The other two theories has been extremely useful in the analysis of mass transfer accompanied by a chemical reaction.

## Mass transfer at fluid surfaces

Velocity of a fluid surface, as in the contact of a gas and liquid, is not zero. Therefore, a number of theories have been developed to replace the film theory.

Penetration Theory

This theory explain the mass transfer at fluid surface and this was proposed by Higbie (1935). Higbie emphasized that in many situations the time of exposure for mass transfer is too short and hence, concentration gradient of film theory does not achieve steady state.

This theory describe the contact of two fluids as shown in figure. A bubble of gas rises through a liquid which absorbs the gas.
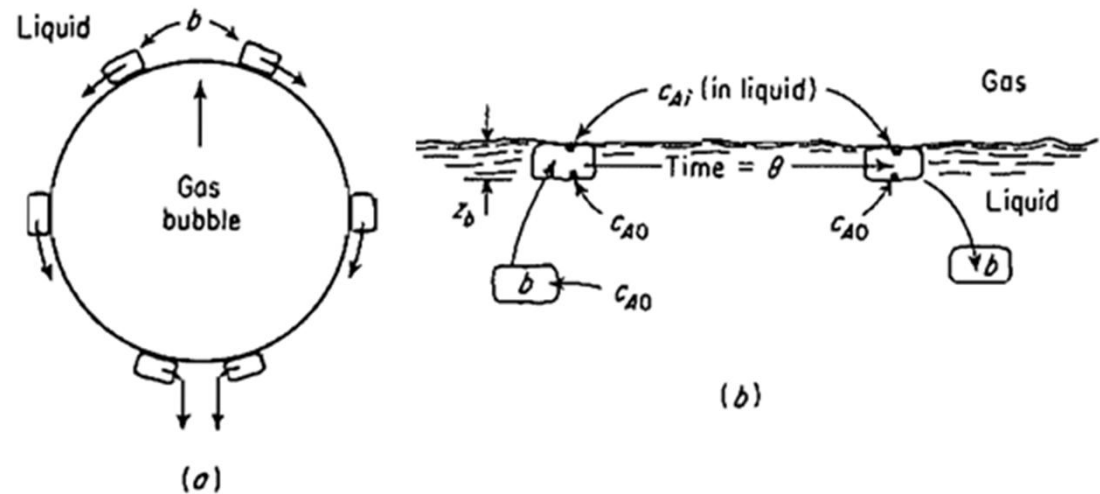
A particle of liquid b, initially at the top of the bubble, is in contact with the gas for the time θ required for the bubble to rise a distance equal to its diameter while the liquid particle slips along the surface of the bubble.

In an another case liquid may be in turbulent motion, shown in figure. An eddy b rising from the turbulent depths of the liquid and remain exposed for a time θ to the action of the gas.

In this theory the time of exposure is taken as constant for all such eddies or particles of liquid.

Initially, the concentration of dissolved gas in the eddy is uniformly c_{A0}, and internally the eddy is considered to be stagnant.

When the eddy is exposed to the gas at the surface, the concentration in the liquid at the gas-liquid surface is c_{Ai}, which may be taken as equilibrium solubility of the gas in the liquid.

During the time θ, the liquid particle is subject to unsteady state diffusion or penetration of solute in the z direction is

$$\frac{\partial c_A}{\partial \theta} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}$$

For short exposure times, and with slow diffusion in the liquid, the molecules of dissolving solute are never able to reach the depth zb corresponding to the thickness of the eddy, so that from the solute point of view, zb is essentially infinite.

The conditions on equation then are

$$c_A = \begin{cases} c_{A0} & \text{at } \theta = 0 & \text{for all } z \\ c_{A,i} & \text{at } z = 0 & \text{for } \theta > 0 \\ c_{A0} & \text{at } z = \infty & \text{for all } \theta \end{cases}$$

Solving equation and proceeding in the manner described earlier for falling liquid film. The average flux can be described as

$$N_{A,av} = 2(c_{A,i} - c_{A0})\sqrt{\frac{D_{AB}}{\pi\theta}}$$

And comparison with equation

$$k_{L,av} = 2\sqrt{\frac{D_{AB}}{\pi\theta}}$$

This indicated dependence on D is typical of short exposure times, where depth of solute penetration is small relative to the depth of the absorbing pool.

Surface Renewal Theory

In reality, the time of exposure of all eddies as proposed in penetration is not constant .This phenomena visualized by Danckwert (1951) in his work. He assumed that

1. The liquid elements at the interface are being randomly replaced by fresh elements from the bulk.
2. At any moment each of the liquid elements at the surface has the same probability of being replaced by a fresh element.
3. Unsteady state mass transfer occurs to an element during its stay at the interface.

Hence, Danckwerts modified the penetration theory to account for varying length time of exposure.

If S is the fractional rate of replacement of elements,

Then
$$N_{A,av} = (C_{Ai} - C_{A0})\sqrt{D_{AB}S}$$

Hence
$$k_{L,\,av} = \sqrt{D_{AB}S}$$

$k_{L,av}$ proportional to $D_{AB}{}^{0.5}$ regardless of the nature of the surface renewal rate S.

Combination of Film-Surface Renewal Theory

Dobbins concerned with the rate of absorption of oxygen into flowing streams and rivers and pointed out that the film theory ($k_L \propto D_{AB}$) assume a time of exposure of the surface elements within the film, formed at steady state, sufficiently long.

Whereas, the penetration and surface renewal theories ($k_L \propto D_{AB}^{0.5}$) assume the surface elements to be essentially infinitely deep, the diffusing solute never reaching the region of constant concentration below.

Therefore, observed dependence, $k_L \propto D_{AB}^n$, with 'n' dependent upon circumstances.

Dobbins replaced the third boundary condition used in penetration theory by $C_A = C_{A0}$ at $z = z_b$, where z_b is finite depth.

$$k_{L,av} = \sqrt{D_{AB}S} \ \coth \sqrt{\frac{SZ_b^2}{D_{AB}}}$$
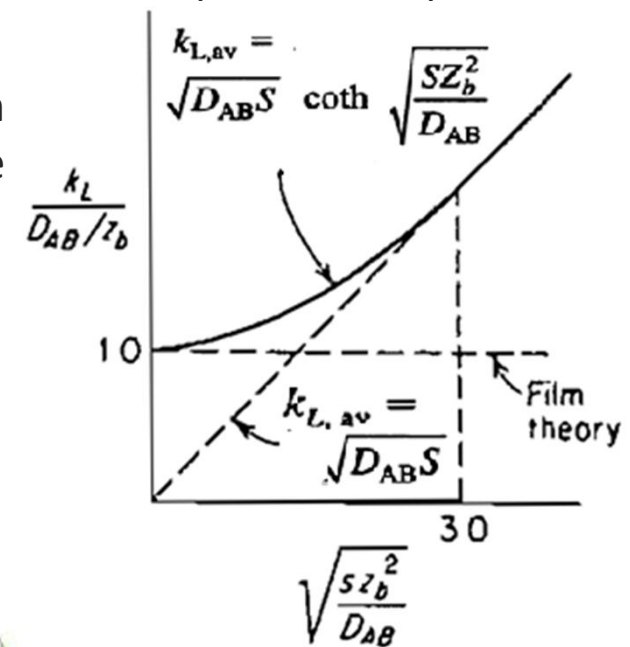
Surface-stretch Theory

Lightfoot and his coworkers explained this theory where they found that the mass transfer at the interface varies with time periodically.

For Example: A liquid drop such as ethyl acetate rising through a denser liquid such as water, with mass transfer of a solute such as acetic acid from water to the drop. Such a drop, if relatively large, wobbles and oscillates, changing its shape as shown schematically in figure.

If the central portion of the drop is thoroughly turbulent, the mass transfer resistance of the drop resides in a surface layer of Varying thickness.

Similar situation occur while drops and bubbles form at nozzle and when liquid surface are wavy or rippled.

