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# **ONLINE COURSE WARE**

# **SUBJECT NAME: Unit Operation of Chemical Engineering II**

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### **MODULE:I**

## Lecture 1

**Diffusion** : A random thermal movement occurs during diffusion where the molecules collide with each other and their speed and directions change. So it is evident that the rate of diffusional movements depends upon the number of collisions between the molecules and the process of diffusion continues until uniformity of concentration is reached. So this is summed up that the diffusion stops at the onset of equilibrium and then the state of uniform concentration is reached. But in this case also, the thermal movements of molecules happen

So diffusion can be defined as the net movement of molecules from a region of high concentration to one of low concentration at a fixed temperature and pressure, without the help of any external force. *Molecular diffusion* occurs due to heat transfer by conduction.

On the other hand, if the movements of molecules occur with the help of an external force, it is called *convective* flow or bulk flow and the process is called *eddy diffusion*.

The rate of diffusion naturally differs in solids, liquids, gases and vapours, depending upon the density of the mediums as well as mobility of the phases. The following table will show the comparative mobility rate observed in different phases:

State of the matter	Description	Mobility rate
Solid	High density and limited mobility	$1 \times 10^{-7}$
Liquid	Lower density and greater mobility	$5 \times 10^{-4}$
Gas and Vapour	Very low density and highest mobility	$1 \times 10^{-1}$

As diffusive mobility is a function of the number of collisions, diffusivity increases with decrease in pressure, because, number of collisions is less at lower pressure. Again, movement of the molecules increase with the increase in temperature and so it can be said that diffusivity increases with the rising temperature. The following table will show the values of diffusivity of matter in different phases :

Phase of the matter	Diffusivity
Solid	$10^{-13} - 10^{-5}$
Liquid	$10^{-10} - 10^{-9}$
Gas and Vapour	$5 \times 10^{-5} - 10^{-5}$

Lecture 2

### **Role of Concentration Difference in Diffusion:**

In case of diffusion of two ideal gases, where an equal number of moles of gases diffusing counter-current to each other, the flux equation at steady state is given Fick's law of diffusion–

 $N_A = D_{AB}(p_{A1} - p_{A2}) / RTZ$  .....(2)

Where,  $N_A = flux \text{ of } A \text{ in } kmol/m^2 s$ 

 $Z = (Z_2 - Z_1)$  = the distance through which diffusion occurs (m)

 $p_{A1}, p_{A2}$  = the partial pressure of component A at pt. 1 and 2 respectively

So, it is evident from the above equation that concentration difference means the difference in partial pressure and so, flux is directly proportional to the difference of concentration and inversely proportional to the distance through which diffusion occurs.

#### **Resistance to Diffusion :**

Random thermal movement of molecules is the main cause of diffusion. The moving molecules randomly collide with other molecules and a resistance occurs, which, in turn, depends upon (a) the number of collisions during its movement and, (b) the distance through which the diffusion occurs.

Consider the case of diffusion of an ideal gas A through a stagnant gas B, the steady state flux equation is –

 $N_A = D_{AB}P / RTZp_{BM} (p_{A!} - p_{A2}) \dots (3)$ 

 $[p_{BM} = log-mean partial pressure of stagnant gas B]$ 

Therefore,  $p_{BM} = (p_{B2} - p_{B1}) / \ln(p_{B2}/p_{B1})$ .

Therefore, it is stated that the flux is inversely proportional to the distance (Z), through which diffusion occurs and the concentration of the stagnant gas ( $p_{BM}$ ), because with the increase in Z and  $p_{BM}$ , resistance increases as well as flux decreases.

When we consider a pure phase,  $p_{BM}$  approaches zero and resistance to diffusion becomes very small. But the flux  $N_A$  is finite due to the fact that difference in partial pressure is almost zero.

### Lecture 3

## **Mass Transfer Operation :**

Many unit operations are based on mass transfer.

Mass transfer may occur :-

- 1) in one direction,
- 2) in opposite direction,

- 3) with the exchange of a single component,
- 4) with the exchange of multicomponents,
- 5) with a simultaneous chemical reaction,
- 6) with simultaneous heat transfer,
- 7) isothermally and
- 8) non-isothermally.

In a mass transfer operation, the following phenomena must be occurred -

- a) Two or more phases must come in contact with each other.
- b) Materials should flow from one phase to the other.
- c) A part of the total flow must be by molecular motion or molecular diffusion.

Phases in Contact	Mass Transfer Operations
Solid – solid	Solid diffusion
Solid – liquid	Dissolving, crystallization
Solid – vapour	Sublimation, adsorption
Liquid – liquid	Extraction, liquid thermal diffusion
Liquid – gas	Gas absorption
Liquid – vapour	Distillation
Gas – gas	Gas diffusion, thermal diffusion
Solid – liquid – solid	Leaching
Solid – liquid - vapour	Adsorption

There are few similarities between various mass transfer operations which are as follows-

- a) After a considerably long period of contact, the phase equilibrium is reached.
- b) Rate of transfer is calculated by deviation from equilibrium concentration.
- c) Equilibrium exists at phase interface or there is no resistance to mass transfer at the interface, of course with some exceptions.
- d) Material transfer occurred due to combined effect of molecular diffusion and turbulence.

There are few differences between various mass transfer operations which are summed up as follows:

a) Usually, there are two active components for distillation, thermal diffusion, adsorption, gas diffusion and leaching, but there may be three or more components present. But at least three or more components must be involved in extraction, gas absorption

b) Distribution of components between phases is another difference.

c) Temperature is also a point of difference between operations.

## **Interphase Mass Transfer :**

A phase is a part of an entirely homogenous system, bounded by a surface, which separates it from the other parts of the system.

The process of mass transfer from the bulk of one phase to the interphase surface and then from the interphase to the bulk of another phase is termed as *interphase mass transfer*. This can be exemplified as follows-

A solute, if diffuse through a gas phase and then pass through interphase between phases it finally diffuse through adjacent immiscible liquid. Adsorption of SO2 from air by water is such type of case, where mass transfer occurs due to concentration gradient. An equilibrium exists at the interface between two fluid phases.





The above diagram shows that mass transfer occurs in the gas phase from  $P_{AG}$  to  $P_{Ai}$  at the interface and  $C_{Ai}$  to  $C_{AL}$  in the liquid phase.

So, as the equilibrium exists at the interface, there is no resistance to mass transfer and  $p_{Ai}$  and  $C_{Ai}$  are related by the equilibrium relationship.

Therefore,  $p_{Ai} = H.C_{Ai}$  [H = constant for Henry's law for the given system]

### Lecture 4

## **Mass Transfer Coefficient**

Now, let's consider the case of turbulent mass transfer from a surface to a fluid in a conduit. As the fluid is in turulent motion, there must be 3 regions of mass transfer :

- 1. through a laminar sublayer,
- 2. through the transition or buffer layer,
- 3. through the turbulent region.

As we know that the turbulent motion is a complex phenomenon, the value of the distance in turbulent region, through which the diffusion proceeds, is very difficult to ascertain. So in all practical purposes, an effective laminar film thickness,  $Z_G$ , is taken, whose resistance to mass transfer is approximately the same as the combined resistance shown by the real laminar sublayer + buffer region + the turbulent region.

Therefore, the flux equation :

 $N_A = D_{AB} / RTZ_G (p_{A1} - p_{A2}) \dots (1)$ 

As,  $D_{AB} / RTZ_G$  = constant = K'<sub>G</sub> = mass transfer film coefficient for gas

Therefore, equation (1) becomes,  $N_A = K'_G (p_{A1} - p_{A2})$  .....(2)

*Case I*: Flux equation for the steady state diffusion of A through stagnant B is :

 $N_A = D_{AB} P / RTZ_G p_{BM} (p_{A1} - p_{A2}) \dots (3)$ 

Here,  $D_{AB}P / RTZ_G p_{BM} = K'_G = Constant$ .

<u>Case II</u> : Flux equation for equimolar counter-diffusion of A and B in the case of the liquid is :

 $N_A = D_{AB} / Z_L (C_{A1} - C_{A2}) \dots (4)$ 

Or,  $N_A = K'_L (C_{A1} - C_{A2})$  [K"<sub>L</sub> = liquid film mass transfer coefficient,  $Z_L$  = effective laminar film thickness]

# **Mass Transfer Film Coefficient**

It is defined as the mass of a component, which is transferred in unit time from the bulk ofone phase to an interface of unit area when the volume of the driving force is unity.

It is calculated as the inverse of resistance (as like heat transfer). It is the combination of distance (Z) and the concentration of the other component  $P_{BM}$ 

# Lecture 5

**Different Flux Equations :** 

Phase	Driving Force	Mass Transfer of Component through a Stagnant Compound	Binary Equimolar Counter-mass Transfer	Units of Mass Transfer Coefficien	
Gas	Concentration	$N_{A} = K_{C}(C_{A1} - C_{A2})$	$N_{A} = K'_{C}(C_{A1} - C_{A2})$	m/s	
Liquid	Concentration	$N_A = K_C(C_{A1} - C_{A2})$	$N_A = K'_C(C_{A1} - C_{A2})$	m/s	
Gas	Partial Pressure	$N_A = K_G(p_{A1} - p_{A2})$	$N_A = K'_G(p_{A1} - p_{A2})$	Kmol/m <sup>2</sup> sPa	
Liquid	Concentration	$N_A = K_L(C_{A1} - C_{A2})$	$N_A = K'_L(C_{A1} - C_{A2})$	m/s	
Gas	Mole fraction	$N_A = K_y(y_{A1} - y_{A2})$	$N_A = K'_y(y_{A1} - y_{A2})$	Kmol/m <sup>2</sup> s mol.fract.	
Liquid	Mole Fraction	$N_A = K_x(x_{A1} - x_{A2})$	$N_A = K'_x(x_{A1} - x_{A2})$	Kmol/m <sup>2</sup> s mol.fract.	

# **Relation Between Mass Transfer Coefficients :**

Gases :

K'\_cC = K'\_c P/RT = K\_c p\_{BM}/RT = K'\_GP = K\_Gp\_{BM} = K\_yy\_{BM} = K'y = K\_cy\_{BM}C = K\_GY\_{BM}P

## <u>Liquids</u> :

 $K'_{c}C = K'_{L}C = K_{L}x_{BM}C = K'_{L}\rho/M = K'x = K_{x}X_{BM}$  [ $\rho$  = density of liquid, M = molecular weight]

## **Overall Mass Transfer Coefficient**

Where concentration difference is very small then the value of mass transfer film coefficient ( $K_G$  and  $K_L$ ) can be neglected. In all other cases, these coefficients are difficult to measure.  $K_G$  and  $K_L$  are measured on the basis of phases (gas or liquid).

The overall mass transfer coefficient of gas (KG) is defined as :

 $N_A = K_G (p_{AG} - p_A^*) \dots (1)$  [K<sub>G</sub> = overall driving force for gas phase (Kmol/m<sup>2</sup>sPa),  $p_A^*$  = value of the concentration in gas phase that is in equilibrium with  $C_{AL}$ ]

Similarly, for liquid :

 $N_A = K_L (C_A^* - C_{AL}) \dots (2) [C_A^* = value of concentration in liquid phase that is in equilibrium with p_{AG}]$ 

Mass Transfer film coefficient is expressed in terms of the driving forces :

$$N_A = K_G (p_{AG} - p_{Ai}) = K_L (C_{ai} - C_{AL})$$
 .....(3)

 $p_{AG} - p_{A^*} = (p_{AG} - p_{Ai}) + (p_{Ai} - p_{A^*}) \dots \dots \dots (4)$ 

If H is considered to be the Henry's law constant, then, for a state of equilibrium,

 $p_{A^*} = HC_{AL}$ ,  $p_{Ai} = HC_{Ai}$ ,  $p_{AG} = HC_{A^*}$ 

After putting equilibrium values in in equation (4), we get :

 $p_{AG} - p_{A^*} = (p_{AG} - p_{Ai}) + H(C_{Ai} - C_{AL}) \dots (5)$ 

So, from equation (1),(3) and (4), we get :

 $1/K_G = 1/K_G + H/K_L$  .....(6)  $[1/K_G = \text{total resistance based on overall gas}$  phase driving force and it is the sum of gas film resistance  $(1/K_G)$  and liquid film resistance  $(H/K_L)$ ]

When H is very small, the term  $H/K_L$  is certainly negligible and then the total resistance is equal to the gas film resistance. This system is called gas film controlling. The absorption of  $NH_3$ , which is very soluble in water, is an example of this kind.

So the overall driving force may be written as :

$$\begin{split} C_{A^*} - C_{AL} &= (C_{A^*} - C_{Ai}) + (C_{Ai} - C_{AL}) \quad \dots \dots \dots (7) \\ C_{A^*} - C_{AL} &= (p_{AG} - p_{Ai}) / H + (C_{Ai} - C_{AL}) \quad \dots \dots (8) \\ \text{Similarly, as (6) :} \\ 1/K_L &= 1/HK_G + 1/K_L \quad \dots \dots (9) \end{split}$$

When the value of H is very high, the gas film resistance  $1/HK_G$  is negligible and the total resistance is equal to the liquid film resistance  $1/K_L$ . So the system becomes liquid film controlling. This phenomenon happens in case of the gases having low solubility in water, like CO<sub>2</sub> or O<sub>2</sub>.

# Lecture 6

# ABSORPTION

It is a physical process by which one or more constituents of a gaseous mixture is removed by treating it with a particular liquid which has to have the property of dissolving the gaseous constituents. The soluble constituents of the gas are called *active components* and the partially insoluble constituents are called *inert components*.

The reverse process of removing gas from a solution is called stripping or desorption.

*Example :* Absorption – Removal of SO2 from flue gas by alkaline solution.

Desorption – Removal of volatile components of oil by means of steam.

If the concentration of active component in a gas is higher than its concentration when it is in equilibrium with liquid, mass transfer occurs from gas to liquid phase and vice versa. So it can be said that the direction of mass transfer totally depends on liquid - gas composition.

Absorption or stripping process may run in two ways :

1) Statically – This process is made to run to know the equilibrium state between the phases and the deviation of the actual compositions of the two phases from the equilibrium state.

