

Mass Transfer-I



BIJU PATNAIK UNIVERSITY OF TECHNOLOGY

ROURKELA, ODISHA, INDIA

LECTURER NOTES

PCCH4302 **MASS TRANSFER - I** (3-0-0)

Module - I

Introduction to Mass transfer operations, molecular diffusion in fluids, binary solutions, Fick's law, equation of continuity, steady state equimolar counter current diffusion, Stefan's equation, diffusivity of gases and liquids, application of molecular diffusion, mass transfer coefficients, in laminar and turbulent flow, Film theory, Penetration theory, surface-renewal theories, analogy between mass, heat and momentum transfer.

Module – II

Principle of VLE for binary systems, phase diagrams, relative volatility, ideal solutions, azeotropes, enthalpy concentration diagrams, flash vaporization, partial condensation, differential distillation steam distillation, azeotropic and extractive distillation.

Continuous distillation: Mc Cabe - Thiele method, Ponchon - Savarit method, Tray efficiencies, introduction to multi component distillation.

Module - III

Absorption : Solubility of gases in liquids, two components system, multi component system, ideal and non - ideal solutions, choice of solvent for absorption, single component absorption material balance, counter current multistage operations, dilute gas mixtures, non - isothermal operation, tray efficiency, continuous contact equipment, HETP, HTU, NTU concepts for single component absorption.

Module - IV

Humidification Operations : Definition of fundamental terms, Psychrometric charts, theory of adiabatic saturation and wet bulb temperature, Lewis relation, Gas liquid contact, Dehumidification, Adiabatic Humidification. Equipments: Natural Circulation, Natural draft, Mechanical draft, Spray tower, Spray chamber, Spray pond, Humidity Measurement: Direct chemical method, Hygrometer method, Sling psychrometer, Dew point method, Mirror method

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MODULE-I

1.1 INTRODUCTION TO MASS TRANSFER OPERATION

Mass transfer is a transport of components under a chemical potential gradient. The component moves to the direction of reducing concentration gradient. The transport occurs from a region of higher concentration to lower concentration. Equilibrium is reached when the gradient is zero. The transport or migration of one constituent from a region of higher concentration to that of a lower concentration is known as mass transfer. Mass transfer operations depend on molecules diffusing from one distinct phase to another and are based upon differences in the physico-chemical properties of the molecules, such as vapour pressure or solubility. For interphase mass transfer, there is a concentration gradient between bulk and interface, however under steady state, at interface equilibrium is assumed. Mass transfer operation plays an important role in many industrial processes. A group of operations for separating the components of mixtures is based on the transfer of material from one homogeneous phase to another. These methods is covered by the term mass transfer operations which include techniques like gas absorption and stripping, liquid-liquid extraction, leaching, distillation, humidification, drying, crystallization and number of other separation techniques.

1.1.1 Absorption and stripping- Absorption refers to an operation in which the transfer of material is from a gas phase to a liquid phase. A gas is absorbed by means of liquid in which the solute gas is more or less soluble from its mixture with an inert gas as well as more or less insoluble gas. The liquid is essentially immiscible in the gas phase. The stripping is the separation of gas solute from the liquid phase. The separation of ammonia from an air-ammonia mixture by means of water is a typical example of absorption. The solute is then recovered from the solution by distillation. Depending upon situation, both the fluids (absorbent and absorbing fluid) are reprocessed and/or reused for the operation.

1.1.2 Adsorption and desorption –It exploits the ability of transfer of mass from either a gas or a liquid to the surface of a solid. The adsorption is not a true inter-phase mass transfer operation because the fluid adheres to the solid surface instead of dissolving in the solid. A desorption involves the transfer of mass from the solid surface (adsorbents) to the gas or liquid medium (adsorbates). A few operations of practical applications are (a) elimination of toxic gases and deodorization of air, (b) recovery of solvents, (c) removal of ions from solution, as in demineralization of water, (d) fractionation by selective adsorption of gases,

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vapours from gases, vapors from vapors and liquids from liquids and many other applications.

