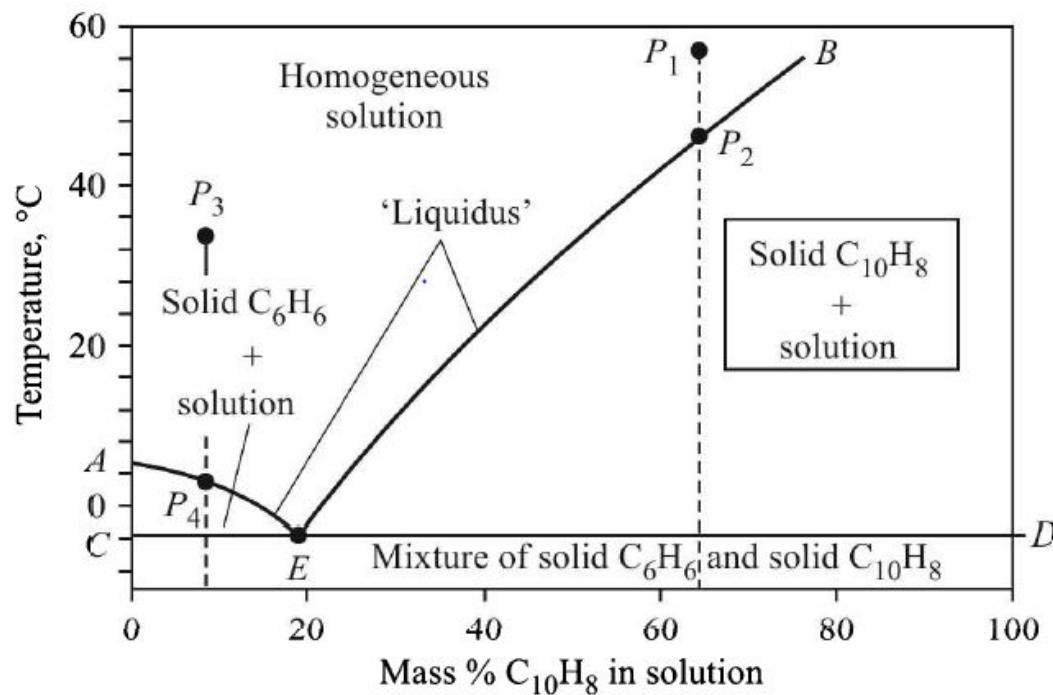


Figure 13.3 Phase equilibrium of the benzene–naphthalene system.

$$B^0 = \bar{k}(T) w^m M_T^n s^p \quad (13.3)$$

where

B^0 = number of nuclei formed per unit time in unit volume of the suspension

w = a measure of mechanical agitation (for example, it may be the agitator speed)

M_T = total mass of crystals per unit volume of the suspension or density of the suspension (kg/m^3)

s = degree of supersaturation

m, n, p = exponents

$\bar{k}(T)$ = a temperature-dependent coefficient.

The degree of supersaturation is defined as $s = (C - C_s)/C_s$, where C = solute concentration in the supersaturated solution, and C_s = solubility of the solute at the given temperature.

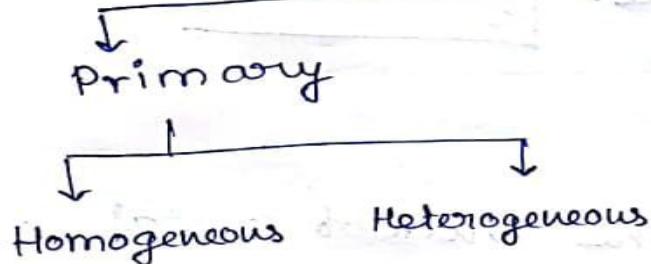
Characteristic length of crystal = L

$$B_0 = \lim_{L \rightarrow 0} \frac{d(N/V)}{dt}$$

$$A_0 = \phi_a L^2$$

$$V = \phi_v L^3$$

Nucleation



Secondary
Occurs due to storage or prolonged action of impellers

Homogeneous \equiv No addition of fine crystals. Occurs without any external interruption

Heterogeneous \equiv Seeds (small fine crystals) are added to facilitate formation of crystals

For primary nucleation: \nearrow crystal size

$$B_0 = A' \exp \left[\frac{16 \pi \sigma^3 v m^2}{3 k^3 T^3 [\ln(s+1)^2]} \right]$$

\nwarrow Boltzmann const.

For heterogeneous nucleation:

$$B_0 = K_1 M_T^{-n}$$

$K_1 \quad \} \text{Experimentally}$
 $n \quad \} \text{determined}$

Mass of suspension

$n = \text{order} \approx 0-5$

$n=2$ if nothing mentioned

B^0 = number of nuclei formed per unit time in unit volume of the suspension

III) Growth of crystals: m_c = mass of crystal

$$\text{Growth rate} = \frac{dL}{dt} = G_1$$

$$G_1 = k' s^n$$

McCabe ΔL law

Growth rate doesn't

$$G \neq f(L)$$

Depend on size

Final size depends on Residence Time