2) Kinetically – This indicates the rate of the process under the given conditions.

### **Design of Packed Absorption Column / Tower**

Absorption is usually carried out in packed columns. A tower is established which is filled up with inert material (tower packing), just to increase the area of contact between the gases and liquid. The liquid is poured through the top to trickle down through the packing and the gas is pumped through the bottom of the tower to move in opposite direction. The two phases come in contact with each other inside the tower column.

The above description clearly states that there are great difficulties to measure the surface area of the liquid from which the mass transfer takes place. So in packed column, the

mass transfer coefficient is expressed only in terms of volume of the packing. It is expressed as  $K_{G,a}$ , where a is the surface area per unit volume of packing.

The designing of a packed column is made keeping in mind the following matters :

1) Overall mole balance  $-G_M(y_2 - y_1) = L_M(x_2 - x_1)$  [  $G_M$  and  $L_M$  = molar flow rate of gas and liquid respectively]

2) Diameter of the column – channeling, loading, flooding.

3) Height of absorption column.



 $G_M, y_1 \qquad L_M, x_1$ 

Lecture 7

**Capacity of the Packed Towers :** 

The material balance equation for the column is :

N'<sub>A</sub>A dZ.a =  $K_G.a(P_{AG} - P_{Ai}) A dz = K_La(C_{Ai} - C_{AL}) A.dZ$ 

[N'A = Kmol of solute absorbed per unit, a = surface area of interface per unit volume of column, A = cross-sectional area of column, Z = height of packed section]

Therefore, interfacial area for transfer = a dv = a.A.dZ

## Height of Column Based on Conditions in the Gas Film

If we consider that :

 $G_M$  = moles of inert gas/(unit time).(unit cross-section of tower),  $L_M$  = moles of solute-free liquor/(unit time).(unit cross-section of tower), y = moles of solute gas A/ mole of inert gas B in gas phase, x = moles of solute A / mole of inert solvent in liquid phase.

If it is assumed that at any plane, the molar ratios of the diffusing material in the gas and liquid phases are y and x respectively, then over a small height dZ, the moles of gas leaving the gas phase will equal to the moles taken up by the liquid.

A.  $G_M.dy = A.L_M.dx$ 

Again,  $G_M$ .Ady = N'A.Adz.a = N'A(a dv) = K\_G.a(P\_{Ai} - P\_{AG}) A.dz

Now, in a gas absorption, gas and liquid concentration will decrease in the upward direction and both dx and dy will be negative

As, 
$$P_{AG} = y/1+y \cdot P$$
  
 $G_{M}dy = K_{G}aP(y_i / 1+y_i - y/1+y)dz$   
Or,  $G_{M}dy = K_{G}aP\{y_i - y/(1+y)(1+y_i)\}dz$ 

So, the height of column Z required to achieve a change in y from  $y_1$  at the bottom to  $y_2$  at the top of the column is given by :

$$\int_{0}^{z} dz = z = G_{M}/K_{G}a.P \int_{y_{1}}^{y_{2}} (!+y)(1+yi)/(yi-y) dy$$

For a dilute mixture, the above equation becomes -

 $z = G_M/K_G.a.P \int_{y_1}^{y_2} dy/(y_i - y)$ 

## Height of Column Based on Conditions in liquid Film

So, for liquid film :

A.LM dx = KL.a.(CAi – CAL) A.dz  $\dots$ (1)

Where CA = moles of solute/unit volume of liquor and CT = (moles of solute+solvent)/unit volume of liquor.

Therefore, CA/(CT - CA) = moles of solute/moles of solvent = x

 $CA = X/(1+X) \cdot CT$ 

So, the equation (1) can be written as :

 $L_M dx = K_L.a.CT\{x/(1+x) - x_i/(1+x_i)\}dz$ 

Or,  $L_M dx = K_L \cdot a \cdot CT \{x - x_i / (1+x)(1+x_i)\} dz$ 

$$\int_{0}^{z} dz = z = L_{M}/K_{L}.a.C_{T}\int_{x_{1}}^{x_{2}} (1+x)(1+x_{i})/(x-x_{i}) dx$$

Therefore, for dilute concentration,

 $z = L_M/K_L.a.C_T \int_{x_1}^{x_2} dx/(x - x_i)$ 

### **Height Based on Overall Coefficients**

If the driving force based on the gas concentration is written as (y - ye) and the overall gas transfer coefficient as KG, then the height of tower for dilute concentration becomes :

 $z = G_M/K_G.a.P \int_{y_1}^{y_2} dy/(y_e - y)$ 

Or, in terms of liquor concentration

 $z = L_M/K_L.a.C_T \int_{x_1}^{x_2} dy / (x - x_e)$ 

# Lecture 8

# **Operating Line and Graphical Integration for the Height of a Column**

From material balance, we can get :

$$G_{M}(y_{1}-y) = L_{M}(x_{1}-x)$$

Or,  $(y_1 - y) = L_M/G_M (x_1 - x)$ 

This is the equation of a straight line of slope LM/GM, passes through the point (x1, y1) and (x2, y2). This line is known as *operating line*.



If the gas film is controlling, the process  $y_i = y_e$  and is given by a point  $F(x, y_e)$ . The driving force causing transfer is then given by the distance DF and is given by  $\int_{y_1}^{y_2} \frac{dy}{(y_i - y_i)} dy$ . if the liquid film controls the process  $x_i = x_e$  and the driving force  $x_i - x$  is given by line DR

The evaluation of the integral :  $\int_{x_1}^{x_2} dx/(x - x_i)$ 

### Number of Transfer Unit

ye - y = overall driving force expressed in terms of y

x - xe = overall driving force expressed in terms of x

Thus, the number of overall gas transfer unit =  $N_{OG} = \int dy / (y_e - y)$ 

So, the number of liquid transfer unit =  $N_{OL} = \int dx / (x - x_e)$ 

The heights of the overall transfer units are :  $H_{OG} = G'/K'_G a$ ,  $H_{OL} = L'/K_L a [G' = mass velocity of vapour (Kg/m<sup>2</sup>)]$ 

Over a small height dz, the partial pressure of the diffusing component A will change by an amount  $dP_{AG}$ . Then the moles of A transferred are given by : (change of mole fraction) × (total moles of gas) Therefore,  $K_G a (P_{AG} - P_{AC}) dz = -dP_{AG}/p \times G'_M$ So,  $\int^{PAG_1}_{PAG_2} dP_{AG} / (P_{AC} - P_{AG}) = \int^z_0 K_G a P / G'_M dz$ In terms of mole fractions :  $N_{OG} = \int^{y_2}_{y_1} dy / (y_e - y) = \int^z_0 K_G a P / G'_M dz = K_G a P / G'_M z$  $N_{OG} = \int^{y_2}_{y_1} dy / (y_e - y) = \int^{y_2}_{y_1} y d(\ln y) / (y_e - y)$  $N_{OG} =$  Height of column / Height of transfer unit = Z/ H<sub>OG</sub>  $H_{OG} = G'_M/PK_G a$ ; and similarly  $H_{OL} = L_M/K_L.a.C_T$ 

## **MODULE:II**

#### Lecture 9

#### Distillation

It is a method to separate two or more liquid components of a liquid solution into a pure fraction. The components separate due to their different vapour pressure at a given temperature. There are marked differences between distillation and absorption or stripping. In distillation, the mass transfer occurs at both the direction, where more volatile components vaporizes and then passes from the liquid to the vapour phase and less volatile components condense. The resulting vapour is rich in one component and poor in another component (distillate product). The liquid effluent is called bottom product.

## Vapour – Liquid Equilibrium

The composition of the vapour in equilibrium with a liquid of given composition is determined experimentally using an equilibrium. The results are shown on a temperature composition diagram.



So, a liquid of composition  $x_1$  will boil at temperature  $T_1$  and the vapour in equilibrium is indicated by point D of composition  $y_1$ . Here, x = mole fraction of the more volatile component and y = mole fraction of the volatile component in the vapour.

In Fig B and C, there is a critical composition of  $x_g$ , where the liquid as well as vapour have same composition and so no change occurs when the mixture is kept for boiling. This critical mixture is called *azeotropes*.

In the distillation diagram, the more suitable way is to plot y against x at a constant pressure, as most of the industrial distillations is done at constant pressure.

#### **The Boiling Point Diagram**

Equilibrium in vapour – liquid system is usually expressed in terms of y (mole fraction of a component in vapour) and x (mole fraction of that component in the liquid. Boiling point diagrams are meant for observing the progressive change of equilibrium values with temperature. The following figure shows the boiling point diagram for a benzene-toluene system at a pressure at 101.32 KPa.

The lower curve is the saturated liquid curve and is called *Bubble point curve*. The upper curve is the saturated vapour curve and is called *dew Point curve*. The region encapsulated between two curves is called *two-phas region*, where the mixture remains as partially liquid and partially vapours. So it is clear that any point above the upper curve means mixture of vapours and any point below the curve means the mixture of liquids. So, at the point x and y, lying at same horizontal line, denotes equilibrium compositions at a temperature of  $95^{\circ}C$ .



The boiling point diagram can be drawn from the pure component vapour pressure data for the systems, which follow the Raoult's *law*.

#### Partial Pressure and Dalton's, Raoult's & Henry's Laws

The partial pressure PA of component A in a mixture of vapours is the pressure that would be exerted by component A at the same temperature if present in the same volumetric concentration as in the mixture.

According to Dalton's law of partial pressure,  $P = \sum P_A$ , i.e., total pressure of the gas mixture is equal to the sum of the partial pressures of its components.

As, in an ideal gas or vapour, the partial pressure is proportional to the mole fraction of the constituent, then –  $PA = y_A P$ 

For an ideal mixture, the partial pressure is related to the concentration in the liquid phase by *Raoult's law*, which is usually written as  $-P_A = P_A^O x A [P_A^O = vapour pressure of pure A at the same temperature]$ 

This relation is true only when  $x_A$  value is high. For low  $x_A$  value, a linear relation exists between  $P_A$  and  $x_A$ .

For a liquid solute A in a liquid solvent B, Henry's law takes the form -  $P_A = H.'x_A$ 

If the mixture follows *Raoult's law*, the values of yA for various values of xA may be calculated from a knowledge of the vapour pressure of the components at various temperature.

So,  $P_A = P_A^O x_A$  $P_A = P y_A$  Therefore,  $y_A = P_A^o x_A/P$ ,  $y_B = P_B^o x_B$ But,  $y_A + y_B = 1$   $P_A^o x_A/P + P_B^o(1 - x_A) / P = 1$   $p_A^o x_A + p^o_B (1 - x_A) = P$   $p_A^o x_A - p_B x_A = p - p_B^o$ Or,  $x_A = (p - p_B) / (p_A^o - p_B^o)$ 

Lecture 10

#### **Relative Volatility**

The relative volatility is defined as the ratio of the pure component vapour pressure to that of other at same temperature. In case of the ratio of the relative volatility ( $\alpha$ ) of a pure component A's vapour pressure and vapour pressure of another component B can be expressed as –

 $\alpha AB = PAo / PBo$ 

The relative volatility of the components of a multi-component system A-B-C-D , arranged in the order of increasing boiling point can be expressed as –

 $\alpha AD = PAo / PDo; \quad \alpha BD = PBo / PDo, \quad \alpha CD = PCo / PDo$ 

In case of the system obeys Raoult's law –

 $\alpha AB = (pA/xA) / (pB/xB) [pA \& pB = partial pressure of component A and B in the vapour; xA \& xB = mole fraction in the liquid]$ 

pA = PyA; pB = PyB [yA & yB = mole fractions of component A and B respectively (in vapour)]

 $\alpha AB = yA.xB / yB. xA = yA (1 - xA) / xA(1 - yA)$ 

Or,  $yA = \alpha ABxA / 1 + (\alpha AB - 1)xA$ 

Relative volatility is the measurement of the case with which the components may be separated.

So, when  $\alpha AB$  1, then separation is not possible.

#### **Distillation Methods**

There are three different methods for distillation of two component mixtures :-

- 1) Differential distillation
- 2) Flash or equilibrium distillation,

3) Rectification.

#### 1. Differential Distillation

In this type of distillation, the liquid mixture is boiled slowly in a hot kettle. When the vapour is formed, it is quickly channelled to a condenser. Then the distillate is collected from the condenser. It is quite clear that at the initial stage of vaporisation, the distillate is rich in A, but it becomes less after some time.



If we consider a batch of L1 moles of a liquid mixture consisting of A and B components (as shown in above figure) and x1 is the mole fraction of A and after some predetermined time, L moles of liquid is left in the container, x and y are the amount of A in the liquid, then x and y must be in equilibrium.

If we take an example where a very small amount of liquid, dL is vaporised, and during vaporisation, the composition of the liquid changes from x to (x - dx) and the change in the amount of liquid from L to (L - dL), then by material balance, we get –

xL = (x - dx)(L - dL) + ydL

 $Or, xL = xL - xdL - Ldx + dxdL + ydL \qquad (1)$ 

As the value of dxdL is very low, it can be neglected. So the equation (1) becomes –

$$dL/L = dx/(y-x)$$

Integrating :  $\int_{L_2}^{L_1} dL/L = \ln L_1/L_2 = \int_{x_2}^{x_1} dx/(y-x)$  ....... (2) [L<sub>1</sub> = original moles in the container, L<sub>2</sub> = moles left in the container, x<sub>1</sub> and x<sub>2</sub> = original and final composition of liquid respectively]

Equation (2) is known as Rayleigh's equation.

The average composition of the total material distilled,  $y_{av}$ , is usually calculated by material balance.

$$L_1 x_1 = L_2 x_2 + (L_1 - L_2) y_{av}$$

### 2. Flash or Equilibrium Distillation

This type of distillation is done to a liquid mixture, which is partially vaporised. Then this vapour-liquid mixture is kept for some time so that equilibrium is reached. Then, the mixture I separated. The total operation is carried out in a single stage and it can be carried out continuously or batch wise.



A binary mixture consisting of components A and B flows t heater at the rate of F mol/h and there it is vaporised partially. Then the mixture reaches equilibrium and separated. The total material balance gives - F = V + W ......(1) [V = moles of vapour/hr., W = moles of liquid/hr]Material balance for the more volatile component gives -  $Fx_F = Vy_D + Wx_W$  ......(2) [x<sub>F</sub>, y<sub>D</sub> and x<sub>W</sub> = mole fractions of more volatilecomponents in feed, vapour and liquid respectively.]