1.1.3 Extraction- It refers to a separation of the constituents of a liquid solution by contact with another insoluble liquid. The liquid which is added to the solution to bring about the extraction is known as the solvent. The solution which is to be extracted is called the feed. The solvent-rich product of the operation is called the extract and the residual liquid from which the solute is separated is called the raffinate. The separation of aromatics from kerosene based fuel oils, the production of fuels in the nuclear industry and the separation of penicillin from fermentation mixtures are examples of techniques of extraction.

1.1.4 Leaching- It is a treatment of a finely divided solid with a liquid. Some examples of leaching operations are oilseed extraction, extraction of sugar beets with hot water and extraction of medicinal compounds from plant roots, leaves and stems.

1.1.5 Distillation- It is an operation whereby a liquid mixture of miscible and volatile substances is separated into individual components or into group of components by partial vaporization. The separation of a mixture of methanol and water into its components, and separation of petroleum crude into gasoline, kerosene, fuel oil and lubricating stock are examples of distillation process.

1.1.6 Humidification and dehumidification- In humidification, the enrichment of vapour content in a gas stream takes place by passing the gas over a liquid. The transfer of water from the liquid phase to the gas phase of a mixture of air and water vapour is a widespread application of humidification. Dehumidification involves the transfer of water vapour from the gas phase to the liquid phase. Removal of water vapour from air by condensation of a cold surface and condensation of carbon tetrachloride out of a stream of nitrogen are examples of dehumidification.

1.1.7 Drying and Evaporation- Drying refers to removal of relatively small amount of water or other liquid from a solid material whereas evaporation refers to the removal of relatively large amount of water from solutions. In evaporation the water is removed as vapour at its boiling point. Drying involves the removal of water at temperature below the boiling point by circulating air or some other carrier gas over the material.

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1.2 CONCENTRATIONS AND FLUX

1.2.1 Concentrations The concentration of particular species is expressed in variety of ways. In mass transfer operation, the concentration gradient is the driving force when other driving forces (temperature, pressure gradients, etc.) are kept constant. The actual driving force for mass transfer to occur is to create gradient of chemical potential (between two points) which is a function of all external forces. The concentration gradients are generally expressed in terms of mass concentration of component, molar concentration of component and mass or mole fraction of species.

Mass concentration

The mass concentration of species i is expressed as ρ_i . It is defined as the mass of i per unit volume of a multi-component mixture; that is:

$$\rho_i = \frac{m_i}{V} \quad (1.1)$$

It has the same unit as density. Total mass concentration within a mixture is equal to overall density which can be expressed as

$$\rho = \sum_{i=1}^n \rho_i \quad (1.2)$$

where n is the number of species in the mixture.

Mass fraction

The mass fraction of species i is defined by the ratio of mass concentration of species i to the total mass density. It can be expressed as:

$$w_i = \frac{\rho_i}{\sum_i \rho_i} = \frac{\rho_i}{\rho} \quad (1.3)$$

From Equations (1.2) and (1.3), it is shown that

$$\sum_{i=1}^n w_i = \sum_{i=1}^n \frac{\rho_i}{\rho} = 1 \quad (1.4)$$

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Molar Concentration

The molar concentration of component is denoted by C_i . It is defined as moles of i th component per unit volume of mixture. The total concentration in the system can be obtained by sum up all molar concentrations for all species which can be represented as

$$C = \sum_{i=1}^n C_i \quad (1.5)$$

Sometimes it is required to convert from mass to molar concentration. This can be accomplished by dividing the mass concentration of species i by the molar weight of that species. For an ideal gas mixture the molar concentration of species i can be obtained from the ideal gas law ($PV = nRT$) as

$$C_i = \frac{P_i}{RT} \quad (1.6)$$

where p_i is the partial pressure of species i in the mixture, T is the absolute temperature and R is the universal gas constant. So total concentration in the gaseous system can be represented by

$$C = \frac{1}{RT} \sum_{i=1}^n P_i = \frac{P_t}{RT} \quad (1.7)$$

where P_t is the total pressure of the system which is sum of partial pressures of all components.