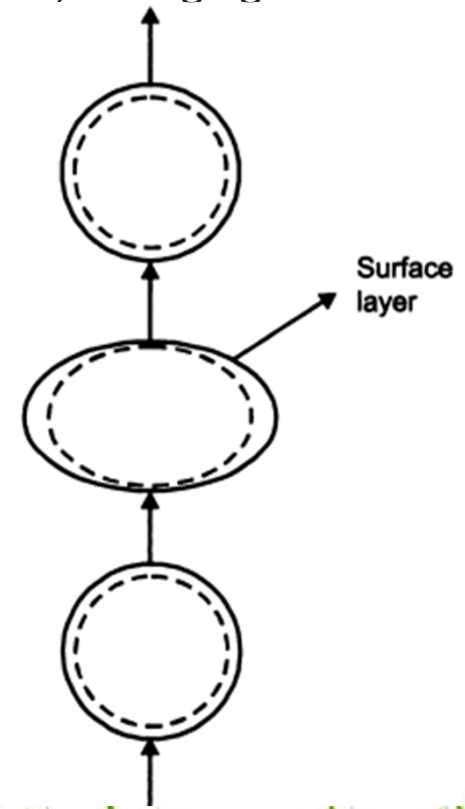For these case the theory leads to

$$k_{L,av} = \frac{\left[(A/A_r)\sqrt{\dfrac{D_{AB}}{\pi\theta_r}}\right]}{\sqrt{\displaystyle\int_0^{\theta/\theta r} (A/A_r)^2 \, d\theta}}$$

Where

A = time dependent interfacial surface

A_r = is reference value of A, defined for every situation

θ_r = constant with dimensions of time or drop formation time

The Boundary Layer Theory

The theories discussed so far related to interfacial surface formed between two fluids where the velocity at that surface will not normally be zero.

However, when one phase is a solid the fluid velocity parallel to the surface at the interface must be zero.

A fluid with uniform velocity u_0 and uniform solute concentration c_{A0} meets up with a flat solid surface AK shown in figure. Velocity u_x is zero at the surface and rises to u_0 at some distance above the plate.
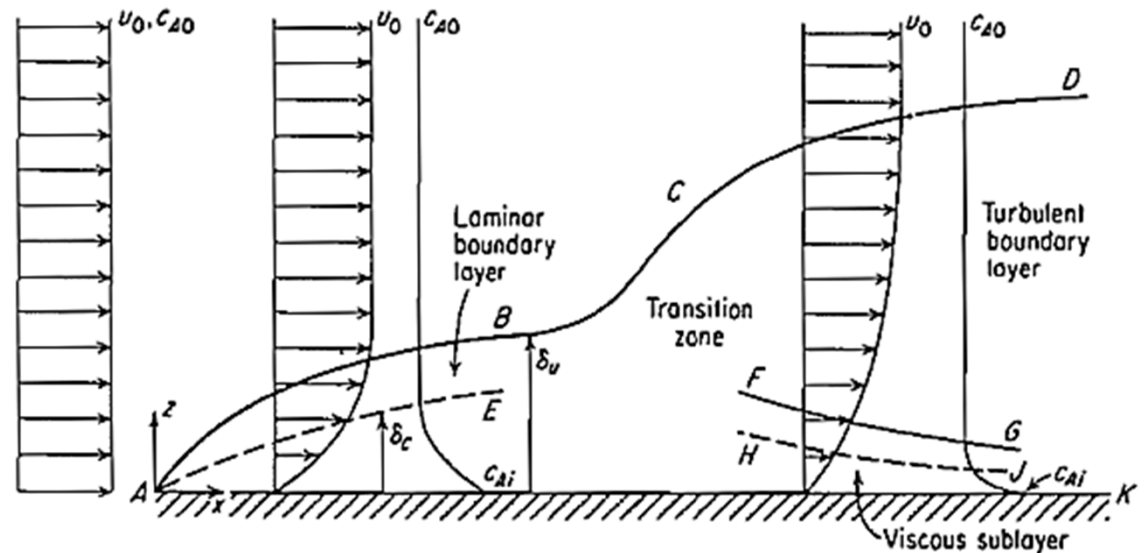
- The curve ABCD separates the region of velocity u_0 from the region of lower velocity called the boundary layer.

- The boundary layer may be characterized by laminar flow, as below curve AB.

- If the velocity u_0 is sufficiently large (Re approximately 5 x 10^5) the flow in the bulk of the boundary layer will be turbulent, as below the curve CD.

- Below the turbulent boundary layer there will be a thinner region, the viscous sublayer, extending from the plate to the curve FG.

- Well-developed boundary layers form at very low rates of flow.

- At higher rates of flow the boundary layer separates from the surface and eddies form in the wake behind the object.

- If the mass transfer from the surface into fluid occurs, as with a solid subliming into gas or a solid dissolving into liquid, the solute concentration in the fluid at the solid surface is everywhere $c_{A,i}$ grater than c_{A0}.

- The curve AE and HJ represent and separate the region of uniform concentration c_{A0} from regions of higher values of c_A, corresponding to a concentration boundary layer.

- In this region only a laminar velocity boundary layer exists. The equation of motion and mass transfer can be solved simultaneously to yield the concentration profile and slope of the curve gives laminar mass transfer coefficient.

- If mass transfer begins at the leading edge A it develops the velocity boundary layer of thickness δ_u and concentration boundary layer δ_c. The ratio of $\delta_u/\delta_c = Sc^{1/3}$.

In laminar flow with low mass transfer rates and constant physical properties past a solid surface, as for the two dimensional laminar boundary layer. The momentum balance or equation of motion for x direction becomes

$$u_x \frac{\partial u_x}{\partial x} + u_z \frac{\partial u_x}{\partial z} = \nu \left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial z^2} \right)$$

If there is mass transfer without chemical reaction, the equation of continuity for substance A

$$u_x \frac{\partial c_A}{\partial x} + u_z \frac{\partial c_A}{\partial z} = D_{AB} \left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial z^2} \right)$$

And if there is heat transfer between plate and fluid

$$u_x \frac{\partial t}{\partial x} + u_z \frac{\partial t}{\partial z} = \alpha \left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial z^2} \right)$$

Solving these equation simultaneously with dimensionless forms of variable

$$\frac{u_x - (u_{x,z=0} = 0)}{u_0 - (u_{x,z=0} = 0)} \qquad \frac{c_A - c_{A,i}}{c_{A0} - c_{A,i}} \qquad \text{and} \qquad \frac{t - t_i}{t_0 - t_i}$$

Then the boundary condition become identical. Thus for z = 0 all three dimensionless variables are zero, and at z = ∞, all three equal unity.

Therefore, the form of solution, which provide dimensionless velocity, concentration, and temperature profiles, are the same.

If three diffusivity are equal than Sc = Pr = 1, the profiles in dimensionless form are identical.

The initial slopes of the concentration, temp, and velocity profiles provide the means of computing the corresponding local transfer coefficients

$$N_A = -D_{AB}\left(\frac{\partial c_A}{\partial z}\right)_{z=0} = k_L(c_{A,i} - c_{A0})$$

$$q = -\alpha\left[\frac{\partial(t C_p \rho)}{\partial z}\right]_{z=0} = h(t_i - t_0)$$

$$\tau_i g_c = \nu\left[\frac{\partial(u_x \rho)}{\partial z}\right]_{z=0} = \frac{f}{2} u_0(\rho u_0 - 0)$$

Where f is the dimensionless friction factor and $f u_0/2$ might be considered a momentum transfer coefficient.

At low mass transfer rates

$$\frac{Nu}{Re_x \, Pr^{1/3}} = \frac{Sh}{Re_x \, Sc^{1/3}} = \frac{f}{2} = 0.332 \, Re_x^{-1/2}$$

And the average coefficient provide Nu_{av} and Sh_{av} given by the same expression with 0.332 replaced by 0.664. These show the mass transfer coefficient to vary as $D_{AB}^{2/3}$, which is typical result of boundary layer calculations

Mass, Heat and Momentum Transfer Analogies

Reynold Analogy

In this analogy, the assumption considered are:

(i)   Only turbulent core is present.

(ii) Velocity, temperature and concentration profiles are perfectly matching.

(iii) All diffusivities are same.