 $x_{F} = V/F y_{D} + (F - V)x_{W}/F \qquad (3)$ If we put V/F = f [f = fraction of the vaporised feed], Therefore,  $y_{D} = -(1 - f)/f x_{w} + x_{F}/f \qquad (4)$ After replacing  $y_{D}$  and  $x_{w}$  by y and x, we get –  $y = e - (1 - f)/f x + x_{F}/f \qquad (5)$ 

The intersection of this line and the  $45^{\circ}$  diagonal line represented by the equation y = x on the xy equilibrium can be obtained by simultaneous solution of these two equation.

Putting y = x;  $x = -(1-f)/f x + x_F/f$ Solving for x,  $x = x_F$ 

So, if a line is drawn starting from the point  $(x_F, x_F)$  on the 45° diagonal line with a slope -(1 - f)/f, it will intersect the equilibrium curve at the point  $(y_D, X_w)$ . Since  $y_D$  and  $x_w$  are in equilibrium, the composition of the vapour and liquid leaving the separator can be calculated from the value.

## Lecture 11

# 3. Rectification

In the earlier two processes, the vapour leaving the container at any time is in equilibrium with the liquid remaining and normally there will be only a small increase in concentration of the more volatile component. The main advantage of rectification is that it enables a vapour to be obtained that is substantially richer in more volatile component than the liquid left in the container. This is achieved by an arrangement known as fractionating column which enables successive vaporisation and condensation to be accomplished in one unit.

#### **Azeotropic and Extractive Distillation**

Here the composition of a liquid mixture and its corresponding liquid mixture is same. This type of liquid mixture is called azeotropic or constant boiling mixture. So the boiling point of the mixture remains constant as long as the vapour is generated. Azeotropes are of two types -i) homogeneous and ii) heterogenous.

*i) Homogeneous* : Here one liquid phase is in equilibrium with vapour.

*ii) <u>Heterogeneous</u>* : Here two liquid phases are in equilibrium with the vapour.

A homogeneous azeotrope may be separated by incorporating a third component which will form a ternary mixture. This ternary mixture is now separated with one component in the distillate and the other in the bottom product.

When the third component is found in an appreciable amount in the distillate product, the operation is known as azeotropic distillation.

But when the concentration of third product is high in the bottom product, the operation is called extractive distillation.

# Reflux

The purpose of fractional distillation is to extract the product in as pure a form as possible from the condenser. In practice, all the condensate is not returned to the last still. A position of the condensate, *forward flow* is taken out as product, while another portion is returned to the last still to get the desired separation. The portion which is returned, is called reflux. The portion of the vapour going to the condenser from the last still in the series, which must be returned to keep the system functioning properly is called the *reflux ratio*. This is usually expressed as percentage reflux, or kilogram of reflux per kg of forward flow.

## Lecture 12

#### **Calculation of Number of Theoretical Stages by McCabe – Thiele Method**

McCabe and Thiele's metyhod for calculation of the number of theoretical stages in the case of the separation of a binary mixture is a mathematical graphical method. According to this method, the tower, above the feed plate is called *rectifying section* and the lower part below the feed plate is called *stripping section*. The material balance around two parts provide two operating lines. These operating lines nd the equilibrium curve for the system are used to calculate the number of theoretical stages.

The main assumption in this method are -i) constant molal vaporisation and ii) constant molal overflow. This means that the molal flow rate of vapour and liquid are

constant throughout the tower between the i) feed inlet and top plate and ii) feed inlet and bottom feed.

Therefore, a material balance equation for n-th plate gives -

 $V_{n+1} + L_{n-1} = V_n + L_n$  ......(1) [V = number of moles of vapour/r.; L = number of moles of liquid overflow/hr.; n = indicating the particular plate]

Therefore, material balance for more volatile component gives -

 $V_{n+1}y_{n+1} + L_{n-1}x_{n-1} = V_ny_n + L_nx_n$  .....(2) [y and x = mole fraction of more volatile component in vapour and liquid respectively.]

A heat balance can be considered for the same plate. Let  $T_n$  be the temperature of the n-th plate. If the sensible heats in vapour and liquid, as well as the heat of mixing, radiation and other heat losses are negligible, only latent heats are important.



As the molar latent heats for chemically similar compounds are almost the same, there is constant molal vaporisation and constant molal overflow in the tower.



Feed is introduced into the column at an intermediate point and the products are taken out from the top and bottom. The rectifying section is sometime called the *enriching section*, because the feed is enriched in this section, so that the top product is richer in more volatile component than the feed.

So, at steady state, the overall material balance gives [Fig A] - F = D + W ..... (1)

So, overall material balance for more volatile component gives -  $Fx_F = Dx_D + Wx_w \dots (2)$ 

From [Fig B] in rectifying section, the vapour from the top plate goes to a condenser for its condensation, so that the resulting liquid is at its boiling point. The reflux stream and the top product D have the same composition, i.e.,  $y_1 = x_D$ 

For constant molal vaporisation and overflow -

 $L_1 = L_2 = L_n = L (taken)$  and  $V_1 = V_2 = V_n = V_{n+1} (taken)$ 

So the overall material balance over the dashed line section of Fig B gives -

 $V_{n+1} = L_n + D$  .....(3)

Or, V = L + D .....(4)

So, material balance for the more volatile component gives -

 $Vy_{n+1} = Lx_n + Dx_D$  .....(5)

Combining equation (4) and (5), we have –

 $y_{n+1} = L/(L+D) x_n + D/(L+D) x_D \dots (6)$ 

Equation (6) is called the equation for the operating line for rectifying section which is the equation of a straight line on a plot of y/x diagram with slope L/(L+D) and intercept  $D/(L+D) x_D$ .

The intersection of the line with  $45^{\circ}$  diagonal line (y - x) can be obtained by simultaneous solution of two equation.

Therefore, putting y = x in equation (6), it is obtained that –

 $x = L/((L+D) x + Dx_D/(L+D)$ 

Or,  $x = x_D$ 

So, the operating line intersects the  $45^{\circ}$  diagonal line at point ( $x_d$ ,  $x_D$ ).

# Lecture 13 Stripping Section:



#### Material Balance for Stripping Section

A material balance over the dashed line section of the figure gives –  $V_{m+1} = L_m - W$  .....(1)

For constant molal vaporisation and overflow –  $L_m = L_{m+1} = L(-)$  [assumed] and  $V_m = V_{m+1} = V(-)$  [assumed]

Therefore, V(-) = L(-) - W .....(2)

Material balance for the more volatile component gives –  $V(-)y_{m+1} = L(-) x_m - wx_m \dots (3)$ 

Combining equation (2) and (3), it is found that

 $Y_{m+1} = L(-)/(L(-) - w).x_m - w/(L(-) - w).x_w \quad \dots \dots \dots (4)$ 

This is the equation of a straight line on a plot y versus x. it is called *equation of the* operating line for stripping section. The line has the slope L(-)/(L(-) - w) and intercept  $wx_w/(L(-) - w)$  at x = 0. Like the rectifying section, it intersects the 45° diagonal line at point( $x_w, x_w$ ).

#### Locus of Intersection of the Two Operating Lines (q line equation)

If the feed is partially liquid and partially vapour, the vapour will add to Vm to give Vn and the liquid will add to  $L_n$  to make  $L_m$ .

### Relationship Between Straems above and Below the Feed Plate

Now the condition of the feed may be represented by q.

q = heat required to vaporise 1 cond. mole of feed at entering temperature / molar latent heat of vaporisation of feed.

q = number of moles of saturated liquid produced on the feed plate by each moloes of feed added to the tower.

So, from above figure –  $L_m = L_n + qF$  .....(1)

Similarly,  $V_n = V_m + (1-q)F$  .....(2)

For constant molal vaporisation and overflow –  $L(-) = L + q_F$  .....(3) And, V = V(-) + (1 - q)F .....(4)

The operating lines for the rectifying and stripping sections can be written as -

 $y = L/(L+D) x + Dx_D/(L+D)$  .....(5)

From equation (5) –  $L(y - x) = D(x_D - y)$  .....(7)

From equation (6) with the help of (3) –  $L(y - x) = q_F(x - y) + w(y - x_w)$ ......(8)

From equation (7) and (8) –  $D(x_D - y) = q_F(x - y) + w(y - x_w)$  .....(9)

Substituting, F = D + W and  $Fx_F = Dx_D + Wx_w$  in equation (9), it is obtained –

 $Dx_D - Dy = qF_x - qF_y + w_y - Wx_w$ 

Or,  $Dx_D + Qx_w = y(D - qF + w) + qF_x$ 

Or,  $Fx_F = y(D + w - qF) + qF_x$ 

$$= y(F - q_F) + qF,$$

$$= F{y(1-q) + q_x}$$

Or,  $x_F = y(1-q) + q_x$ 

Or,  $y(q-1) = q_x - x_F$ 

Or,  $y = q/(q-1)x - x_F/(q-1)$  ------(##)

This (##) equation is known as *q-line equation*. The line has the slope q/(q-1) and intersects the  $45^{\circ}$  diagonal line at (x<sub>F</sub>, x<sub>F</sub>)

## Lecture 14

### **Calculation of Number of Plates and Location of Feed Plates**

To calculate the total number of plates required in a tower for a given separation, qline is drawn starting from point ( $x_F$ ,  $X_F$ ) in the 45° diagonal line with a slope of q/(q - 1). The operating line for the rectifying section bis drawn with a slope L/(L + D) and intercept DxD/(L+D) at x = 0. this line starts from the point ( $x_D$ ,  $X_d$ ) on the 45° diagonal line.

The operating line for stripping section starts from the point  $(x_w, x_w)$  on 45° diagonal line and ust pass through the intersection between the operating line for rectifying section and q-line.

Then the rectangular steps are drawn starting from the point  $(x_D, x_D)$  between the operating line for rectifying section and equilibrium curve until the q-lines passed and between the operating line for stripping section and the equilibrium curve until  $x = x_w$  is passed. The total number of steps is the total number of theoretical plates required.



# Mole Fraction of A in liquid x

Since the vapour and liquid leaving the reboiler are in equilibrium and therefore considered a theoretical step, the number of theoretical plates in a tower is equal to the number of theoretical steps minus one.

The feed plate is located y the triangle that has one corner on the rectifying operating line and one on stripping operating line.

## Lecture 15

#### **Reflux Ratio**

This reflux ratio is expressed either as percentage reflux or kg of reflux per kg of top product. The ratio of L/D is the ratio of the top overflow to the quantity of product.

*Example* : 75% reflux means that 75% of the vapour entering into the condenser is returned as reflux and 25% is taken out as top product.

A reflux ratio of 4 means that 4 kg of condensate is returned for every kg taken off as product.

The operating line for rectifying section is -

 $y_{n+1} = L/(L+D) xn + D/(L+D) xD$ 

Or, 
$$y_{n+1} = L/D / (L/D+1) xn + 1 / (L/D+1) xD$$
 .....(1)

Putting L/D = R = reflux ratio equation becomes –

 $y_{n+1} = R/(R+1) x_n + 1/(R+1) xD$ 

So the operating line can also be drawn in terms of reflux ratio, where the line has a slope R/(R+1) and intercept  $x^{D}/(R+1)$  at x = 0

<u>Total Reflux</u> : One of the limiting values of the reflux ratio is the total reflux, i.e.,  $R = \infty$  [as D = 0]

In a total reflux, the slope of operating line for rectifying section is R/(R+1) = 1 - 1/(R+1) = 1

So, the operating lines of both sections coincide with 45° diagonal line. This gives rise to minimum number of theoretical plates required for a given separation. In actual practice, however, no tower is operated under total reflux.



The tower under total reflux also requires infinite sizes of condenser, reboiler and tower diameter for a given feed rate.

## Minimum Reflux Ratio (R<sub>m</sub>)

If the reflux ratio is reduced, the slope of the operating line is reduced and more stages are required to pass from  $x_f$  to  $x_D$  as shown by the AK line in figure. Further reduction in R will eventually bring the operating line to AE where an infinite number of stages are required to pass from  $x_D$  to  $x_f$ . This arises from the fact that under these conditions, the stops come very close together at liquid composition near to  $x_f$ . These conditions are known as

minimum reflux ratio ( $R_m$ ). Any small increase in R beyond  $R_m$  will give a workable system, although a large number of plates are required.



So there is a minimum reflux ratio below which it is impossible to obtain desired enrichment, however many plates are used.

The slope of the line AE is – AO/OE =  $R_m/(R_{m+1}) = (x_D - y_f)/x_D - x_f$ 

Therefore,  $R_m = (x_d - y_f)/(y_f - x_f)$ 

If the q line is horizontal, for minimum reflux the enrichment line is AC

So, 
$$R_m/(R_{m+1}) = (x_d - y_c)/x_d - x_c$$

So, 
$$R_m = (x_d - y_c)/(y_c - x_c) = (x_d - x_f)/x_f - x_c$$
 [As,  $y_c = x_f$ ]

# Lecture 16

#### **Plate Efficiency**

Although it is assumed that the vapour leaving a plate is in equilibrium with the liquid which leaves it, actually complete equilibrium is never reached on any plate. This is due to the short contact time and incomplete mixing on the plate. So actual number of plates in a column is always greater than the theoretical number of plates and the plate efficiency is less than 100%.

<u>Overall plate efficiency</u> is defined as the ratio of the number of theoretical or ideal plates required for a given separation in the entire column to the actual number of plates used.

Two more types of plate efficiency are also used. They are -

i) Murphree plate efficiency

ii) Point / local plate efficiency

**Murphree Plate Efficiency** 

The proportion of liquid and vapour and the physical properties of the mixture on the trays, will vary up the column and conditions on individual trays must be examined as suggested by Murphree. For a single ideal tray, the vapour leaving is in equilibrium with the liquid leaving, and the ratio of the actual change of composition achieved to that which would occur if equilibrium between yn and xn were attained is known as *Murphree plate efficiency (EM)*.