Mole fraction

The mole fraction of species i is found by dividing the molar concentration of species i by total concentration in the system which is expressed as

$$x_i = \frac{C_i}{C} \quad \text{for liquid and solid} \quad (1.8)$$

and

$$y_i = \frac{P_i}{P_t} \quad \text{for gases} \quad (1.9)$$

If it is summed over all species, then one can get $\sum_i x_i = 1$ and $\sum_i y_i = 1$.

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1.2.2 Fluxes

The flux is defined as the rate of transport of species i per unit area in a direction normal to the transport. The flux is calculated with respect to a fixed reference frame. The molar flux of species i can be represented as

$$N_{i-mol} = C_i u_i \quad (1.10)$$

Here $N_{i-molar}$ is the molar flux of species i and u_i is the velocity of i with respect to a fixed reference frame. In the same fashion, a mass flux, N_{i-mass} can be represented as

$$N_{i-mass} = \rho_i u_i \quad (1.11)$$

The units of the molar and mass fluxes are moles/m².s and mass/m².s. Sometimes it is convenient to interpret the total flux of species i with respect to an arbitrary reference frame rather than a fixed set of reference frame. The molar flux of species i based on arbitrary reference velocity u_0 is denoted by J_{i-mol} which can be defined as

$$J_{i-mol} = C_i (u_i - u_0) \quad (1.12)$$

Similarly mass flux of species i based on arbitrary reference velocity u_0 is denoted by J_{i-mass} which can be expressed as

$$J_{i-mass} = \rho_i (u_i - u_0) \quad (1.13)$$

In a system, since several molecular species move with different average velocities, a frame of moving reference must be chosen. The important moving references are mass average, molar average and volume average velocities.

Mass-average velocity

The mass average velocity can be defined in terms of the mass concentration and the velocity of species i based on fixed axis. It is expressed as

$$U_{mass} = \frac{\sum_{i=1}^n \rho_i u_i}{\sum_{i=1}^n \rho_i} \quad (1.14)$$

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Molar average velocity

The molar average velocity can be expressed by the expression analogous to the mass average velocity. It can be represented by replacing mass concentration of species i , ρ_i with molar concentration of species i , C_i :

$$U_{mol} = \frac{\sum_{i=1}^n C_i u_i}{\sum_{i=1}^n C_i} \quad (1.15)$$

Volume average velocity

For experimental analysis the volume average velocity is important due to a fixed system of constant volume. The volume average velocity can be expressed by

$$U_{vol} = \sum_{i=1}^n \bar{v}_i C_i u_i \quad (1.16)$$

where \bar{v}_i is the partial molar volume of species i .

Relation between fluxes

One can obtain the molar flux of i expressed in Equation (1.12) with respect to the molar average velocity as

$$J_{i-mol} = C_i (u_i - U_{mol}) \quad (1.17)$$

Substituting the Equation (1.10) into the Equation (1.17) and rearranging gives

$$N_{i-mol} = J_{i-mol} + C_i U_{mol} \quad (1.18)$$

Again substituting the definition of molar average velocity defined in Equation (1.15) into the Equation (1.18) we get

$$N_{i-mol} = J_{i-mol} + C_i \frac{\sum_{i=1}^n C_i u_i}{\sum_{i=1}^n C_i} \quad (1.19)$$

Or

$$N_{i-mol} = J_{i-mol} + x_i \sum_{i=1}^n N_{i-mol} \quad (1.20)$$

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For binary system of component A and B, $\sum_{i=1}^{\infty} N_{i-mol} = N_A + N_B = N$. Therefore the

Equation (1.20) can be written for binary system as

$$N_{A-mol} = J_{A-mol} + x_A N \quad (1.21)$$

References:

1. Treybal, R. E., "Mass-Transfer Operations", 3rd Edition, McGraw-Hill, 1981
2. Geankoplis, C.J., "Transport Processes and Separation Process Principles". 4th Edition, Prentice-Hall of India, New Delhi, 2005.
3. Dutta, B.K., "Principles of Mass transfer and Separation Processes". Prentice-Hall of India, New Delhi, 2007.