Hence

$$(\alpha) = (D_{AB}) = \left(\frac{\mu}{\rho}\right)$$

$$Pr = Sc = 1$$

The basic equations of heat, mass and momentum can be written as follows:

$$q = h(t_i - t_0) = -\alpha \frac{d}{\partial z}\ (\rho C_P t)$$

$$N_A = k_c\ (C_{Ai} - C_{A0}) = -D_{AB}\frac{\partial C_A}{\partial z}$$

$$\tau_i = \left(\frac{\mu}{g_c}\right)\frac{\partial u}{\partial z}$$

Let us consider heat and momentum transfer and from first equation

$$h(t_i - t_0) = -\alpha\ \frac{\partial}{\partial z}\ (\rho C_P t) = -\left(\frac{K}{\rho C_P}\right)(\rho C_P)\ \frac{dt}{dz}\ \text{since } \alpha = \left(\frac{K}{\rho C_P}\right)$$

$$h \, (t_i - t_0) = -K\left(\frac{d}{dz}\right)(t - t_i)$$

$$\therefore \quad \frac{h}{K} = \left(\frac{d}{dz}\right)\left[\frac{t - t_i}{t_0 - t_i}\right]$$

As per assumption (ii) velocity and temperature profile match and hence

$$\left[\frac{d}{dz}\right]\left[\frac{u_x}{u_0}\right] = \left(\frac{d}{dz}\right)\left[\frac{(t - t_i)}{(t_0 - t_i)}\right]$$

Multiplying by $C_p \, \mu$ on both sides of equation, we get

$$\left(\frac{C_P \mu}{u_0}\right)\left(\frac{du_x}{dz}\right) = K\left(\frac{d}{dz}\right)\left[\frac{(t - t_i)}{(t_0 - t_i)}\right]$$

Since $K = C_p \, \mu$ by assumption (iii), and rearranging gives

$$\left(\frac{C_P \mu}{K u_0}\right)\left(\frac{du_x}{dz}\right) = \left(\frac{d}{dz}\right)\left[\frac{t - t_i}{t_0 - t_i}\right]$$

Combining equation h/K to this

$$\left(\frac{C_P \mu}{K u_0}\right)\left(\frac{du_x}{dz}\right) = \frac{h}{K}$$

Therefore
$$\mu\left(\frac{du_x}{dz}\right)=\left(\frac{hu_0}{C_P}\right)=\left(\frac{f}{2}\right)\rho u_0^2$$

i.e.
$$\left(\frac{f}{2}\right)=\frac{h}{\rho\,C_P u_0}$$

Similarly considering mass and momentum transfer, we get

$$\left(\frac{f}{2}\right)=\left(\frac{k_c}{u_0}\right)$$

Hence Reynold analogy equation is

$$\left(\frac{f}{2}\right)=\frac{h}{\rho C_P u_0}=\frac{k_c}{u_0}$$

Chilton-Colburn Analogy

In this analogy, the assumption considered are:
(i)   Only turbulent core is present.
(ii) Velocity, temperature and concentration profiles are same.
(iii) Pr and Sc are not equal to unity.
In this analogy, the equation obtained is

$$\left(\frac{f}{2}\right) = \left(\frac{k_c}{u_0}\right)(\text{Sc})^{2/3} = \frac{h}{(\rho C_p u_0)}(\text{Pr})^{2/3}$$

Taylor-Prandtl Analogy

In this analogy, the assumption considered are:

(i)   Presence of turbulent core and laminar sublayer.

(ii) Pr and Sc are not equal to unity.

In this analogy, the equation obtained is

$$\frac{k_c}{u_0} = \frac{h}{\rho C_p u_0} = \frac{\left(\dfrac{f}{2}\right)}{\left[1 + 5\sqrt{\dfrac{f}{2}}(\text{Sc}-1)\right]} = \frac{\left(\dfrac{f}{2}\right)}{\left[1 + 5\sqrt{\dfrac{f}{2}}(\text{Pr}-1)\right]}$$

Von-Karman Analogy

In this analogy, the assumption considered are:

(i)   Presence of turbulent core, laminar sublayer and buffer layers.

(ii) Universal velocity profile equation are applicable.

(iii) Pr and Sc are not equal to unity.

In this analogy, the equation obtained is

$$\frac{k_c}{u_0} = \frac{\frac{f}{2}}{1 + 5\sqrt{\frac{f}{2}}\left[(Sc - 1) + \ln\left(\frac{5Sc + 1}{6}\right)\right]}$$

$$= \frac{\frac{f}{2}}{1 + 5\sqrt{\frac{f}{2}}\left[(Pr - 1) + \ln\left(\frac{5Pr + 1}{6}\right)\right]}$$

Simultaneous Mass and Heat Transfer

Mass transfer along with the heat transfer occurs, either as a result of an externally imposed temperature difference or because of the absorption or evolution of heat which generally occurs when a substance is transferred from one phase to another.

In such cases, within one phase, the heat transferred is a result not only the conduction (convection) caused by virtue of the temperature difference in the absence of mass transfer but also includes the sensible heat carried by the diffusing matter.

Consider the situation shown in figure. Here a fluid consisting of substance A and B flows past a second phase under conditions causing mass transfer.

The total mass transferred is given by the following variation of equation

$$N_A + N_B = F \ln \frac{N_A/(N_A + N_B) - c_{A,i}/c}{N_A/(N_A + N_B) - c_{A1}/c}$$
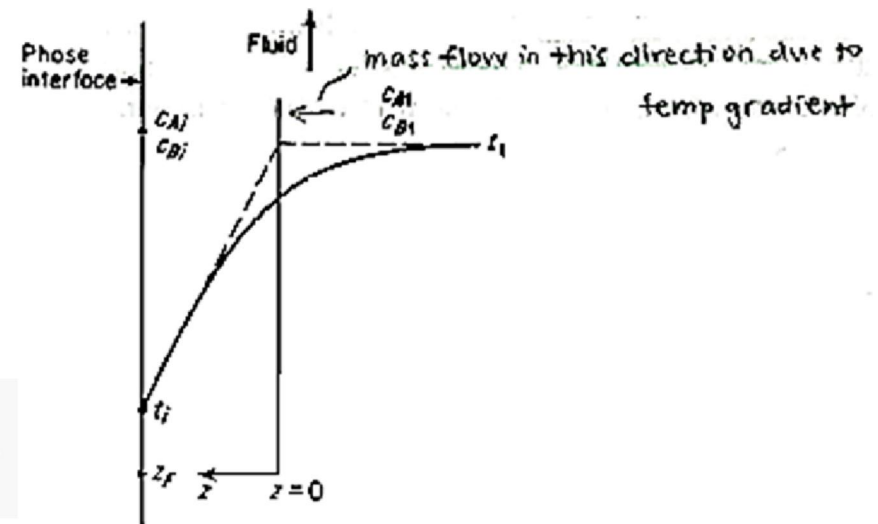
The relationship between N_A and N_B is fixed by other considerations. There is a heat flux described by the ordinary heat transfer coefficient h in the absence of mass transfer.

According to film theory heat flux is $h(-dt/dz)z_f$. The total sensible heat flux q_s to the interface is summation of sensible heat brought there by the movement of matter through the temperature difference and heat flux due to film. Thus,

$$q_s = h\left(-\frac{dt}{dz}\right)z_F + (N_A M_A C_{p.A} + N_B M_B C_{p.B})(t - t_i)$$

Rearranging and integrating the above equation

$$\int_{t_i}^{t_1} \frac{dt}{q_s - (N_A M_A C_{p,A} + N_B M_B C_{p,B})(t - t_i)} = \frac{1}{hz_F} \int_{z_F}^{0} dz$$

$$q_s = \frac{N_A M_A C_{p,A} + N_B M_B C_{p,B}}{1 - e^{-(N_A M_A C_{p,A} + N_B M_B C_{p,B})/h}}(t_1 - t_i)$$

Heat transfer coefficient
corrected for mass transfer

It will be larger if the mass transfer is in the same direction as the heat transfer, smaller if the two are in opposite direction.

It can be applied for condensation of component A in the presence of noncondensing B ($N_B = 0$).

The total heat release at the interface q_t must include the effect produced (may be latent heat of vaporization, a heat of solution, or both, depending upon the circumstances) when the transferred mass passes through the interface.

$$q_t = q_s + \lambda_A N_A + \lambda_B N_B$$

Interphase Mass Transfer

- We have so far discussed the theoretical principles of diffusion and mass transfer from one point to another in a single phase or in a homogeneous medium by using either the equation of molecular diffusion or the phenomenological mass transfer coefficients.

- However, most mass transfer operations in practice involve transport of one or more solute from one phase to another.