In vapour terms :  $E_{Mv} = (y_n - y_{n-1})/(y_e - y_{n-1})$  [y<sub>e</sub> = composition of the vapour that would be in equilibrium with the liquid of composition xn actually leaving the plate.

In liquid terms :  $E_{ML} = (x_{n+1} - x_n)/(x_{n+1} - x_e)$ 

## **Equipment for Gas Liquid Operation**

Industrial gas-liquid contactors are used for transferring mass heat and momentumbetween phases in various separation operations. They are classified into two main groups -i) Differential contactors and ii) Stage wise contactors.

In differential contactors, mass transfer occurs throughout the entire length and equilibrium is not reached at any point between the phases. Each consists of a vertical column usually filled up with packing. The tow phases are allowed to flow counter currently through the interstices between the packing. Packing are used to increase the gas liquid contact area for mass transfer between the phases. The designing of such contactors mainly involves the calculation of height for a given separation.

In stagewise contactors, two phases come in contact with each other intermittently and equilibrium is established between two phases at a number of discreet stages. The stages are plates or trays of different constructions which are placed vertically above each other in a column. Designing of such contactors requires the calculation of the number of stages for a given separation.

## 1. Bubble-Cap Plate Column

The column is a stagewise contactors in which two phases are allowed to come in contact with each other in each stage. A bubble-cap plate column consists of a vertical column which is divided into sections by a number of horizontal plates. Each plate is considered to be a stage. Here gas is broken up into little bubbles which pass through a volume of liquid. The column diameter should be such that it can permit sufficiently large gas and liquid velocities without flooding. (Ghosal Pg 254)

### 2. Sieve Plate Column (Ghosal pg 255)

This is the most common type of plate or tray contacting device. Here mass transfer between gas or vapour and liquid occurs as the vapour bubbles up through the simple holes in the plate and then through the flowing liquid on each plate. The size of the holes varies from 3 - 12 mm. in diameter with 5 mm being a common size. The total area of the holes ranges from 5 - 15 % of the plate area.

#### **HETP : Height Equivalent of a Theoretical Plate (CR 639)**

With plate columns, the vapour leaving an ideal plate is richer in the mere volatile component than the vapour entering the plate by one equilibrium step. It has been suggested that this same enrichment of the vapour will occur in a certain height of packing, which is termed the HETP. As all sections of packing are physically the same, it is assumed that one equilibrium stage is represented by a given height of packing. Thus the required height of packing for any desired separation is given by : HETP x number of ideal stages required.

## **MODULE:III**

#### Lecture:17

### **EXTRACTION**

#### **Liquid-Liquid Extraction**

Extraction is an operation by means of which one or more components of a liquid or a solid are transferred to another liquid.. In case of liquid-liquid extraction, one of the components must be sufficiently insoluble so that the two liquid phases are formed. The phases are then separated to recover the desired product. Separation of certain compounds of petroleum-base components of the oil by acetone is an example of extraction.

The liquid added to bring about the extraction is known as solvent. The solvent takes up part of the component of the original solution and forms an immiscible layer over the remaining solution. The solvent layer is called extract and the other layer, composed of the remaining of the original solution is termed as *raffinate*.

This operation is used particularly when the separation by distillation is difficult due to the formation of azeotropic mixture or nonvolatility, or in the case of substances which are thermally unstable.

## **Extraction Schemes**

There are number of ultistage schemes that can be used in the case of liquid-liquid extraction. they are -i) cross-current, ii) counter-current, iii) fractional extraction.

i) Cross-current Extraction : In this case, two liquid phases are mixed together in an equilibrium stage for a period of time until equilibrium is reached. The phases are then allowed to settle and separated by decanting. Fresh solvent is usually fed to each stage. Raffinate from each stage goes to the next stage as feed. The scheme has disadvantage that a large volume of the solvent is required and extract of low concentration is produced. It is not widely used in commercial process.

ii) Counter-current Extraction : Here solvent is usually fed to the last stage, while the feed is introduced into the first one, counter-current to the solvent. One or more components can be separated from the feed liquid.

iii) Fractional Extraction : Four components are present in this scheme. Two immiscible liquid phases flow counter-current to each other in order to separate at least two components from feed mixture. Here a primary solvent, S, preferentially extracts one of the components from the feed F and a wash solvent, w, preferentially scrubs the extract free from the unwanted solute. The washing in effect, enriches the component being extracted. So, two components in a feed mixture can be fractionated quite like stripping and rectification in continuous distillation.

## Lecture:18

# **Distribution Coefficient**

The distribution of a solute between two immiscible liquids is very important in liquid-liquid extraction, particularly in the separation and purification of organic solutions. When a solute is added to a system of two immiscible liquids, it gets distributed between the liquids until equilibrium is reached between two phases. In dilute solutions at equilibrium, the ratio of the concentrations of the solute in two phases is called the distribution coefficient K. So,  $K = C_0/C_w [C_0 \& C_w = Concentrations of the solute in organic phase and aqueous phase respectively]$ 

If sufficient solute is present to saturate the system, the distribution coefficient gives the ratio of the solubilities of the solute in two phases corresponding to its normal saturation conditions. Therefore, K for concentrated solutions, the distribution coefficient is expressed as -

 $K = (kg of solute/kg of solvent)_o / kg of solute/kg of solvent)_w$ 

#### **Triangular Diagram**



A and B are pure, substantially insoluble liquids, and C is the distributed solute. Mixtures to be separated by extraction are composed of A and C, B is the extracting solvent.

In some liquid-liquid systems, the relative miscibility of the two solvents changes a a function of the solute concentration. This results in the production of the three components both in extract and the raffinate phases. The three-component system is usually represented on an equilateral triangle that the sum of the perpendicular distances from any point within the triangle to the opposite three sides equals the altitude of the triangle. Let the altitude represent 100% composition and the distances to the three sides the percentage or fractions of the three components. Each apex of the triangle represents one of the pure components. The perpendicular distance from K to the base AB represents the percentage of B and that to the base CB, the percentage of A. Point D is a binary mixture containing 80% of A and 20% of B. All points on the line DC represent mixtures with some ratio of A to B and considered as a mixture originally at D to which C has been added.

If R lb of a mixture at point R is added ti E lb of mixture at point E, the new mixture is shown on the straight line RE at point M. The so called lever rule gives the relative amount of the two phases (amount of E to that of R) in the mixture as the ratio of the lengths MR to EM.

So, R/E = line ME/line MR =  $x_E - x_M / x_M - x_R$ .

### Lecture:19

# **Single Stage Equilibrium Extraction**

When the solvent is immiscible with one of the solution components, it is easy to determine the fraction of separation from simple material balance equations.

Let us consider a dilute solution of acetaldehyde in toluene. Acetaldehyde may be extracted from this solution using water as the extracting solvent. Toluene and water are practically immiscible in mixtures containing up to 15% by weight acetaldehyde. When water is added to the solution, acetaldehyde dissolves in it and two layers are formed. The extract layer contains acetaldehyde and water and the raffinate layer contains acetaldehyde and toluene. If the two layers are in equilibrium at a given temperature, then it is easier to find out the fraction of extraction for a stage.

Let, xf = amount of acetaldehyde (kg) per kg of toluene in the feed solution.

S = amount of water (kg) added

Ao = amount of toluene (kg) in feed solution.

 $y_1, x_1 =$  equilibrium concentrations of acetaldehyde in the extract and raffinate in kg/kg of water and kg/kg of toluene respectively.

At equilibrium, material balance in terms of acetaldehyde gives -

 $Aoxf = Aox1 + Sy1 \dots (1)$ 

Ao = Sy1/(xf - x1) .....(2)

For a single stage operation, the values of Ao, Bo and xo are known. Then the equilibrium relationship between x1 and y1 permits the calculation of the fraction of separation performed in the stage.

Lecture:20

## **Multistage Extraction Process**

Let us consider a liquid mixture consisting of components A and B. A can be separated from B and vice versa in a multistage batch liquid-liquid extraction operation. The above figure shows an operation in 3 vessels numbered 1,2 and 3. Let us consider 100 kg of A and 100 kg of B are taken in  $100m^3$  of aqueous solution in vessel 1. then 100 m<sup>3</sup> of an immiscible organic solvent is added to vessel 1. The two phases are mixed vigorously until equilibrium is reached. At equilibrium, the composition of A and B in the two phases will depend on the partition or distribution coefficient.

The equilibrium distribution ratio for A :  $K_A = CA_o/CA_w$  and for B :  $K_B = CB_o/CB_w$  [CA<sub>o</sub> and CB<sub>o</sub> = concentrations of A and B in organic phase; Caw and CBw = concentrations of A and B in aqueous phase.]

Let us consider that component A is more extracted by organic phase than component B.

Let KA = 3 and Kb = 0.5

## 5.4 Continuous multistage countercurrent extraction

#### Countercurrent process and overall balance



#### Multistage Extraction Process

At equilibrium, the compositions of A and B in the organic and aqueous phases of vessel 1 will be as shown in figure. These are obtained from the following equations :

CAo = 3.0 Caw ......(1) CBo = 0.5 CBw ......(2) VoCAo + VwCAw = 100 .....(3) VoCBo + VwCbw = 100 .....(4) [Vo and Vw are the known volumes of the organic and aqueous phases respectively (Ghosal pg 267)]

By repetition of this procedure, i.e., by transferring the organic phase and aqueous phase component A and B can be separated.

### Lecture:21

#### Calculation of the number of stages

#### A. Co-current Contact With Immiscible Solvents :

If the initial solution contains a mass A of solvent A with a mass fraction  $x_f$  of solute, then the selective solvent to be added will be a mass S of solvent S. On mixing and separating a raffinate is obtained. With the solvent A containing a mass fraction  $x_1$  of solute and an extract with the solvent S containing a mass ratio  $y_1$  of the solute.

A material balance on solute gives :  $Ax_f = Ax_1 + Sy_1$ 

 $y_1/(x_1 - x_f) = -A/S$  .....(1)

#### When both phases are flowing:



Mass fraction of solute in raffinate (x)

Graphical representation can be done by locating the point F to represent the feed solution and drawing a line FE<sub>1</sub> of slope (–A/S). to cut the equilibrium curve at E<sub>1</sub>. this point gives the composition of extract and raffinate  $(y_1, x_1)$ . If a second stage is carried out by the addition of solvent S to the stream Ax<sub>1</sub>, then point E<sub>2</sub> is found on the equilibrium curve by drawing GE<sub>2</sub> of slope (–A/S)<sub>2</sub>. Point E<sub>2</sub> gives the composition of final extract6 and raffinate  $(y_2 \text{ and } x_2)$ 

If If the distribution law law is followed, then the equilibrium curve becomes a straight line given by y = mx.

The material balance on the solute may then be rewritten as :  $Ax_f = Ax_1 + Sy_1 = Ax_1 + S_mx_1 = (A + S_m)x_1$ 

 $x_1 = (A/A+S_m)x_f$ 

If a further mass S of solvent is added to raffinate  $Ax_1$  to give an extract of composition  $y_2$  and a raffinate  $x_2$  in a second stage, then :

 $Ax_{1} = Ax_{2} + S_{m}x_{2} = (A + S_{m})x_{2} \text{ and}$   $X_{2} = (A/A + S_{m})x_{1} = (A/A + S_{m})^{2}.x_{f}$ So, for n-stages :  $x_{n} = (A/A + S_{m})^{n}.x_{f}$ So,  $n = \log x_{n}/x_{f} / \log[A/A + S_{m}]$ 

#### Lecture:22

## **B.** Counter Current Contact with Immiscible Solvents :



If a series of mixing and separating vessels is arranged so that the flow countercurrent, then the conditions of flow may be represented as shown in above figure, where each circle corresponds to a mixer and separator. The initial solution F of the solute B in solvent A is fed to the first unit and leaves as raffinate R1. this stream passes through the units and leaves from the nth unit and passes in the reverse direction through the units, leaving as extract  $E_1$  [Here, x and y = ratio of solute to solvent in raffinate and extracts respectively]

If the two solvents are immiscible, the solvent in the raffinate remains as  $A_1$  and the added solvent in the extract stream as S.

The material balance for the solute gives:

i) For the first stage :  $Ax_f + Sy_2 = Ax_1 + Sy_1$ 

ii) For the nth stage :  $Ax_{n-1} + Sy_{n+1} = Ax_n + Sy_n$ 

iii) For the whole unit :  $Ax_f + Sy_{n+1} = Ax_n + Sy_1$ Therefore,  $y_{n+1} = A/S(x_n - x_f) + y_1$  .....(1)

This is the equation of a straight line of slope A/S, known as operating line, which passes through the point  $(x_f, y_1)$  and  $(x_n, y_{n+1})$ .

The equilibrium relation  $y_n$  against  $x_n$  and the operating line are drawn. The number of stages required to pass from  $x_f$  to  $x_n$  is found by drawing steps. In this example, three stages are required and  $(x_n, y_{n+1})$  corresponds to  $(x_3, y_4)$ 

## **Classification of Industrial Liquid-Liquid Contactors**

All industrial liquid-liquid contactors can be classified into two main categories, based on their operations :- 1) Stage wise; and 2) Differential

<u>Stage wise Contactors</u>: In this type of contactors, two phases are allowed to mix together so as to reach equilibrium and then separated before being passed counter-current to each other.

The advantages of this process are -

i) Simplicity of design and scale up,

ii) Absence of aerial mixing

iii) High stage efficiency

The disadvantagre of this process is the requirement of a setting unit for the separation of the phasesafter each equilibrium which makes the overall unit large and bulky.

<u>Differential Contactors</u>: This design is compact for a given throughput. In a majority of cases, it takes the form of a vertical column occupying little ground area. Since the two phases are always in continuous contact, equilibrium is never reached and the design and scale-up of such contactors are complicated.

Stage-wise and differential contactors can be further divided according to the techniques adopted for the production of phase dispersion and counter-current flow.

# Lecture:23

# <u>DRYING</u>

The drying of materials is often the final operation in a manufacturing process, carried out immediately prior to packaging or dispatch. Drying refers to the final removal of water or other solute and the operation often follows evaporation, filtration or crystallization.