DIFFUSION

2.1 FICK'S LAW OF DIFFUSION

2.1.1 First law of diffusion (Steady state Law)

Adolf Fick (1955) first described the molecular diffusion in an isothermal, isobaric binary system of components A and B. According to his idea of molecular diffusion, the molar flux of a species relative to an observer moving with molar average velocity is proportional to the concentration gradient in a certain direction.

$$J_A \propto \frac{dC_A}{dZ} \quad (2.1)$$

Or

$$J_A = -D_{AB} \frac{dC_A}{dZ} \quad (2.2)$$

Where, J_A is the molar flux of component A in the Z direction. C_A is the concentration of A and Z is the distance of diffusion. The proportionality constant, D_{AB} is the diffusion coefficient of the molecule A in B. This is valid only at steady state condition of diffusion. The Equation (2.2) is called Fick's first law of diffusion. If the concentration gradient is expressed as the gradient of mole fraction and in three dimensional cases, the molar flux can be expressed as

$$J_A = -CD_{AB} \left(\frac{\partial x_A}{\partial x} + \frac{\partial x_A}{\partial y} + \frac{\partial x_A}{\partial Z} \right) \quad (2.3)$$

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2.1.2 Prove that mutual diffusivities of species A and B are equal if gas mixture is ideal when total pressure is constant.

Substituting the Equation (2.2) for J_A into Equation (1.21), the molar flux with negligible bulk movement of component A of the binary gas mixture can be represented as

$$N_A = -CD_{AB} \frac{dy_A}{dZ} + y_A N \quad (2.4)$$

Similarly for component B, it can be written as

$$N_B = -CD_{BA} \frac{dy_B}{dZ} + y_B N \quad (2.5)$$

Since $N_A + N_B = N$ and $y_A + y_B = 1$, addition of Equations (2.4) and (2.5) gives,

$$CD_{AB} \frac{dy_A}{dZ} = -CD_{BA} \frac{dy_B}{dZ} \quad (2.6)$$

Differentiation of the equality, $y_A + y_B = 1$ with respect to Z , gives

$$\frac{dy_A}{dZ} = -\frac{dy_B}{dZ} \quad (2.7)$$

Substituting the Equation (2.7) into Equation (2.6) one can get

$$D_{AB} = D_{BA} \quad (2.8)$$

From Equation (2.8) it is seen that for a binary gas mixture, the diffusivity of A in B equals the diffusivity of B in A.

2.1.3 Unsteady state Diffusion

If the change of concentration of a component A of the diffusive constituents in a mixture occurs over a time at a point, the Fick's law of diffusion at unsteady state condition can be expressed for Z-direction as

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial Z^2} \quad (2.9)$$

Both the diffusive and non-diffusive constituents affect the rate of unsteady state diffusion. The diffusivity at unsteady state condition can be expressed in terms of activation energy and the temperature as

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$$D_{AB} = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (2.10)$$

The activation energy (E_D) for the diffusion decreases the rate of diffusion whereas temperature increases the diffusion rate.

2.2 STEADY STATE MOLECULAR DIFFUSION IN FLUIDS UNDER STAGNANT AND LAMINAR FLOW CONDITIONS

2.2.1 Steady state diffusion through a constant area

(Steady state diffusion through a stagnant gas film)

Assume steady state diffusion in the Z direction without any chemical reaction in a binary gaseous mixture of species A and B. For one dimensional diffusion of species A, the Equation of molar flux can be written as

$$N_A = -CD_{AB} \frac{dy_A}{dZ} + y_A(N_A + N_B) \quad (2.11)$$

Separating the variables in Equation (2.11), it can be expressed as

$$\frac{-dy_A}{N_A - y_A(N_A + N_B)} = \frac{dZ}{CD_{AB}} \quad (2.12)$$

For the gaseous mixture, at constant pressure and temperature C and D_{AB} are constant, independent of position and composition. Also all the molar fluxes are constant in Equation (2.12). Therefore the Equation (2.12) can be integrated between two boundary conditions as follows:

$$\begin{array}{lll} \text{at} & Z = Z_1, & y_A = y_{A1} \\ \text{at} & Z = Z_2, & y_A = y_{A2} \end{array}$$