- Since diffusion and mass transfer occur in both the phases, we need to make use of two mass transfer coefficient-one for each phase.

- Here the driving force is not merely the difference of the concentrations of the solute in the two phases. The driving force is rather measured by how far the phases are away from equilibrium.
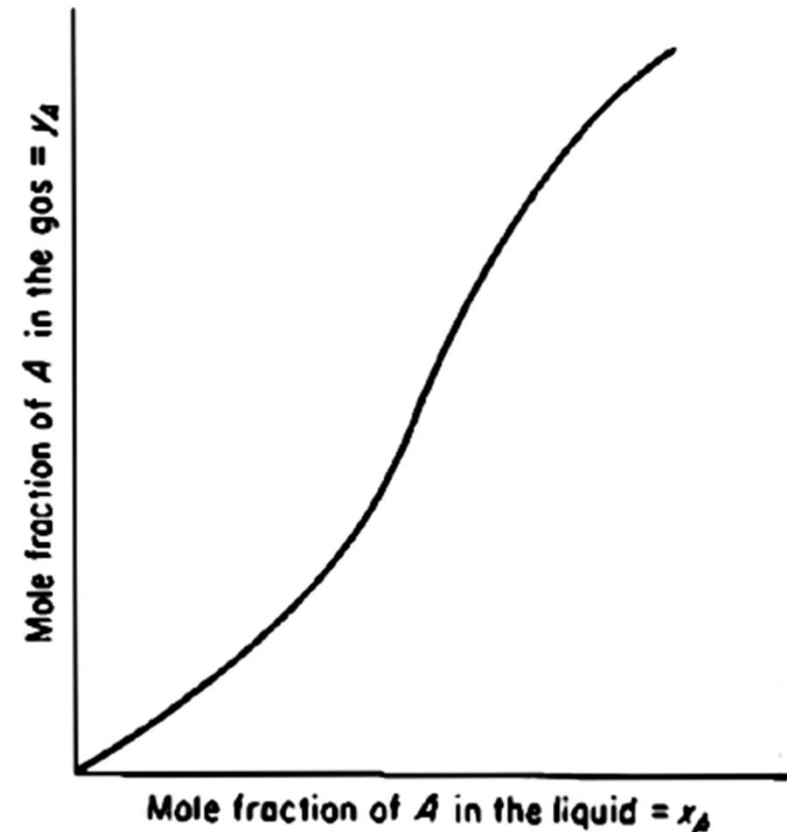
Equilibrium

To generalize the equilibrium characteristics, consider that an amount of solute from a gaseous mixture is dissolved in solvent. After sufficient time, the system will attain equilibrium with respect to a particular temperature and pressure.

- The concentration of solute in both gas and liquid phase may not be equal but the chemical potential of solute will be equal at equilibrium.

- At the same temperature and pressure, if some more amount of solute is introduced, then once again a new equilibrium will be attained in the same system.

- For Example: When ammonia is dissolved from an air-ammonia mixture by liquid water. Suppose a fixed amount of liquid water is placed in closed container together with a gaseous mixture of ammonia and air and system can be maintained at constant temperature and pressure.

- Since ammonia is very soluble in water, some ammonia molecules will instantly transfer from the gas into the liquid, crossing the interfacial surface separating the two phases.

- A portion of ammonia molecules escape back into the gas, at a rate proportional to their concentration in the liquid.

- As more ammonia enters the liquid, ammonia concentration increases in liquid and the rate of ammonia returns to the gas increases, this continue until the rate of absorption of ammonia in liquid exactly equals to rate of desorption of ammonia.

- At the same time, through diffusion mechanics the concentration throughout each phase become uniform. The dynamic equilibrium exist between the phases and net transfer of ammonia falls to zero.

- If additional ammonia inject into the container, a new set of equilibrium concentrations will be established, with higher concentrations in each phase compare to previous.
- In this manner we can obtain the complete relationship between the equilibrium concentration in both phases.
- If the ammonia is designated as substance A, the equilibrium concentration in the gas and liquid, y_A and x_A mole fractions, respectively, give rise to an equilibrium-distribution curve of the type shown in figure.

The extent of deviation from the equilibrium state is a measure of the 'driving force' for mass transfer. For a system at equilibrium, the driving force is zero.

The Raoult's and The Henry's Law

The equilibrium data or the equilibrium distribution of a solute between two immiscible (or partial miscible) phases are determined experimentally, although there have been numerous attempts with varying degrees of success to predict the equilibrium data theoretically.

Two important laws of equilibrium between phases are described as follows:

Raoult's Law

For an ideal gas-liquid or vapor-liquid system, the equilibrium relationship obeys the Raoult's law. This law is mathematically expressed as

$$p_A^* = x_A P_A$$

Where

P_A = vapor 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 solution are, however, non-ideal. There are some solutions which are nearly ideal in their behavior.

Henry's Law

Equilibrium data for many non-ideal gas-liquid system at low concentrations can be expressed by the Henry's law.

$$p_A^* = H x_A$$

Where H is the Henry's law constant and p_A^* and x_A have stated before.
The constant H for a given solute-solvent pair is a strong function of temperature (it increases with temperature).

Diffusion between Phases

Local Two-Phase Mass Transfer

- Generally the two phase systems occur in most of the mass transfer operations. Suppose two phases are immiscible with each other, then an interface is seen between the two phases.

Consider a solute A which is in bulk gas phase G and diffusing into the liquid
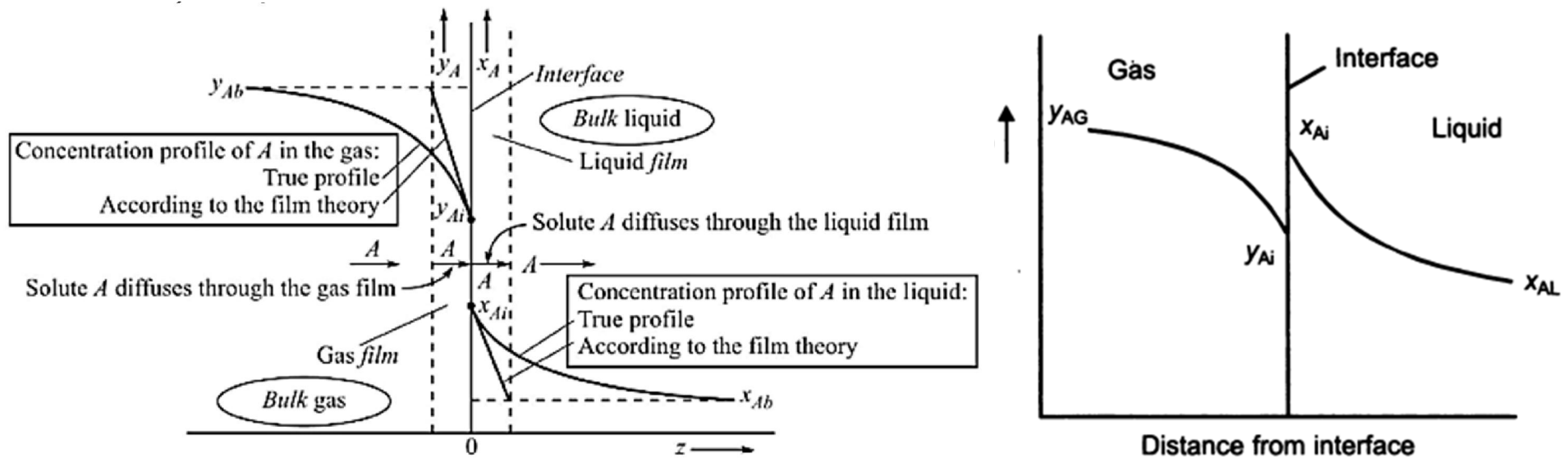
certainly not at equilibrium. This enables diffusion to occur.

- At the interface, there is no resistance to transfer of solute and the concentration y_{Ai} and x_{Ai} are in equilibrium .

They are related by the equilibrium distribution relation as

$$y_{Ai} = f(x_{Ai})$$

The concentration driving forces can be shown graphically as in figure.

If we consider a steady state mass transfer, the rate at which molecules reach the interface will be the same rate at which the molecules are transferred to the liquid phase.