## Humidification and Dehumidification

Moisture content of a material is usually expressed in terms of water content as a percentage of the mass of the dry material, though moisture content is sometimes expressed on a wet basis. If a material will either lose or gain water until an equilibrium condition is established. This equilibrium moisture content varies widely with the moisture content and the temperature of the air as given in the figure.

Moisture may be present in three forms -

*i) Bound Moisture*; This is water retained, so that it exerts a vapour pressure less than that of free water at the same temperature. Such water may be retained in small capillaries, absorbed on surfaces or as a solution in cell walls.

*<u>ii</u>) Free Moistures* : This is the water which is in excess of the equilibrium moisture content.

The water removed by vaporisation is generally carried away by air or hot gases and the ability of these gases to pick up water is determined by their temperature and humidity. So far air-water system, the following definitions are important –

1. <u>Humidity(H)</u> : Mass of water per unit mass of dry air.

As, moles of water vapour/moles of dry air =  $P_w/(P - P_w)$ 

So,  $H = 18P_w/(P - P_w).0.29$  [P<sub>w</sub> = partial pressure of water vapour, P = total pressure.]

2. <u>Humidity of Saturated Air  $(H_S)$ </u>: This is the humidity of air, when it is saturated with water vapour. The air then is in equilibrium with water at the given temperature and pressure.

Percent Humidity = Humidity of air/humidity of saturated air X 100

= H/H<sub>s</sub> X 100

Percentage of relative humidity (R) = Partial pressure of water vapour in air/vapour pressure of water at the same temperature X 100

The distinction between percent humidity and percent relative humidity is of significance though the difference in values does not usually exceed 7 - 8%

3. <u>Humid Volume (vH)</u> : The humid volume, in  $m^3/kg$  dry air is equal to the volume of 1 kg dry air plus the volume of the air it contains at 101.325 kpa absolute pressure and given gas temperature.

So, using ideal gas law :

 $v_H = 22.4m^3/1kmol X 1kmol air/29 kg air X T/273 + 22.4m^3/1kmol X 1kmolH<sub>2</sub>O/18kg H<sub>2</sub>O X H X T/273$ 

= (2.83 X 10 - 3 + 4.56 X 10 - 3H) T

For a saturated air-water vapour mixture,  $H = H_S$ , and so  $v_H$  would be the saturated volume.

4. <u>Humid Heat  $(C_S)$ </u>: it is the heat required to raise the unit mass of dry air and associated vapour through 1K at constant pressure.

So,  $C_S = 1.005 + 1.88H \{KJ/kg dry air - k\}$  [1.005 = specific heat of dry air, KJ/kg-k; 1.88 = specific heat of water vapour, KJ/kg-k

5. <u>Dew Point</u> : It is the temperature at which condensation will first occur when the air is cooled.

6. <u>Wet Bulb Temperature</u> : When a drop of liquid comes in contact with an amount of unsaturated air, some of the liquid evaporates. The heat required for this evaporation is taken from the liquid and the liquid tends to cool. However, when, liquid becomes colder than air,

heat flows from the air to the liquid. Ultimately a dynamic equilibrium is reached, when heat absorbed by the liquid exactly equals the amount of heat transferred from the surrounding air to the liquid. Since, at this point, there is no net loss or gain of heat in the surroundings, adiabatic evaporation of the liquid occurs. Under such conditions, the temperature of the liquid attains a definite equilibrium value. This temperature is lower than the temperature of ai but higher than its dew point.

The thermometer with the wetted bulb gives the equilibrium temperature. The equilibrium vaporisation temperature determined in this manner is called the wet-bulb temperature ( $\theta$ w).

The rate of heat transfer from gas to liquid is given by :

The mass rate of vaporisation is given by :

 $G_v = h_D.A.M_w \left(P_{wo} - P_w\right) / RT \quad [As, N_A = h_D.(P_{wo} - P_w); N_A \to kmol/m^2.s \text{ and } G_v \to kg/s]$ 

Or.,  $G_v = hD.A.MA/RT [(P - Pw)mean (Hw - H)]$ 

Or,  $G_v = h_D.A.\rho_A(H_w - H)$  ......(2) [As we know, PV = RT and so, 1/V = RT/P; therefore, MA/V =  $\rho_A$ ]

The rate of heat transfer required to effect vaporisation at this rate is given by :

 $Q' = h_D.A.\rho$ 

At equilibrium rate of heat transfer is obtained by equating equation (1) and (3) –

Therefore,  $H - H_w = -h/h_D.\rho_A.\lambda(\theta - \theta_w)$ .....(4)

air at temperature  $\theta_w$ ;  $\rho_A$  = density of air at its mean partial pressure;  $\lambda$  = latent heat of vaporisation of unit mass of water.]

So, wet bulb temperature  $(\theta_w)$  depends only on the temperature and humidity of the dryin(

 $Q = Q'H_w H).\lambda$  .....(3)

A g air. [h and  $h_D$  = heat and mass transfer coefficients respectively; A = surface area;  $\theta$  = temperature of air stream;  $\theta_w$  = wet bulb temperature;  $P_{wo}$  = vapour-pressure of water at  $\theta_w$ ;  $M_A$  and  $M_w$  = molecular weights of air and water respectively; T = absolute temperature; R = universal gas constant; H = humidity of gas stream;  $H_w$  = humidity of saturated

7. <u>Total Enthalpy</u> : The total enthalpy  $H_y$  in KJ/kg dry air is defined as the enthalpy of 1 kg of dry air plus the water vapour it contains. If  $T_b$  is the datum temperature for both the components, then it can be determined by the relationship –

 $H_y = C_s(T - T_b) + H.\lambda_b$ 

Or,  $H_y = (1.005 + 1.88H)(T - T_b)^{o}C + H\lambda_b [\lambda_b = latent heat in KJ/kg of water vapour at T_b]$ 

<u>Humidifiers</u> : When the temperature of liquid water is higher than the dew point of air, the air is humidified by spraying it with water or steam. This may be done by intimate contact between air to water in packed or bubble capped towers. This is required to get air at known temperature and humidity. In this case, since the temperature of the water is higher than the wet-bulb temperature of the air.

<u>Dehumidifiers</u> : When the temperature of the water is less than the dew point of the air, some of the water vapour condenses out of air and the air is dehumidified. This process is carried out by bringing the water in contact with air and takes place in a dehumidifier.

<u>Free Moisture Content</u> : It is the moisture content of a material that can be removed by drying under the given temperature and humidity. It may include both bound and unbound moisture.

<u>Unbound Moisture</u> : It is the water held by a material in excess of equilibrium moisture content corresponding to saturation in the surrounding atmosphere. It exerts a vapour pressure as high as that of ordinary water at the same temperature. It is primarily in the voids of the solid. All water present in non-hydroscopic material is unbound moistures.

### Lecture:24



#### **Drying Characteristics**

The drying characteristics of wet solids are usually described by the drying rate curve for constant drying conditions. Figure A and B are the drying rate curves with free moisture and time as the axes and drying rate and free moisture content as axes respectively. During drying of different solids, two major portions of the drying rate curve are observed : a) constant rate period and b) falling rate period.

At time zero, point A represents the initial free moisture content. At first, the evaporation rate is fast because the solid is usually at a lower temperature than its ultimate

temperature. Ultimately, the surface temperature reaches its equilibrium value at B. The drying rate curve starts at point A if the solid is quite hot at the beginning. This unsteady state adjustment period is usually very short and may be ignored for drying time calculation. In Figure A, line B to C is straight and the slope and rate are constant during this period. In Figure B, the constant rate of drying is represented by line BC.

During this period, a continuous film of water exists on the drying surface and evaporation occurs from this film of water. The solid, to be dried, is initially very wet and the film of water is entirely unbound water. Saturated condition at the surface is maintained due to rapid moisture movement within the solid. The rate of heat transfer is therefore controlled by heat transfer to the evaporating surface. The rate of heat transfer balances the rate f mass transfer and the temperature of the saturated surface remains constant.

The duration of constant rate period depends on three external factors -

i) Heat on mass transfer coefficient.

ii) Exposed area,

iii) Temperature and humidity difference between the gas stream and wet surface of the olid.

PointC on both Figure A and B represents the critical moisture content. At this point, the water present on the surface cannot maintain a continuous flim and the wet area continuously decrease in this first filling rate period until the surface is completely dry at point D. Line CD represents the first falling rate period in both Figure. At point D, the second filling rate period starts. The drying rate is now controlled by the rate of internal moisture movements and virtually independent of external variables. The time of falling rate period is longer than constant rate period though the amount of water evaporated is smaller. The entire drying process occurs in the falling rate period when the initial moisture content is less than the critical moisture content.

### Lecture:25

### Material and Heat Balance Equation in Continuous Drying Operation



The above Figure shows the flow diagram of a continuous counter-current dryer, where the drying gas and solid flow counter-current to each other. [S = solid enters at a rate of kg dry solid/hr.;  $x_1$  = initial free moisture content in solid;  $t_{S1}$  = initial temperature of solid;  $x_2$  = moisture content at outlet in solid;  $t_{S2}$  = outlet temperature of solid; G = gas enters at a rate of G kg dry air/hr; H<sub>2</sub> = initial humidity of gas(kg H<sub>2</sub>O/kg dry air);  $t_{G2}$  = initial temperature of gas; H<sub>1</sub> = final humidity of gas;  $t_{G1}$  = outlet temperature of gas.]

By material balance in terms of moisture content :  $GH_2 + Sx_1 = GH_1 + Sx_2$ ..... (1)

For heat balance, let toC be the datum temperature. In most cases, the datum temperature selected is 0oC.

So, the equation for the enthalpy of the gas in KJ/kg of dry air is :

 $H_G = C_S(t_G - t_0) + H \lambda_0$  .....(2) [ $\lambda_0$  = latent heat of water at t<sup>0</sup>C and C<sub>S</sub> = humid heat in KJ/kg of dry air]

Again,  $C_S = 1.05 + 1.88H$ 

The enthalpy of the wet solid, HS in KJ/kg dry solid is the sum of enthalpy of the dry solid and that of the liquid as free moisture and can be written as :

 $H_S = C_{pS}(t_s - t_0) + xC_{pA}(t_s - t_0)$  .....(3) [ $C_{pS}$  and  $C_{pA}$  = heat capacities of the dry solid and liquid moisture respectively (KJ/kg dry solid.K and KJ/kgH<sub>2</sub>O.K respectively)].

Neglecting heat of wetting, heat balance on the dryer gives :

 $GH_{G2}$  +  $SH_{G1}$  =  $GH_{G1}$  +  $SH_{S2}$  + Q .....(4) [Q = loss of heat in dryer, KJ/hr].

Q = 0 (for adiabatic process) and Q = negative (when the heat is added to the dryer)

Lecture:26

# **CRYSTALLIZATION**

Crystallization refers to a solid-liquid separation process in which solid particles are formed within a homogenous phase. It can occur as –

- 1. Formation of solid particles in a vapour,
- 2. Formation of solid particles from a liquid melt and
- 3. Formation of solid crystals from a solution.

The process usually happens in two steps :

i) Concentration of solution.

ii) Cooling of solution until the solute concentration becomes greater than its solubility at that temperature.

Then the solute comes out from the solution in the form of pure crystals.

# **Crystal Geometry**

A crystal is a highly organised type of matter, the constituents particles of which arranged in a orderly or repetitive manner. The constituent particles may be atoms, molecules or ions. They are arranged in an orderly, 3-dimensional array called space lattice.

Crystals of a particular material are classified according to the arrangement of the axes to which large angles are referred. The seven classes of crystals are -1) cubic, 2) tetragonal, 3)orthorhombic, 4) hexagonal, 5) monoclinic, 6) triclinic, 7) trigonal.

## Supersaturation

Let us consider an equilibrium solution of a solid and liquid phase. If the equilibrium is disturbed either by cooling or by evaporating some of the liquid, the amount of dissolved solid will exceed its equilibrium concentration and the system will try to attain equilibrium by removing excess solid present in it. The resulting process is called crystallization and the solution is now supersaturated. Crystallization cannot occur without supersaturation.

Supersaturation is expressed as coefficient :

S = parts of solute/100 parts of solvent / parts of solute at equilibrium/100 parts of solvent.

There are five basic methods of generating supersaturation :

- 1) Evaporation,
- 2) Cooling,
- 3) Vacuum cooling
- 4) Reaction,
- 5) Salting

# **Mechanism of Crystallization Process**

There are two basic steps in the overall process of crystallization from a supersaturated solution. They are -a) nucleation and b) crystal growth.

If the solution is free of the crystallizing or any foreign substance, nucleation occurs before crystal growth. The driving force for both the steps is supersaturation. Nucleus formation and crystal growth do not occur in a saturated or unsaturated solution.

a) Nucleation : It may occur in 3 different mechanisms : i) Homogenous or primary, ii) heterogeneous and iii) secondary or contact. (Ghosal – Pg 289)

b) Crystal Growth : Crystal growth is a layer-by-layer process and occurs in two steps : i) Solute diffusion to the suspension-crystal interface and ii) surface reaction for absorbing solute into the crystal lattice.

# Material and Heat Balance in Crystallization

When the solute crystals are anhydrous, the material balance4 calculations are very simple. But when the crystals are hydrated, the material balance equation takes into account some of water present in the crystals and hydrate.

So solute balance gives :  $Fx_F = Lx_L + Cx_C$  ..........(2) [x = weight fraction of solute in liquid or solid phase]

In the case of anhydrous crystals,  $x_C = 1$ , but for hydrated crystals,  $x_C$  will be less than 1.

Heat balance equation in a crystallization process is necessary in order to know the cooling requirements or to determine the final conditions.

Let  $H_1$  be the enthalpy of the feed solution at the initial temperature and  $H_2$  be the enthalpy of the final mixture of crystals and mother liquor at the final temperature. If  $H_v$  be the enthalpy of water vapour, which is formed due to evaporation, then the total heat absorbed (q) is –

 $q = (H_2 + H_v) - H_1$  .....(3)

When heat is added to the system, then q is positive and when heat is evolved from the system, q is negative

#### **MODULE:IV**

Lecture 27

## **CLASSIFICATION OF MEMBRANE PROCESSES**

SI. No	Name of the process	Driving Force	Separation Size Range	Examples of Materials Separated
1.	Microfiltration	Pressure gradient	10 – 0.1µm	Small particles, large coloids, microbial cells.
2.	Ultrafiltration	Pressure gradient	<0.1µm – 5nm	
3.	Nanofiltration	Pressure gradient	≈1nm	Emulsions, colloids, proteins.
4.	Reverse Osmosis	Pressure gradient	<1nm	
5.	Electrodialysis	Electric field gradient	<5nm	Dissolved salts, small organics
6.	Dialysis	Concentration gradient	<5nm	Treatment of renal failure.