Where 1 indicates the start of the diffusion path and 2 indicates the end of the diffusion path. After integration with the above boundary conditions the Equation for diffusion for the said condition can be expressed as

$$N_A = \frac{N_A}{(N_A + N_B)} \frac{CD_{AB}}{Z_2 - Z_1} \ln \left[\frac{\frac{N_A}{(N_A + N_B)} - y_{A2}}{\frac{N_A}{(N_A + N_B)} - y_{A1}} \right] \quad (2.13)$$

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For steady state one dimensional diffusion of A through non-diffusing B, $N_B = 0$ and $N_A = \text{constant}$. Therefore $N_A / (N_A + N_B) = 1$. Hence Equation (2.13) becomes

$$N_A = \frac{CD_{AB}}{Z_2 - Z_1} \ln \left[\frac{1 - y_{A_2}}{1 - y_{A_1}} \right] \quad (2.14)$$

Since for an ideal gas $C = \frac{P}{RT}$ and for mixture of ideal gases $y_A = \frac{P_A}{P}$, the

Equation (2.14) can be expressed in terms of partial pressures as

$$N_A = \frac{PD_{AB}}{(Z_2 - Z_1)RT} \ln \left[\frac{P - p_{A_2}}{P - p_{A_1}} \right] \quad (2.15)$$

Where P is the total pressure and p_{A_1} and p_{A_2} are the partial pressures of A at point 1 and 2 respectively. For diffusion under turbulent conditions, the flux is usually calculated based on linear driving force. For this purpose the Equation (2.13) can be manipulated to rewrite it in terms of a linear driving force. Since for the binary gas mixture of total pressure P, $P - p_{A_2} = p_{B_2}$; $P - p_{A_1} = p_{B_1}$;

$p_{A_1} - p_{A_2} = p_{B_2} - p_{B_1}$. Then the Equation (2.15) can be written as

$$N_A = \frac{PD_{AB}}{(Z_2 - Z_1)RT} \left[\frac{p_{A_1} - p_{A_2}}{p_{B_2} - p_{B_1}} \right] \ln \left[\frac{p_{B_2}}{p_{B_1}} \right] \quad (2.16)$$

Or

$$N_A = \frac{PD_{AB}}{(Z_2 - Z_1)RT p_{B,M}} (p_{A_1} - p_{A_2}) \quad (2.17)$$

Where $p_{B,M}$ is called logarithmic mean partial pressure of species B which is defined as

$$p_{B,M} = \frac{p_{B_2} - p_{B_1}}{\ln \left(\frac{p_{B_2}}{p_{B_1}} \right)} \quad (2.18)$$

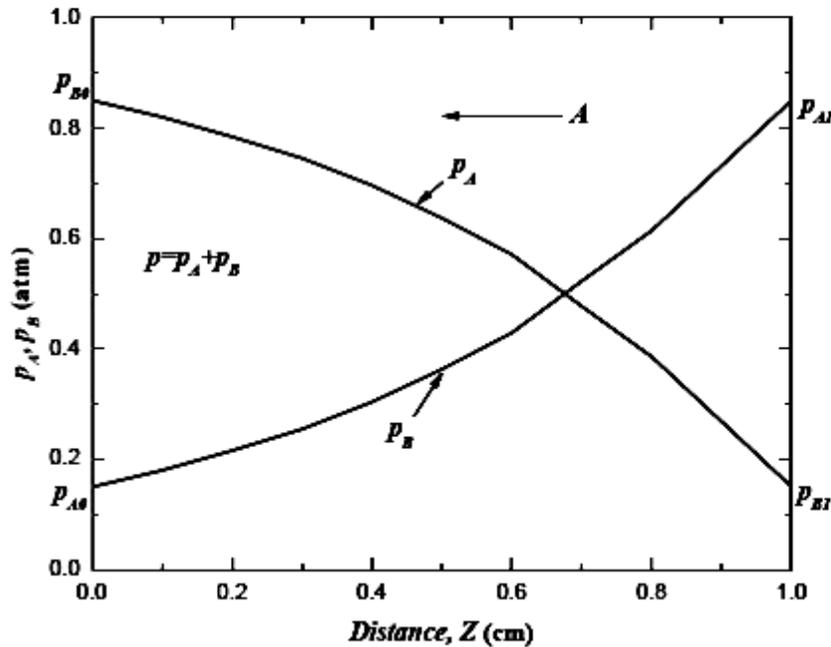
A schematic concentration profile for diffusion A through stagnant B is shown