Since interface has no resistance, the flux of each phase can be expressed in term of mass transfer coefficient.
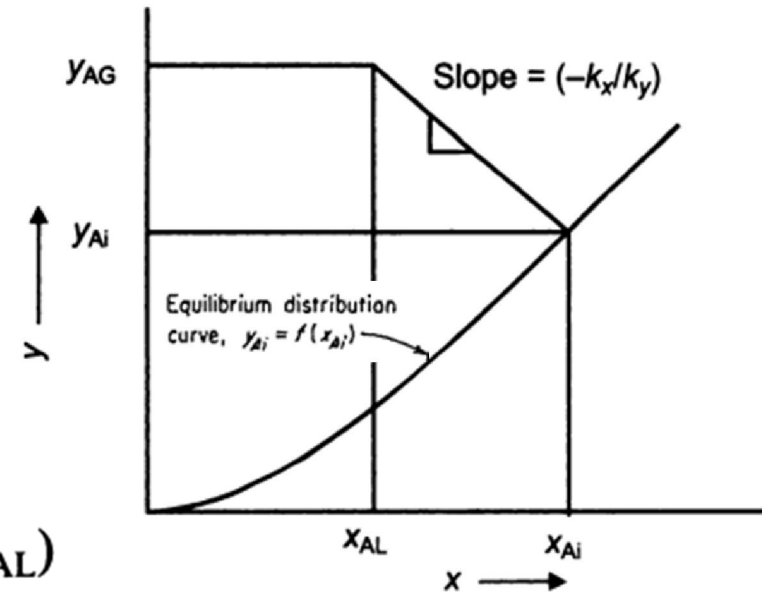

$$N_A = k_y (y_{AG} - y_{Ai}) = k_x (x_{Ai} - x_{AL})$$

Where k_y and k_x are local gas and liquid mass transfer coefficients.

i.e.
$$\frac{y_{AG} - y_{Ai}}{x_{AL} - x_{Ai}} = -\left(\frac{k_x}{k_y}\right)$$

Hence, the interface compositions can be determined if k_x, k_y, y_{AG} and x_{AL} values are known.

Local Overall Mass Transfer Coefficient

- Experimentally determining the rate of mass transfer is very difficult since it is not possible to evaluate the interface compositions.

- However, bulk concentrations are easily measured and measuring x_{AL} is as good as measuring y_A^* because both have the same chemical potential.

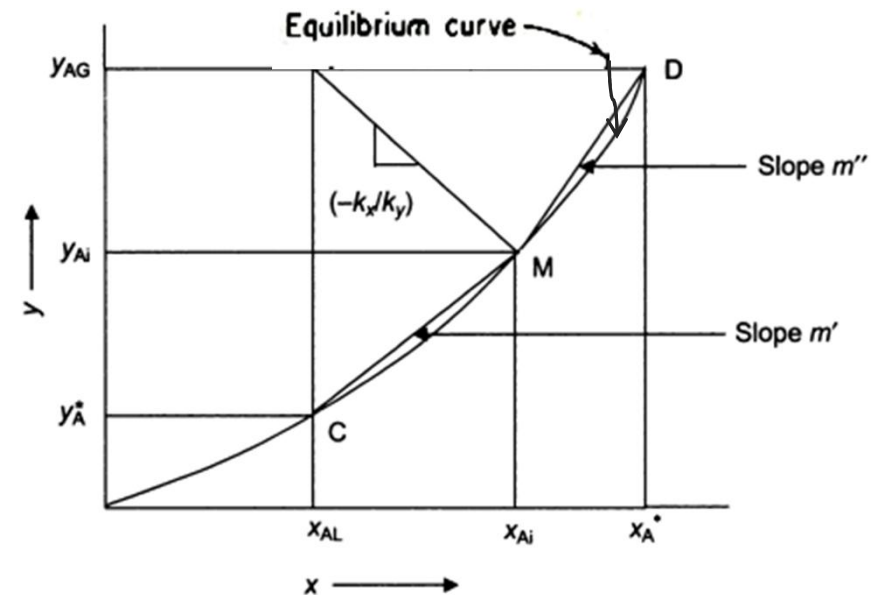- Similarly y_{AG} is as good as measuring x_A^*. The concentration driving forces can be shown as in figure.

The flux can be written in terms of overall mass transfer coefficient for each phase.

$$N_A = K_y \left(y_{AG} - y_A^* \right)$$

Where K_y is overall mass transfer coefficient.

From the geometry of the figure.

$$\left(y_{AG} - y_A^* \right) = \left(y_{AG} - y_{Ai} \right) + \left(y_{Ai} - y_A^* \right)$$
$$= \left(y_{AG} - y_{Ai} \right) + m' \left(x_{Ai} - x_{AL} \right)$$

Where m' is the slope of the chord CM in figure. Substituting the concentration difference form the previous equations.

$$\left(\frac{N_A}{K_y}\right) = \left[\left(\frac{N_A}{k_y}\right) + \left(\frac{m'N_A}{k_x}\right)\right]$$

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

individual gas-phase mass transfer resistance

individual liquid-phase mass transfer resistance
(on gas phase basis)

Similarly, for the liquid side

$$N_A = K_x(x_A^* - x_{AL})$$

On simplification we get

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

individual gas-phase mass transfer resistance
(on liquid-phase basis)

individual liquid-phase mass transfer resistance

Where m'' is the slope of the chord MD in figure. The above two equations show the relationship between the individual and overall mass transfer coefficients. These equation also lead to the following relationships between the mass transfer resistances.

$$\frac{\text{Resistance in gas phase}}{\text{Total resistance}} = \frac{1/k_y}{1/K_y}$$

$$\frac{\text{Resistance in liquid phase}}{\text{Total resistance}} = \frac{1/k_x}{1/K_x}$$

Assuming that k_x and k_y are same and if m' is small so that solute A is highly soluble in liquid (i.e. equilibrium curve will be flat), the term m'/k_x will be negligible when compares to $1/k_y$.

Hence

$$\frac{1}{K_y} \approx \frac{1}{k_y}$$

This condition says that overall resistance lies only in the gas phase, conversely when m'' is very large, then solute A is relatively insoluble in liquid. Under this condition, the term $(1/m'' k_y)$ will be negligible compared to $1/k_x$. Then

$$\frac{1}{K_x} \approx \frac{1}{k_x}$$

In this case the entire rate of mass transfer is controlled by liquid phase. For case where k_x and k_y are not nearly equal, then it will be relative size of the ratio (k_x/k_y) and of m' or m'' which will determine the location of the controlling mass transfer resistance.

Local Coefficients-General Case

When we deal with situations which do not involve either diffusion of only one substance or equimolar counter-diffusion, or if mass transfer rates are large, the F-type coefficients should be used.

The general approach is the same, although the resulting expressions are more cumbersome. Thus, for similar situation shown in previous figures, the mass transfer flux

$$N_A = \frac{N_A}{\Sigma N} F_G \ln \frac{N_A/\Sigma N - y_{A,i}}{N_A/\Sigma N - y_{A,G}} = \frac{N_A}{\Sigma N} F_L \ln \frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - x_{A,i}}$$

Where F_G and F_L are the gas and liquid phase coefficient of substance A and ΣN = N_A + N_B + N_C + ...

Equation becomes

$$\frac{N_A/\Sigma N - y_{A,i}}{N_A/\Sigma N - y_{A,G}} = \left(\frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - x_{A,i}} \right)^{F_L/F_G}$$

The interfacial composition $y_{A,i}$ and $x_{A,i}$ can be found by plotting the above equation (with $y_{A,i}$ replaced by y_A and $x_{A,i}$ by x_A) on the distribution diagram. Determining the intersection of the resulting curve with the distribution curve.

This is in general a trial-and-error procedure, since $N_A/\Sigma N$ may not be known, and must be done in conjunction with first equation .

In the special cases for diffusion only of A and of equimolar counter-diffusion in two components phases, no trial and error is required.