Industrial membrane processes may be classified according to the size range of the materials which they are to separate and the driving force used in the separation.

# ULTRAFILTRATION

Ultrafiltration is one of the most widely used pressure driven membrane separation processes. The solute retained or rejected by ultrafiltration embranes are those with molecular weight of 103 or greater, depending mostly on the MWCO(moleculer weight cert-off) of the membrane separation. The process solid, dissolved salts and low molecular weight organic molecules (500 - 1000 kg/kmol) generally pass through the membrane. The pressure difference applied across the membrane is in the range of 0.1 - 0.7 MN/m2 and membrane permeation rates are  $0.01 - 0.2 \text{ m}^3/\text{m}^2\text{h}$ 

The separation of process liquid and solute takes place at the membrane during ultrafiltration gives rise to an increase in solute concentration near the membrane surface. This is called concentration polarization and takes place within the boundary film generated by the applied cross flow. With a greater concentration at the membrane, there will be a tendency for solute to diffuse back into the bulk feed according to Fick's law. At steady state, the rate of back-diffusion will be equal to the rate of removal of solute at the membrane minus the rate of solute leakage through the membrane.

 $J(C - C_p) = -D dc/dy$  .....(1) [C = solute concentration,  $C_p$  = solute concentration in the permeate expressed as mas fraction, y = distance from the membrane]

Now,  $C = C_f$ , when y = 1 and  $C = C_w$ , when y = 0 at membrane wall.

So integrating equation (1), we have,  $-\int_{Cw}^{Cf} dc/(C - C_p) = J/D \int_{0}^{l} dy$ 

 $(C_w - C_p)/(C_f - C_p) = exp(Jl/D)$ 

If it is assumed that the membrane completely rejects the solute, that is R = 1 and  $C_p = 0$ , then,  $C_w/C_f = exp(Jl/D)$ 

R =solute rejection coefficient  $= 1 - (C_p/C_f)$ 

The ratio of  $C_w/C_f$  is called the polarisation modulus.

#### Lecture 28

#### **REVERSE OSMOSIS**

Reverse osmosis (RO) is a separation process that uses pressure to force a <u>solution</u> through a <u>membrane</u> that retains the <u>solute</u> on one side and allows the pure <u>solvent</u> to pass to the other side. More formally, it is the process of forcing a solvent from a region of high solute concentration through a membrane to a region of low solute concentration by applying a pressure in excess of the <u>osmotic pressure</u>. This is the reverse of the normal <u>osmosis</u>

process, which is the natural movement of <u>solvent</u> from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied. The membrane here is semi permeable, meaning it allows the passage of solvent but not of solute.

The membranes used for reverse osmosis have a dense barrier layer in the polymer matrix where most separation occurs. In most cases the membrane is designed to allow only water to pass through this dense layer while preventing the passage of solutes (such as salt ions). This process requires that a high pressure be exerted on the high concentration side of the membrane, usually 2-17 bar (30-250 psi) for fresh and brackish water, and 40-70 bar (600-1000 psi) for seawater, which has around 24 bar (350 psi) natural osmotic pressure which must be overcome.

This process is best known for its use in <u>desalination</u> (removing the salt from <u>sea</u> <u>water</u> to get <u>fresh water</u>), but it has also been used to purify fresh water for medical, industrial and domestic applications since the early 1970s.

When two solutions with different concentrations of a solute are mixed, the total amount of solutes in the two solutions will be equally distributed in the total amount of solvent from the two solutions.

Instead of mixing the two solutions together, they can be put in two compartments where they are separated from each other by a <u>semi permeable membrane</u>. The semi permeable membrane does not allow the solutes to move from one compartment to the other, but allows the solvent to move. Since equilibrium cannot be achieved by the movement of solutes from the compartment with high solute concentration to the one with low solute concentration, it is instead achieved by the movement of the solvent from areas of low solute concentration to areas of high solute concentration. When the solvent moves away from low concentration areas, it causes these areas to become more concentration will decrease. This process is termed osmosis. The tendency for solvent to flow through the membrane can be expressed as "osmotic pressure", since it is analogous to flow caused by a pressure differential.

In reverse osmosis, in a similar setup as that in osmosis, pressure is applied to the compartment with high concentration. In this case, there are two forces influencing the

movement of water: the pressure caused by the difference in solute concentration between the two compartments (the osmotic pressure) and the externally applied pressure.

#### Applications

## Drinking water purification

Around the world, household <u>drinking water purification</u> systems, including a reverse osmosis step, are commonly used for improving water for drinking and cooking.

Such systems typically include a number of steps:

- a sediment filter to trap particles including rust and calcium carbonate
- optionally a second sediment filter with smaller pores

• an <u>activated carbon</u> filter to trap organic chemicals, and chlorine which will attack and degrade TFC reverse osmosis membranes

• a reverse osmosis (RO) filter which is a <u>thin film composite membrane</u> (TFM or TFC)

• optionally a second carbon filter to capture those chemicals not removed by the RO membrane.

• optionally an <u>ultra-violet</u> lamp is used for disinfection of any microbes that may escape filtering by the reverse osmosis membrane.

In some systems, the carbon pre-filter is omitted and <u>cellulose triacetate</u> membrane (CTA) is used. The CTA membrane is prone to rotting unless protected by the chlorinated water, while the TFC membrane is prone to breaking down under the influence of chlorine. In CTA systems, a carbon post-filter is needed to remove chlorine from the final product water.

Portable reverse osmosis (RO) water processors are sold for personal water purification in various locations. To work effectively, the water feeding to these units should best be under some pressure (40 psi or greater is the norm). Portable RO water processors can be used by people who live in rural areas without clean water, far away from the city's water pipes. Rural people filter river or ocean water themselves, as the device is easy to use (Saline water may need special membranes). Some travelers on long boating trips, fishing, island camping, or in countries where the local water supply is polluted or substandard, use RO water processors coupled with one or more UV sterilizers. RO systems are also now extensively used by marine aquarium enthusiasts. In the production of bottled mineral water, the water passes through an RO water processor to remove pollutants and microorganisms. In European countries, though, such processing of Natural Mineral Water (as defined by a European Directive) is not allowed under European law. (In practice, a fraction of the living bacteria can and do pass through RO membranes through minor imperfections, or bypass the membrane entirely through tiny leaks in surrounding seals. Thus, complete RO systems may include additional water treatment stages that use ultraviolet light or <u>ozone</u> to prevent microbiological contamination.)

#### Lecture 29

#### Water and wastewater purification

Rain water collected from storm drains is purified with reverse osmosis water processors and used for landscape irrigation and industrial cooling in Los Angeles and other cities, as a solution to the problem of water shortages.

In industry, reverse osmosis removes minerals from boiler water at power plants. The water is boiled and condensed repeatedly. It must be as pure as possible so that it does not leave deposits on the machinery or cause corrosion. It is also used to clean effluent and brackish groundwater.

The process of reverse osmosis can be used for the production of deionized water.

In July 2005, Singapore announced that a process named NEWater would be a significant part of its future water plans. It involves using reverse osmosis to treat domestic wastewater before discharging the NEWater back into the reservoirs.

#### Dialysis

Reverse osmosis is similar to the technique used in <u>dialysis</u>, which is used by people with <u>kidney</u> failure. The kidneys filter the blood, removing waste products (e.g. urea) and water, which is then excreted as <u>urine</u>. A <u>dialysis</u> machine mimics the function of the kidneys. The blood passes from the body via a catheter to the dialysis machine, across a filter.

### **Food Industry**

In addition to desalination, reverse osmosis is a more economical operation for concentrating food liquids (such as fruit juices) than conventional heat-treatment processes. Research has been done on concentration of orange juice and tomato juice. Its advantages include a low operating cost and the ability to avoid heat treatment processes, which makes it suitable for heat-sensitive substances like the protein and enzymes found in most food products.

Reverse osmosis is extensively used in the dairy industry for the production of whey protein powders and for the concentration of milk to reduce shipping costs. In whey applications, the whey (liquid remaining after cheese manufacture) is pre-concentrated with RO from 6% total solids to 10-20% total solids before UF (ultrafiltration) processing. The UF retentate can then be used to make various whey powders including WPI (whey protein isolate) used in bodybuilding formulations. Additionally, the UF permeate, which contains lactose, is concentrated by RO from 5% total solids to 18–22% total solids to reduce crystallization and drying costs of the lactose powder.

Although use of the process was once frowned upon in the wine industry, it is now widely understood and used. An estimated 60 reverse osmosis machines were in use in Bordeaux, France in 2002. Known users include many of the elite classed growths (Kramer) such as Château Léoville-Las Cases in Bordeaux.

Reverse osmosis is used globally throughout the wine industry for many practices including wine and juice concentration, taint removal; such as acetic acid, smoke taint and brettanomyces taint; and alcohol removal. The patent holder for these processes, Vinovation, Inc., claims to have served over 1000 wineries worldwide, either directly or through one if its licensed partners, in the last 15 years. Its use has become so widely accepted that patent infringers have sprung up on several continents.

#### **Car Washing**

Because of its lower mineral content, Reverse Osmosis water is often used in car washes during the final vehicle rinse to prevent water spotting on the vehicle. Reverse osmosis water displaces the mineral-heavy reclamation water (municipal water). Reverse Osmosis water also enables the car wash operators to reduce the demands on the vehicle drying equipment such as air blowers.

# **Maple Syrup Production**

Starting in the 1970s, some maple syrup producers started using reverse osmosis to remove water from sap before being further boiled down to syrup. The use of reverse osmosis allows approximately 75–80% of the water to be removed from the sap, reducing energy consumption and exposure of the syrup to high temperatures. Microbial contamination and degradation of the membranes has to be monitored.

## **Hydrogen production**

For small scale production of hydrogen, reverse osmosis is sometimes used to prevent formation of minerals on the surface of electrodes and to remove organics and chlorine from drinking water.

## Lecture 30

## Desalination

Areas that have no or limited surface water or groundwater may choose to desalinate seawater or brackish water to obtain drinking water. Reverse osmosis is the most common method of desalination, although 85 percent of desalinated water is produced in multistage flash plants.<sup>[2]</sup> Large reverse osmosis and multistage flash desalination plants are used in the Middle East, especially Saudi Arabia. The energy requirements of the plants are large, but electricity can be produced relatively cheaply with the abundant <u>oil</u> reserves in the region. The desalination plants are often located adjacent to the power plants, which reduces energy losses in transmission and allows waste heat to be used in the desalination process of multistage flash plants, reducing the amount of energy needed to desalinate the water and providing cooling for the power plant.

Sea Water Reverse Osmosis (SWRO) is a reverse osmosis desalination membrane process that has been commercially used since the early 1970s. Its first practical demonstration was done by Sidney Loeb and Srinivasa Sourirajan from UCLA in Coalinga, California. Because no heating or phase changes are needed, energy requirements are low in comparison to other processes of desalination, though still much higher than other forms of water supply (including reverse osmosis treatment of wastewater).<sup>[citation needed]</sup>

The typical single pass SWRO system consists of the following components:

- Intake
- Pre-treatment
- High-pressure pump
- Membrane assembly
- <u>Remineralization</u> and pH adjustment
- Disinfection

### **Pre-treatment**

Pre-treatment is important when working with RO and nanofiltration (NF) membranes due to the nature of their spiral wound design. The material is engineered in such a fashion to allow only one way flow through the system. As such the spiral wound design doesn't allow for backpulsing with water or air agitation to scour its surface and remove solids. Since accumulated material cannot be removed from the membrane surface systems they are highly susceptible to fouling (loss of production capacity). Therefore, pretreatment is a necessity for any RO or NF system. Pretreatment in SWRO system has four major components:

## Screening of solids

Solids within the water must be removed and the water treated to prevent fouling of the membranes by fine particle or biological growth, and reduce the risk of damage to highpressure pump components.

Cartridge filtrationation - Generally string-wound polypropylene filters that remove between 1 - 5 micrometre sized particles.

Dosing of oxidizing biocides such as chlorine to kill bacteria followed by bisulfite dosing to deactivate the chlorine which can destroy a thin-film composite membrane. There are also biofouling inhibitors which do not kill bacteria but simply prevent them from growing slime on the membrane surface.

Prefiltration pH adjustment

If the pH, hardness and the alkalinity in the feedwater result in a scaling tendency when they are concentrated in the reject stream, acid is dosed to maintain carbonates in their soulble carbonic acid form.

$$CO_3^{-2} + H_3O^+ = HCO_3^- + H_2O$$

 $HCO_3^- + H_3O^+ = H_2CO_3 + H_2O$ 

Carbonic acid cannot combine with calcium to form calcium carbonate scale. Calcium Carbonate Scaling tendency is estimated using the Langelier Saturation Index. Adding too much sulfuric acid to control carbonate scales may result in calcium sulfate, barium sulfate or strontium sulfate scale formation on the RO membrane.

#### Prefiltration Antiscalants

Scale inhibitors (also known as antiscalants) prevent formation of all scales compared to acid which can only prevent formation of calcium carbonate and calcium phosphate scales. In addition to inhibiting carbonate and phosphate scales, antiscalants inhibit sulfate and fluoride scales, disperse colloids and metal oxides and specialty products exist to inhibit silica formation.

## High pressure pump

The pump supplies the pressure needed to push water through the membrane, even as the membrane rejects the passage of salt through it. Typical pressures for brackish water range from 225 to 375 lbf/in<sup>2</sup> (1.6 to 2.6 MPa). In the case of seawater, they range from 800 to  $1,180 \text{ lbf/in}^2$  (6 to 8 MPa).

#### **Membrane assembly**

The membrane assembly consists of a pressure vessel with a membrane that allows feedwater to be pressed against it. The membrane must be strong enough to withstand whatever pressure is applied against it. RO membranes are made in a variety of configurations, with the two most common configurations being **spiral-wound** and a **hollow-fiber**.

### **Reinmineralisation and pH adjustment**

The desalinated water is very corrosive and is "stabilized" to protect downstream pipelines and storages usually by adding lime or caustic to prevent corrosion of concrete or

cement lined surfaces. Liming material is used in order to adjust pH at 6.8 to 8.1 to meet the potable water specifications, primarily for effective disinfection and for corrosion control.

## Disinfection

Post-treatment consists of stabilizing the water and preparing for distribution. Desalination processes are very effective barriers to pathogenic organisms, however disinfection is used to ensure a "safe" water supply. Disinfection (sometimes called germicidal or bactericidal) is employed to kill any bacteria protozoa and virus that have bypassed the desalination process into the product water. Disinfection may be by means of ultraviolet radiation, using UV lamps directly on the product, or by chlorination or chloramination (chlorine and ammonia). In many countries either chlorination or chloramination is used to provide a "residual" disinfection agent in the water supply system to protect against infection of the water supply by contamination entering the system.

#### Disadvantages

Reverse osmosis units sold for residential purposes offer water filtration at the cost of large quantities of waste water.

#### New developments

Prefiltration of high fouling waters with another, larger-pore membrane with less hydraulic energy requirement, has been evaluated and sometimes used since the 1970s. However, this means the water passes through two membranes and is often repressurized, requiring more energy input in the system, increasing the cost.

Other recent development work<sup>[4]</sup> has focused on integrating RO with electrodialysis in order to improve recovery of valuable deionized products or minimize concentrate volume requiring discharge or disposal.

#### Lecture 31

### PERVAPORATION

Pervaporation is a method for the separation of mixtures of liquids by partial vaporization through a non-porous or porous membrane.

The name of this membrane-based process is derived from the two basic steps of the process, firstly the permeation through the membrane by the permeate, then its evaporation into the vapor phase. This process is used by a number of industries for several different processes, including purification and analysis, due to its simplicity and in-line nature.

The membrane acts as a selective barrier between the two phases, the liquid phase feed and the vapor phase permeate. It allows the desired component(s) of the liquid feed to transfer through it by vaporization. Separation of components is based on a difference in transport rate of individual components through the membrane.

Typically, the upstream side of the membrane is at ambient pressure and the downstream side is under vacuum to allow the evaporation of the selective component after permeation through the membrane. Driving force for the separation is the difference in the partial pressures of the components on the two sides and not the volatility difference of the components in the feed.

The driving force for transport of different components is provided by a chemical potential difference between the liquid feed/retentate and vapor permeate at each side of the membrane. The retentate is the remainder of the feed leaving the membrane feed chamber, which is not permeated through the membrane. The chemical potential can be expressed in terms of fugacity, given by Raoult's law for a liquid and by Dalton's law for (an ideal) gas. It should be noted that during operation, due to removal of the vapor-phase permeate, the actual fugacity of the vapor is lower than anticipated on basis of the collected (condensed) permeate.

Separation of components (*e.g.* water and ethanol) is based on a difference in transport rate of individual components through the membrane. This transport mechanism can be described using the solution-diffusion model, based on the rate/ degree of dissolution of a component into the membrane and its velocity of transport (expressed in terms of diffusivity) through the membrane, which will be different for each component and membrane type leading to separation.

## Applications

Pervaporation is effective for diluting solutions containing trace or minor amounts of the component to be removed. Based on this, hydrophilic membranes are used for dehydration of alcohols containing small amounts of water and hydrophobic membranes are used for removal/recovery of trace amounts of organics from aqueuous solutions. Hydrophobic membranes are often PDMS based where the actual separation mechanism is based on the solution-diffusion model described above.

A relatively new membrane in the field hydrophylic membranes is the <u>ceramic</u> membranes with the actual separation layer being made of amorphous silica. This is in fact a membrane which is porous, with pores ranging around 4 Å, large enough to let water molecules pass through and retain any other solvents that have a larger molecular size such as ethanol. Recent novell hydrophylic ceramic membranes can also be based on titania or zirconia.

Pervaporations is a very mild process and hence very effective for separation of those mixtures which can not survive the harsh conditions of distillation.

• Solvent Dehydration: dehydrating the ethanol/water and isopropanol/water azeotropes

• Continuous water removal from condensation reactions such as <u>esterifications</u> to enhance conversion and rate of the reaction.

- <u>Membrane introduction mass spectrometry</u>
- Removing organic solvents from industrial waste waters.
- Combination of distillation and pervaporation/vapour permeation

Recently, a number of organophilic Pervaporation membranes have been introduced to the market. Organophilic Pervaporation membranes can be used for the separation of organic-organic mxictures, e.g.:

- Reduction of the Aromatics content in refinery streams
- Breaking of Azeotropes
- Purification of extraction media
- Purification of product stream after extraction
- Purification of organic solvents

## Lecture 32

# **ELECTRODIALYSIS**

Electrodialysis (ED) is used to transport salt ions from one solution through ionexchange membranes to another solution under the influence of an applied electric potential difference. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (diluate) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. In almost all practical electrodialysis processes, multiple electrodialysis cells are arranged into a configuration called an electrodialysis stack, with alternating anion and cation exchange membranes forming the multiple electrodialysis cells. Electrodialysis processes are unique compared to distillation techniques and other membrane based processes (such as reverse osmosis) in that dissolved species are moved away from the feed stream rather than the reverse. Because the quantity of dissolved species in the feed stream is far less than that of the fluid, electrodialysis offers the practical advantage of much higher feed recovery in many applications.

In an electrodialysis stack, the diluate (D) feed stream, brine or concentrate (C) stream, and electrode (E) stream are allowed to flow through the appropriate cell compartments formed by the ion exchange membranes. Under the influence of an electrical potential difference, the negatively charged ions (e.g., chloride) in the diluate stream migrate toward the positively charged anode. These ions pass through the positively charged anion exchange membrane, but are prevented from further migration toward the anode by the negatively charged cation exchange membrane and therefore stay in the C stream, which becomes concentrated with the anions. The positively charged species (e.g., sodium) in the D stream migrate toward the negatively charged cathode and pass through the negatively charged cation exchange membrane. These cations also stay in the C stream, prevented from further migration toward the cathode by the positively charged anion exchange membrane.<sup>[7]</sup> As a result of the anion and cation migration, electric current flows between the cathode and anode. Only an equal number of anion and cation charge equivalents are transferred from the D stream into the C stream and so the charge balance is maintained in each stream. The overall result of the electrodialysis process is an ion concentration increase in the concentrate stream with a depletion of ions in the diluate solution feed stream.

The E stream is the electrode stream that flows past each electrode in the stack. This stream may consist of the same composition as the feed stream (e.g., sodium chloride) or may be a separate solution containing a different species (e.g., sodium sulfate). Depending on the stack configuration, anions and cations from the electrode stream may be transported into the C stream, or anions and cations from the D stream may be transported into the E stream. In each case, this transport is necessary to carry current across the stack and maintain electrically neutral stack solutions.

#### **Anode and Cathode Reactions**

Reactions take place at each electrode. At the cathode,

 $2e^{-} + 2 H_2O \rightarrow H_2(g) + 2 OH^{-}$ 

while at the anode,

 $H_2O \rightarrow 2 H^+ + \frac{1}{2}O_2(g) + 2e^- \text{ or } 2 Cl^- \rightarrow Cl_2(g) + 2e^-$ 

Small amounts of hydrogen gas are generated at the cathode and small amounts of either oxygen or chlorine gas (depending on composition of the E stream and end ion exchange membrane arrangement) at the anode. These gases are typically subsequently dissipated as the E stream effluent from each electrode compartment is combined to maintain a neutral pH and discharged or re-circulated to a separate E tank. However, some (e.g.,) have proposed collection of hydrogen gas for use in energy production.

#### Efficiency

Current efficiency is a measure of how effective ions are transported across the ion exchange membranes for a given applied current. Typically current efficiencies >80% are desirable in commercial stacks to minimize energy operating costs. Low current efficiencies indicate water splitting in the diluate or concentrate streams, shunt currents between the electrodes, or back-diffusion of ions from the concentrate to the diluate could be occurring.

Current efficiency is calculated according to:

where  $\xi = \text{current}$  utilization efficiency, z = charge of the ion, F = Faraday constant, 96,485 <u>Amp-s/|mol</u>,  $Q_f = \text{diluate flow rate}$ ,  $\underline{L}/s$ , = diluate ED cell inlet

concentration, mol/L, = diluate ED cell outlet concentration, mol/L, N = number of cell pairs, I = current, Amps.

Current efficiency is generally a function of feed concentration.

#### Applications

In application, electrodialysis systems can be operated as continuous production or batch production processes. In a continuous process, feed is passed through a sufficient number of stacks placed in series to produce the final desired product quality. In batch processes, the diluate and/or concentrate streams are re-circulated through the electrodialysis systems until the final product or concentrate quality is achieved.

Electrodialysis is usually applied to deionization of aqueous solutions. However, desalting of sparingly conductive aqueous organic and organic solutions is also possible. Some applications of electrodialysis include:<sup>[4][2][5][10]</sup>

• Large scale <u>brackish</u> and seawater desalination and salt production.

• Small and medium scale drinking water production (e.g., towns & villages, construction & military camps, nitrate reduction, hotels & hospitals)

• Water reuse (e.g., industrial laundry <u>wastewater</u>, produced water from oil/gas production, <u>cooling tower</u> makeup & blowdown, metals industry fluids, wash-rack water)

• Pre-demineralization (e.g., <u>boiler</u> makeup & pretreatment, ultrapure water pretreatment, process water desalination, <u>power generation</u>, <u>semiconductor</u>, chemical manufacturing, food and beverage)

• Food processing

• Agricultural water (e.g., water for greenhouses, hydroponics, irrigation, livestock)

• <u>Glycol</u> desalting (e.g., <u>antifreeze</u> / engine-coolants, <u>capacitor</u> <u>electrolyte</u> fluids, oil and gas <u>dehydration</u>, conditioning and processing solutions, industrial <u>heat transfer</u> <u>fluids</u>, secondary coolants from heating, venting, and air conditioning (<u>HVAC</u>))

• <u>Glycerin</u> Purification

The major application of electrodialysis has historically been the desalination of brackish water or seawater as an alternative to RO for potable water production and seawater concentration for salt production (primarily in Japan).<sup>[4]</sup> In normal potable water production without the requirement of high recoveries, RO is generally believed to be more cost-effective when total dissolved solids (TDS) are 3,000 parts per million (ppm) or greater, while electrodialysis is more cost-effective for TDS feed concentrations less that 3,000 ppm or when high recoveries of the feed are required.

Another important application for electrodialysis is the production of pure water and ultrapure water by electrodeionization (EDI). In EDI, the compartments (diluate, concentrate, or both) of the electrodialysis stack are filled with ion exchange resin. When fed with low TDS feed (e.g., feed purified by RO), the diluate can reach very low levels (e.g., 18 Megohms). The ion exchange resins act to retain the ions, allowing these to be transported across the ion exchange membranes. The main usage of EDI systems such as those supplied by Ionpure or SnowPure are in electronics, pharmaceutical, power generation, and cooling tower applications.

#### Limitations

Electrodialysis has inherent limitations, working best at removing low molecular weight ionic components from a feed stream. Non-charged, higher molecular weight, and less mobile ionic species will not typically be significantly removed. Also, in contrast to RO, electrodialysis becomes less economical when extremely low salt concentrations in the product are required and with sparingly conductive feeds: current density becomes limited and current utilization efficiency typically decreases as the feed salt concentration becomes lower, and with fewer ions in solution to carry current, both ion transport and energy efficiently greatly declines. Consequently, comparatively large membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions. Innovative systems overcoming the inherent limitations of electrodialysis (and RO) are available; these integrated systems work synergistically, with each sub-system operating in its optimal range, providing the least overall operating and capital costs for a particular application.<sup>[111]</sup>

As with RO, electrodialysis systems require feed pretreatment to remove species that coat, precipitate onto, or otherwise "foul" the surface of the ion exchange membranes. This fouling decreases the efficiency of the electrodialysis system. Species of concern include calcium and magnesium hardness, suspended solids, silica, and organic compounds. Water softening can be used to remove hardness, and micrometre or multimedia filtration can be used to remove suspended solids. Hardness in particular is a concern since scaling can build up on the membranes. Various chemicals are also available to help prevent scaling. Also, electrodialysis reversal systems seek to minimize scaling by periodically reversing the flows of diluate and concentrate and polarity of the electrodes.

#### DIALYSIS

This article is about renal dialysis; for the laboratory technique, see <u>dialysis (biochemistry)</u>; for the treatment for liver failure, see liver dialysis.

A hemodialysis machine

In medicine, **dialysis** (from Greek "dialusis", meaning dissolution, "dia", meaning through, and "lusis", meaning loosening) is primarily used to provide an artificial replacement for lost kidney function (renal replacement therapy) due to renal failure. Dialysis may be used for very sick patients who have suddenly but temporarily, lost their kidney function (acute renal failure) or for quite stable patients who have permanently lost their kidney function (stage 5 chronic kidney disease). When healthy, the kidneys maintain the body's internal equilibrium of water and minerals (sodium, potassium, chloride, calcium, phosphorus, magnesium, sulfate) and the kidneys remove from the blood the daily metabolic load of fixed hydrogen ions. The kidneys also function as a part of the endocrine system producing erythropoietin and 1,25-dihydroxycholecalciferol (calcitriol). Dialysis is an imperfect treatment to replace kidney function because it does not correct the endocrine functions of the kidney. Dialysis treatments replace some of these functions through diffusion (waste removal) and convection (fluid removal).