We can define the overall coefficients F_{OG} and F_{OL} as

$$N_A = \frac{N_A}{\Sigma N} F_{OG} \ln\frac{N_A/\Sigma N - y_A^*}{N_A/\Sigma N - y_{A,G}} = \frac{N_A}{\Sigma N} F_{OL} \ln\frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - x_A^*}$$

By a procedure similar to that used for the K's, it can be shown that the overall and individual phase F's are related:

$$\exp\left[\frac{N_A}{(N_A/\Sigma N)F_{OG}}\right] = \exp\left[\frac{N_A}{(N_A/\Sigma N)F_G}\right]$$
$$+ m'\frac{N_A/\Sigma N - x_{A,L}}{N_A/\Sigma N - y_{A,G}}\left\{1 - \exp\left[-\frac{N_A}{(N_A/\Sigma N)F_L}\right]\right\}$$

$$\exp\left[-\frac{N_A}{(N_A/\Sigma N)F_{OL}}\right] = \frac{1}{m''}\left(\frac{N_A/\Sigma N - y_{A,G}}{N_A/\Sigma N - x_{A,L}}\right)\left\{1 - \exp\left[\frac{N_A}{(N_A/\Sigma N)FdG}\right]\right\}$$
$$+ \exp\left[-\frac{N_A}{(N_A/\Sigma N)F_L}\right]$$

1. Diffusion of one component ($\sum N = N_A$, $N_A/\sum N = 1$)

$$e^{N_A/F_{OG}} = e^{N_A/F_G} + m' \frac{1 - x_{A,L}}{1 - y_{A,G}}(1 - e^{-N_A/F_L})$$

$$e^{-N_A/F_{OL}} = \frac{1}{m''} \frac{1 - y_{A,G}}{1 - x_{A,L}}(1 - e^{N_A/F_G}) + e^{-N_A/F_L}$$

Can also be written as

$$\frac{1}{F_{OG}} = \frac{1}{F_G}\frac{(1 - y_A)_{iM}}{(1 - y_A)_{*M}} + \frac{m'(1 - x_A)_{iM}}{F_L(1 - y_A)_{*M}}$$

$$\frac{1}{F_{OL}} = \frac{1}{m''F_G}\frac{(1 - y_A)_{iM}}{(1 - x_A)_{*M}} + \frac{1}{F_L}\frac{(1 - x_A)_{iM}}{(1 - x_A)_{*M}}$$

Where

$(1 - y_A)_{iM}$ = logarithmic mean of $1 - y_{A,G}$ and $1 - y_{A,I}$
$(1 - y_A)_{*M}$ = logarithmic mean of $1 - y_{A,G}$ and $1 - y_A^*$
$(1 - x_A)_{iM}$ = logarithmic mean of $1 - x_{A,L}$ and $1 - x_{A,I}$
$(1 - x_A)_{*M}$ = logarithmic mean of $1 - x_{A,L}$ and $1 - x_A^*$

2. Equimolar counter-diffusion [$\sum N = 0$ ($F_G = k'_y$, $F_L = k'_x$)]

$$\frac{1}{F_{OG}} = \frac{1}{F_G} + \frac{m'}{F_L}$$

$$\frac{1}{F_{OL}} = \frac{1}{m'' F_G} + \frac{1}{F_L}$$

Material Balance in a Contacting Equipment

In the case of a steady state process, because of the transfer of solute from one phase to other, the concentration within each phase changes as it moves through the equipment.

Similarly, in the case of a batch process, the concentration in each phase changes with time.

These changes produce corresponding variations in the driving forces, and these can be followed with the help of material balances.

Two modes of contact between the phases will be considered – cocurrent contact (in which the phases move in the same direction) and counter-current contact (in which the phases move in the opposite directions). Another type of contact called the cross-current contact.

Steady State Cocurrent Process

Let consider two insoluble phase E and R and a single substance A diffuses from phase R to phase E during their contact. The other constituents of the phases, solvents for the diffusing solutes, are then considered not to diffuse.

- At the entrance of equipment phase R contains R_1 mol per unit time of total substances, consisting of non-diffusing solvent R_S mol per unit time and diffusing solute A, whose concentration is x_1 mole fraction.

- As phase R moves through the equipment, A diffuses to phase E and total quantity of R falls to R_2 mol per unit time at the exit. However, the rate of flow of non-diffusing solvent R_S is same as at the entrance. The concentration of A fallen to x_2 mole fraction.

- Similarly, phase E at the entrance contains E_1 mol per unit time total substances, of which E_S mol is non-diffusing solvent, and an A concentration of y_1 mole fraction.

- Due to accumulation of A concentration become y_2 mole fraction. Phase E increases in amount to E_2 mol per unit time at the exit. However, the rate of flow of non-diffusing solvent E_S is same as at the entrance.

Schematic diagram for a co-current process is shown in figure.
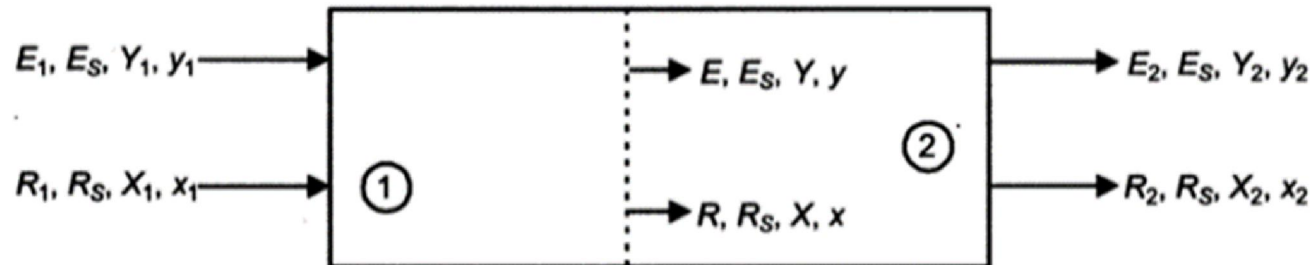
Making a component balance for solute, we get

$$R_1x_1 + E_1y_1 = R_2x_2 + E_2y_2$$

But

$$R_1x_1 = R_S\frac{x_1}{1 - x_1} = R_SX_1$$

$$R_SX_1 + E_SY_1 = R_SX_2 + E_SY_2$$

i.e.

$$R_S(X_1 - X_2) = E_S(Y_2 - Y_1)$$

$$\left(\frac{-R_S}{E_S}\right) = \frac{Y_2 - Y_1}{X_2 - X_1}$$

This indicates a line passing through the points (X_1, Y_1) and (X_2, Y_2) which is called as operating line in the X vs Y plot. The operating line also indicates the material balance in the operation.

Also,

$$R_S X_1 + E_S Y_1 = R_S X + E_S Y$$

$$R_S (X_1 - X) = E_S (Y - Y_1)$$

Figure represent the equilibrium relationship as well as the straight line QP, called an operating line.

At the entrance to the apparatus, the mass transfer coefficient in the two phase may give rise to the driving force line KP, where K represents the interface compositions at the entrance and the distance KM and MP represent the driving forces in phase E and phase R respectively.
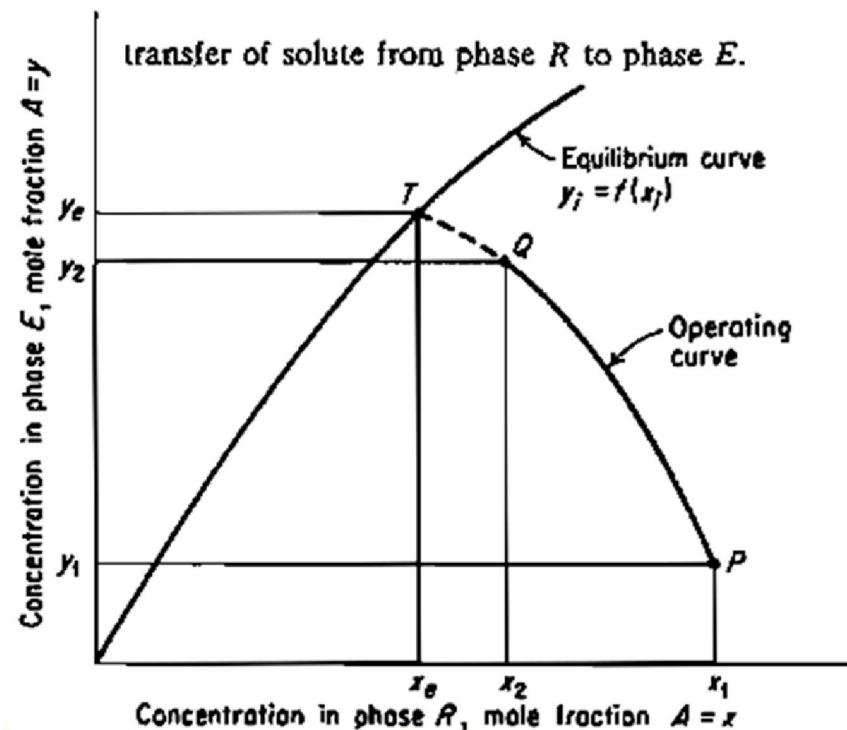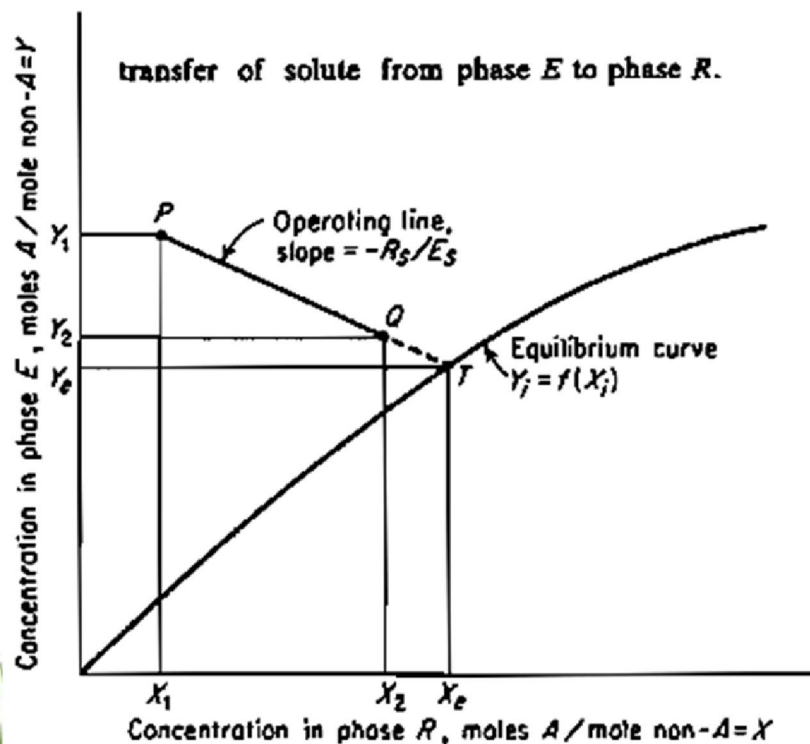
Similarly, at the exit, point L may represent the interface composition and LQ the line representative of the driving forces.
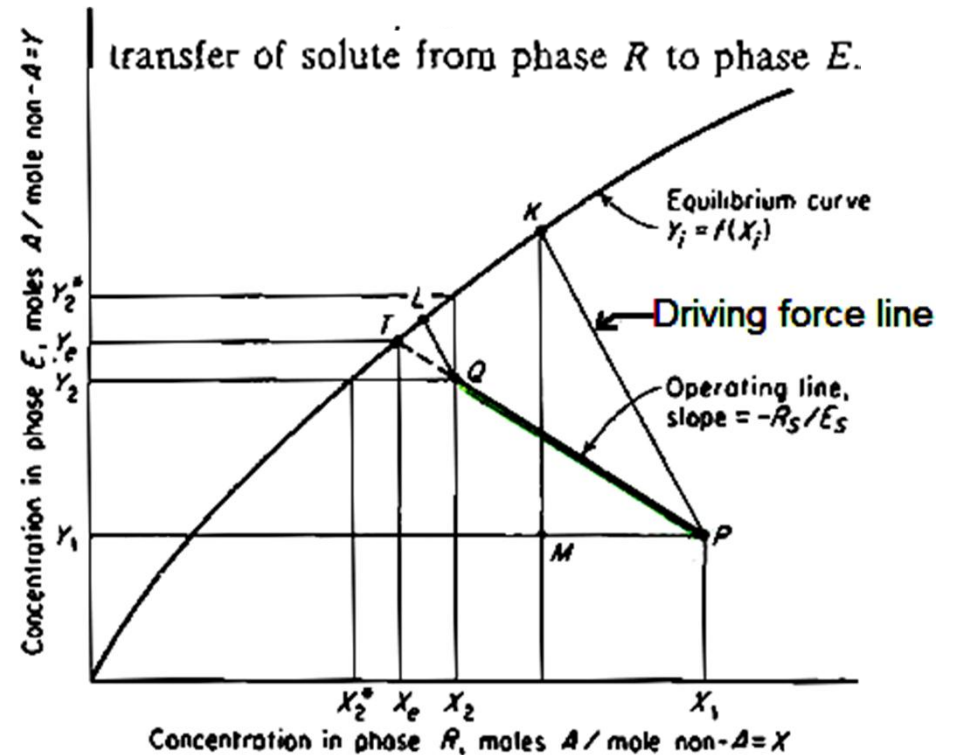
If the apparatus were longer than an equilibrium between the two phases is established, the corresponding equilibrium composition Xe and Ye would be given by an extension of the operating line to the intersection with the equilibrium curve at T.

The operating line as a straight line is greatly dependent upon the units in which the concentrations of the material balance are expressed.

If concentration is expressed in partial pressure term then operating line shown

transfer of solute from phase E to phase R.

Concentration in phase E, moles A / mole non-A = Y

Operating line, slope = $-R_S/E_S$

Equilibrium curve $Y_i = f(X_i)$

Concentration in phase R, moles A / mole non-A = X

transfer of solute from phase R to phase E.

Concentration in phase E, mole fraction A = y

Equilibrium curve $y_i = f(x_i)$

Operating curve

Concentration in phase R, mole fraction A = x

Steady State Counter current Process

If the previously considered process is carried out in countercurrent fashion shown in figure, where phase R enters from location 1 and phase E enters from location 2.

The material balance for solute become
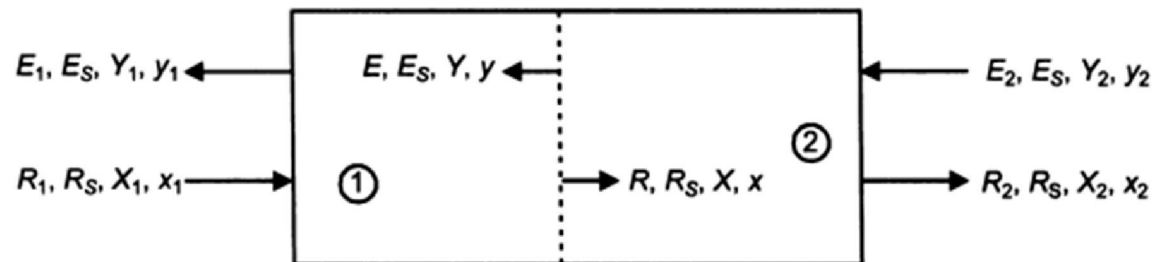
$$E_2 y_2 + R_1 x_1 = E_1 y_1 + R_2 x_2$$

$$E_S Y_2 + R_S X_1 = E_S Y_1 + R_S X_2$$

$$R_S (X_1 - X_2) = E_S (Y_1 - Y_2)$$

i.e.

$$\frac{R_S}{E_S} = \frac{Y_1 - Y_2}{X_1 - X_2}$$

This represents the equation of a line passing through the coordinates (X1, Y1) and (X2, Y2) with a slope of RS/ES in a plot of X vs Y.

Similarly general relationship between concentration in the phase at any location.

$$E_S Y + R_S X_1 = E_S Y_1 + R_S X$$

$$\frac{R_S}{E_S} = \frac{Y_1 - Y}{X_1 - X}$$

This is generalized equation representing the operating line in a counter current process. The following figure graphically shows the operating line and equilibrium for a counter current process.