## Principle

Dialysis works, on the principles of the diffusion of solutes and convection of fluid across a semi-permeable membrane. Blood flows by one side of a semi-permeable membrane, and a dialysate or fluid flows by the opposite side. Smaller solutes and fluid pass through the membrane. The blood flows in one direction and the dialysate flows in the opposite. The concentrations of undesired solutes (for example potassium, calcium, and urea) are high in the blood, but low or absent in the dialysis solution and constant replacement of the dialysate ensures that the concentration of undesired solutes is kept low on this side of the membrane. The dialysis solution has levels of minerals like potassium and calcium that are similar to their natural concentration in healthy blood. For another solute, bicarbonate, dialysis solution level is set at a slightly higher level than in normal blood, to encourage diffusion of bicarbonate into the blood, to neutralise the metabolic acidosis that is often present in these patients.

## **MODEL QUESTIONS**

#### 1. Multiple Choice Question (MCQ) (Answer any ten) 10X1=10

i. The unit of volumetric diffusivity is

a) cm.<sup>2</sup>/sec. b) cm./sec. c) cm.<sup>3</sup>/sec. d) cm.<sup>2</sup>/sec<sup>2</sup>.

- ii. Molecular diffusion is caused by
- a) transfer of molecules from low concentration to high concentration region.
- b) thermal energy of the molecules
- c) activation energy of the molecules
- d) potential energy of the molecules.
- iii. Mass transfer co- efficient is defined as
- a) Flux = Co-efficient / concentration difference
- b) Co-efficient = Flux / concentration difference
- c) Flux = concentration difference / co-efficient
- d) None of these.

iv. Mass transfer co- efficient (K) and diffusivity (D) are related according to film theory as: a)  $K \propto D$ b)  $K \propto \sqrt{D}$  c)  $K \propto D^{1.5}$  d)  $K \propto D^2$ 

- v. Mass transfer co-efficient of liquid is
- a) affected more by temperature than that for gases
- b) affected much less by temperature than that for gases
- c) Not effected by temperature
- d) None of these.
- vi. Relative humidity is the ratio of the
- a) partial pressure of the vapor to the vapor pressure of the liquid at the room temperature.
- b) partial pressure of the vapor to the vapor pressure of the liquid at the gas temperature.
- c) actual humidity to saturation humidity.

d) none of these.

vii. Raoult's law is applicable to

a) ideals solutions b) real solutions c) the mixture of water and alcohol

d) non-ideal gases.

viii. In azeotropic mixture, the equilibrium vapor composition is

a) more than liquid composition

b) less than liquid composition

c) same as liquid composition

d) independent of pressure.

ix. in rectifying section of a continuous distillation column

a) vapor is enriched with low boilers

b) vapor is enriched with high boilers

c) liquid is stripped of high boilers

d) none of these.

x..Which of the following assumes constant molal vaporization and overflow ?

a) McCabe Thiele method , b) Ponchan- Savarit Method ,

c) Enthalpy concentration method , d) Plate absorption column.

xi. The reflux to a distillation column is 100 moles /hour, when the overheat product rate is 50 moles/hour. The reflux ratio is

a) 2, b) 0.5, c) 50, d) 150.

xii . If f=moles of vapor present per mole of feed then the slope of feed line is (McCabe- Thiele method)

a) (1-f)/f, b) -(f-1)/f, c) (-1)/f, d) (f)/(f-1).

xiii. If  $x_D$  = overhead product molal composition and  $R_D$  = reflux ratio, then slope and intercept of the operating line for rectifying section are respectively

a)  $\frac{R_D}{R_D + 1}$ ,  $x_D$ b)  $R_D$ ,  $x_D$   $R_D + 1$ ,  $R_D + 1$ c)  $x_D$ ,  $R_D + 1$   $R_D + 1$   $R_D$ , 1  $R_D + 1$ ,  $x_D + 1$   $R_D + 1$  $R_D + 1$ 

xiv. Rayleigh equation applies to

a) differential distillation, b) flash vaporization,

c) equilibrium distillation, d) molecular distillation.

xv . Tea percolation employs

a) liquid-liquid extraction, b) leaching,

c) absorption, d) none of these.

xvi . The caking of crystals can be prevented by

a)maintaining high critical humidity,

b) maintaining low critical humidity,

c) coating the product with inert material,

d) both (a) and (c) .

xvii. Milk is dried usually in a

a)freeze drier, b) spray drier,

c) tray drier, d) rotary drier.

xviii. In the constant rate period of the rate of drying curve for batch drying

a) cracks develop on the surface of the solid,

b) rate drying decreases abruptly,

c) surface evaporation of unbound moisture occurs,

d) none of these.

xix. In a distillation column when the feed is saturated liquid the value of q is

a) 1.0, b) >1, c) <1, d) 0

xx. For total reflux in distillation the slope of the operating line for rectifying section is

a) 0, b) 1, c) <1, d) >1

xxi. The separation size range for nano-filtration is

a) 10-0.1  $\mu$ m, b) 1-10nm, c) <1nm, d) <1  $\mu$ m

xxii. When the liquid phase and vapor phase of a binary system obeys Raoult's and Dalton's law respectively, the relative volatility is the ratio of

a) vapor pressure of component A to that of component B

b) vapor pressure of component A to the total pressure.

c) vapor pressure of component A to the partial pressure of A

d) partial pressure of component A to the total pressure.

xxiii. Fenske equation determines

- a) maximum no. of ideal plates
- b) height of the distillation column
- c) minimum no. of theoretical plates
- d) optimum reflux ratio

xxiv. At azeotropic composition of a binary mixture, the relative volatility is

a) 0, b) 1, c) <1, d) 2

xxv. A feed mixture for distillation contains 25% liquid and rest is vapour, q value is

a) 3, b) 0, c) ¼, d) ¾

xxvi. Pervaporation differs from other membrane separation process because,

a) it is less expensive

b) It involves phase change in permeate

c) Commercially it is always supplemented to a conventional separation process

d ) Very high pressure is applied in the upstream side of the membrane

#### **GROUP B**

#### Short Question (SQ) (answer any three) 5 X3=15

2 Derive the expression for overall mass transfer coefficient when the system is gas film controlling. (5)

3. Show that for binary gas mixture, the diffusivity of A in B equals to the diffusivity of B in A. (5)

4. Derive the expression of height of absorption column based on conditions in the gas film.

(5)

5. Define diffusivity.  $CH_4$  diffuses at steady state through a tube containing He . At point 1 the partial pressure of  $CH_4$  is  $p_A=55$  kpa & at point 2, 0.03 m apart  $p_A=15$  kpa .

The total pressure is 101.32 kpa & temperature 298 K . At this temperature & pressure the value of diffusivity is  $6.75 \times 10^{-5} \text{ m}^2/\text{S}$ .

Calculate the flux of CH<sub>4</sub> at steady state for equimolar counter diffusion . (2+3)

6. Explain briefly the operating principle of a Fluid Bed Dryer. (5)

7. A hot solution containing 5000Kg of  $Na_2CO_3$  & water with a concentration of 25 wt%  $Na_2CO_3$  is cooled to 293 K and crystals of  $Na_2CO_3.10 H_2O$  are precipitated. At 293 K, the solubility is 21.5 kg anhydrous  $Na_2CO_3/100$ kg of total water. Calculate the yield of crystals obtained if 5% of the original water in the system evaporates on cooling. (5)

8. Show that the relative volatility of a binary system ( $\infty_{AB}$ ) is related to the equilibrium vapour and liquid composition by the following formula:

$$y_A = \alpha_{AB} x_A / \{1 + (\alpha_{AB} - 1) x_A\}$$
 (5)

9. 150 kg nicotine-water solution containing 1 % nicotine is to be extracted with 250 kg of kerosene at 20°C .Water and kerosene essentially immiscible in each other . Determine the percentage extraction of nicotine after one stage operation . At the dilute end of the system, the equilibrium relationship is

 $y^*$ =0.798X where y & x are expressed as kg nicotine/kg kerosene & kg nicotine/kg water , respectively . (5)

10. Discuss the constant rate period and falling rate period of drying with the help of drying rate curves. (5)

11. What is membrane fouling? How it is controlled? (3+2)

12. Answer any three questions

(a) What is extractive distillation?

- (b) What is minimum boiling azeotrope? Give example.
- (c) What is Fenske equation and what is its significance? 2+2+1=5

13. (a)The rejection co-efficient of an ultrafilter is denoted by R=\_\_\_\_\_

(b) What is the difference between crossflow and dead-end flow?

(c) "All membrane fouling are preceded by concentration polarization but all concentration polarization does not lead to membrane fouling" - justify 1+2+2=5

14. Explain the term HETP in case of distillation. Calculate the equilibrium compositions of the liquid & the vapor phases for a mixture of CH<sub>3</sub>OH & H<sub>2</sub>O at 50°C & under a pressure of 40kPa . ( $P^0_{CH3OH}$  =53.32,  $P^0_{H2O}$  =12.33 kPa at 50°C) (2+3)

# GROUP C

Long answer type questions (LQ) (answer any three) 15 X3=45

(5x3=15)

15. Write short notes on any three:

(a) Membrane fouling

(b) Dialysis

(c) Drum drier

(d) Spray Drier

(e) Rotary Drier

16. a) What is Overall & Murphree plate efficiency of a distillation column?

b) Define the term polarization modulus.

c) In respect of membrane separation explain the term MWCO.

d) A limitation to the use of membrane separation process is membrane fouling-explain.

e) A material is to be drier from 16% moisture by weight (wet basis) to 0.5% by circulation of hot air. The fresh air contains 0.02 kg of water/kg of dry air. Find the volume of fresh air required if 1000kg/hr of dried material is top be produced. The exit humidity of air is 0.09 kg of water/kg of dry air. The air enters at 30C & atm pressure. 3+2+3+4+3

17. A hollow fiber permeator with  $d_0$ =300m &  $d_i$ =200m gives a water flux of 10 gal/day-ft<sup>2</sup> with 0.1M NaCl solution at 20C & the salt rejection is 97%. Feed solution flows to the fibers at an average superficial velocity of 0.5cm/s.

(a) Is concentration polarization significant?

(b) For this permeator estimate the exit velocity & the pressure drop within the fibers if the fiber length is  $3m \& average flux is 10 gal/day-ft^2 based on external area.$ 

© What is the pressure drop if fibers are open at both ends? 5+5+5.

18. Derive the equation for the operating line of the rectifying section of a distillation column. Discuss the method of calculation of number of theoretical plates and location of feed plate by McCabe –Thiele method.
 (7+8)

19. (a) Describe the triangular diagram in case of ternary liquid-liquid extraction system.

(b) A continuous fractionation column has been installed to distill 30,000 kg/hr of a mixture of 40 % benzene and 60% toluene. The overhead and bottom products are found to contain 97% benzene and 96% toluene respectively. The feed consists of 3/4<sup>th</sup> vapour and ¼ th liquid. A reflux ratio of 1.5 times the minimum had been used. Determine the number of theoretical plates required using McCabe-Thiele method. All the data for benzene-toluene system: (mm graph paper is required)

Х	0	0.20	0.40	0.60	0.80	1.0
Y	0	0.38	0.61	0.78	0.98	1.0

# (5+10)

20. Describe how minimum reflux ratio can be calculated graphically

A mixture of Benzene and Toluene containing 40 mol % of Benzene is to be separated to give a product of 90 mol% of Benzene at top and a bottom product with not more than 10 mol % of Benzene. Using an average value of 2.4 for the volatility of Benzene relative to toluene, calculate the number of theoretical plates required at total reflux. Also calculate the minimum reflux ratio. (5+10)

21. a) Derive the expression of no. of theoretical stages for liquid-liquid extraction in case of cocurrent contact with immiscible solvents.

100kg/h of a nicotine-water solution containing 0.01 wt. fraction nicotine is extracted with 150kg/h of kerosene containing 0.0006 wt. fraction nicotine in counter current stage column. The concentration of nicotine is 0.001 wt. fraction in the exit water. Determine the no. of theoretical stages required for the above separation.

The equilibrium data for the above system is as follows:

X= kg of nicotine/kg of water	0.001	0.0025	0.005	0.0075	0.0099	0.20
Y= kg of nicotine/kg of kerose	ne 0.00058	0.0019	0.0046	0.0069	0.0091	0.19
			5+10 (mm graph paper required)			

22. a) Define the terms free and bound moisture content.

b) A continuous counter current drier is used to dry 425.6 kg dry solid/h containing 0.035 kg total moisture/kg dry solid to a value of 0.0017 kg total moisture / kg dry solid. The granular solid enters at 25°C & leaves at 60°C. The heating medium is air which enters at 84.2°C, has a humidity of 0.0175 kg water/kg dry air & leaves at 32.8°C. Calculate the air flow rate & the outlet humidity, assuming the heat losses from the dryer to be 9300KJ/h.

(The constant heat capacity of dry solid is 1.465 KJ/kg-K) 3+12

23. a) What do you understand by interphase mass transfer?

b) Derive the expression for the height of a packed absorption tower based on the

condition of liquid film.

c) Ammonia gas (A) diffuses through nitrogen gas under steady state conditions with nitrogen nondiffusing. The total pressure is  $1.013 \times 10^5$  Pa & the temperature is 298K. The diffusion path is 0.15m. The partial pressure of ammonia at point 1 & 2 is  $1.5 \times 10^5$  Pa &  $5 \times 10^3$ Pa respectively. The diffusivity for the mixture at the said temperature & pressure is  $2.30 \times 10^{-5}$  m<sup>2</sup>/s. Calculate the flux of ammonia & the equimolar counter diffusion flux, assuming nitrogen also diffuses. 3+5+7

24. (a)What is the basic difference between absorption and stripping process.

(b) Write notes on choice of solvent for absorption process.

(c) Light oil is being absorbed from a mixture light oil vapour and air by means of a non volatile absorption oil. The absorber is of the plate and bubble cap type. The lean oil entering the absorber contains 0.5% by weight of light oil leaving the absorber contains5% by weight of the light oil. The gas entering the absorber contains 2.25% by volume of light oil and the scrubbed gas leaves the absorber containing 0.18% of light oil by volume. The molecular weight of is 80. The average molecular weight of air is 29.0.

The equilibrium curve for absorbing ,oil-light oil mixture at the temperature of operation is represented by the equation

Yi =0.65 Xi

Yi=kg of light oil per kg of light oil free air

Xi=kg of light oilper kg of light oil free absorption oil

Calculate (a) the kg of light oil free air to kg of light oil free absorption oil.

(b) the number of theoretical plates in the absorber. 2+3+10