The advantage of countercurrent process over the co-current is the higher driving force, which results in reduced size of equipment for a specified transfer condition or lesser flow rates for a given equipment.
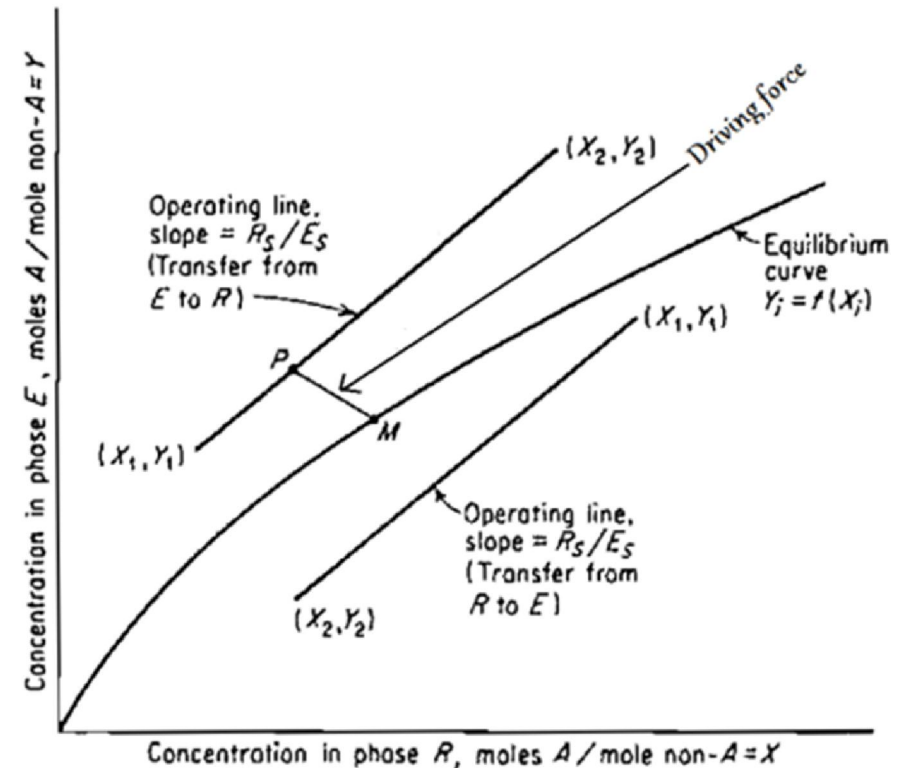
The point where the concentrations in the phases are given by the point P, the driving force line may be indicated by line PM, whose slope depends upon the relative diffusional resistances of the phases.

The driving forces changes in magnitude from one end of the equipment to the other.

If the operating line touch the equilibrium curve anywhere, so that contacted phases are in equilibrium, the driving force and hence the rate of mass transfer would become zero and the time required for a finite material transfer would be infinite.

Stages

A stages is defined as any device or combination of devices in which two insoluble phases are brought into intimate contact and mass transfer occurs between the phases tending to bring them to equilibrium, after that the phases are then mechanically separated.

A process carried out in this manner is a single stage process. An equilibrium, ideal, or theoretical, stage is one where the time of contact between phases is sufficient to bring them in equilibrium.

Stage Efficiency –Continuous Cocurrent Process

It is defined as the fractional approach to equilibrium, which a real stage produces or the ratio of actual solute transfer to that if equilibrium will attained.

The most frequently used expression is the Murphree stage efficiency defined as, the fractional approach of one leaving stream to equilibrium with the actual concentration in other leaving stream.

This can be expressed in terms of concentration in phase E or in phase R

$$E_{ME} = \frac{(Y_2 - Y_1)}{(Y_2^* - Y_1)} \quad \text{and} \quad E_{MR} = \frac{(X_1 - X_2)}{(X_1 - X_2^*)}$$

Cascades

A group of stages interconnected so that the various streams flow from one to the other is called a cascade. Its purpose is to increase the extent of mass transfer over and above the single stage.
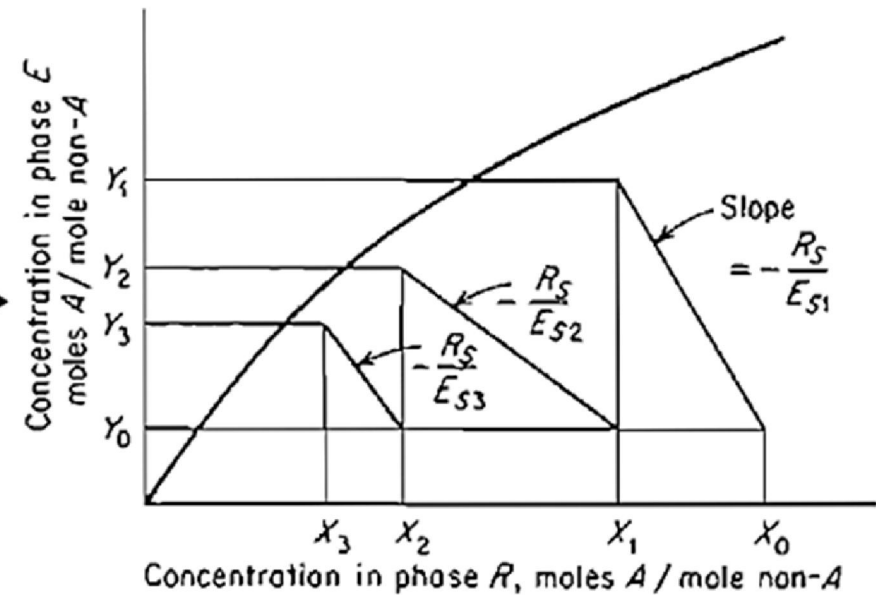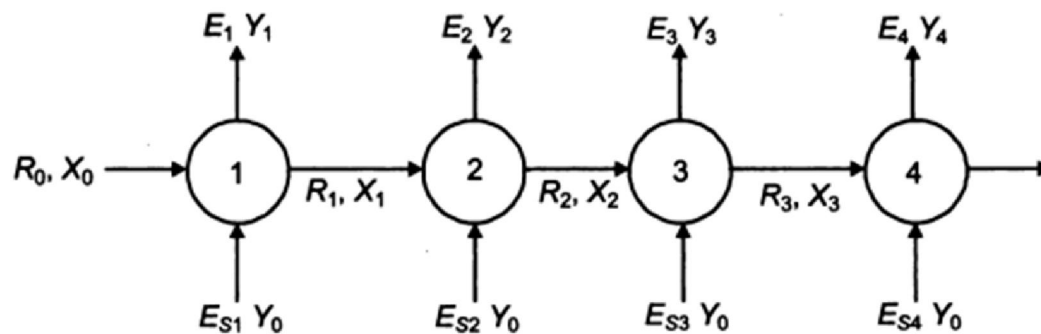
The fractional overall stage efficiency of a cascade is then defined as the number of equilibrium stages to which the cascade is equivalent divided by the number of real stages.

Cross-Flow Cascades

In figure each stage is represented simply by a circle, and within each the flow is cocurrent.

The R phase flow from one stages to the next, being contacted in each stage by a fresh E phase. There may be different flow rates of the E phase to each stage, and each stage may have a different Murphree stage efficiency.

The material balances are simply repetition of single stage. Cross flow is used sometimes in adsorption, leaching, drying and extraction operations but rarely in the others.

Counter-current Cascades

A typical counter-current cascade is shown in figure.

The number of stages N, required for a counter-current cascade ca ne estimated analytically for cases where both the equilibrium relationship and operating line are linear.

If m is the slope of the equilibrium curve and A = RS/mES, the absorption factor then for absorption (transfer from E to R)

For A ≠ 1

$$\frac{(Y_{N+1} - Y_1)}{(Y_{N+1} - mX_0)} = \frac{(A^{N+1} - A)}{(A^{N+1} - 1)}$$

For A = 1

$$N = \frac{(Y_{N+1} - Y_1)}{(Y_1 - mX_0)} = \frac{(Y_{in} - Y_{out})}{(Y_{out} - mX_{in})}$$

For desorption, (transfer from R to E)

For A ≠ 1

$$\frac{(X_0 - X_N)}{\left[X_0 - \left(\dfrac{Y_{N+1}}{m} \right) \right]} = \frac{\left[\left(\dfrac{1}{A} \right)^{N+1} - \left(\dfrac{1}{A} \right) \right]}{\left[\left(\dfrac{1}{A} \right)^{N+1} - 1 \right]}$$

For A = 1

$$N = \frac{(X_0 - X_N)}{\left[X_N - \left(\dfrac{Y_{N+1}}{m} \right) \right]} = \frac{(X_{in} - X_{out})}{\left[X_{out} - \left(\dfrac{Y_{in}}{m} \right) \right]}$$

The above four equations are called Kremser-Brown-Souders equation.