in below. The component A diffuses by concentration gradient, $-\frac{dy_A}{dZ}$. Here flux

is inversely proportional to the distance through which diffusion occurs and the

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concentration of the stagnant gas ($p_{B,M}$) because with increase in Z and $p_{B,M}$, resistance increases and flux decreases.



Partial pressure distribution of A in non-diffusing B

2.2.2 Steady state equimolar counter diffusion:

This is the case for the diffusion of two ideal gases, where an equal number of moles of the gases diffusing counter-current to each other. In this case $N_B = -N_A = \text{constant}$ and $N_A + N_B = 0$. The molar flux Equation (Equation (2.11)) at steady state can then be written as

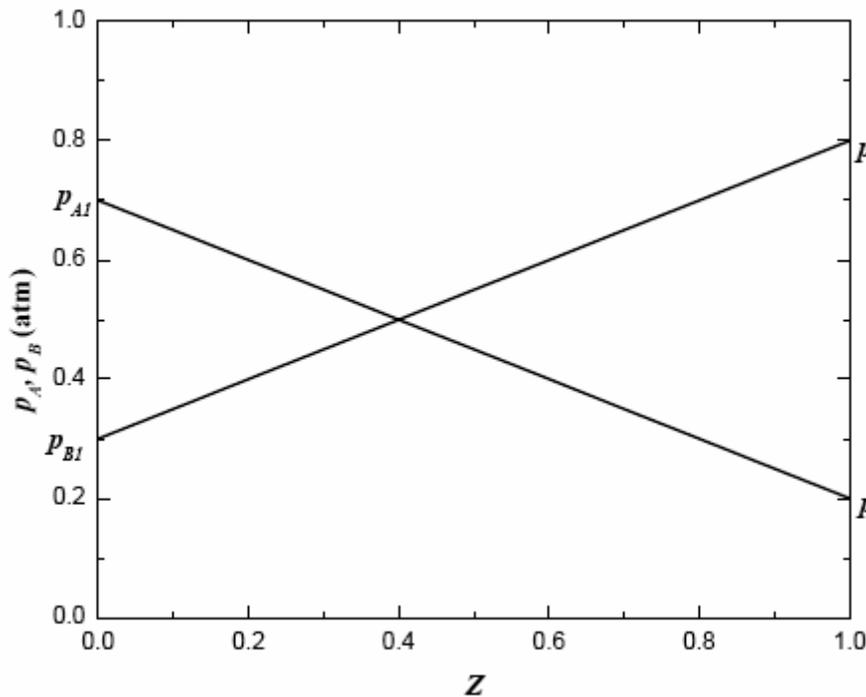
$$N_A = -\frac{D_{AB} P}{RT} \frac{dy_A}{dZ} \quad (2.19)$$

Integrating the Equation (2.19) with the boundary conditions: at $Z = Z_1$, $y_A = y_{A1}$; at $Z = Z_2$, $y_A = y_{A2}$, the Equation of molar diffusion for steady-state equimolar counter diffusion can be represented as

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$$\begin{aligned} N_A &= \frac{D_{AB}P}{RT(Z_2 - Z_1)} (y_{A_1} - y_{A_2}) \\ &= \frac{D_{AB}}{RT(Z_2 - Z_1)} (P_{A_1} - P_{A_2}) \end{aligned} \quad (2.20)$$

It may be noted here also that molar latent heats of vaporization of A and B are equal. So, $\Delta H_A^v = \Delta H_B^v$, where, ΔH_A^v and ΔH_B^v are molar latent heats of vaporization of A and B, respectively. The concentration profile in terms of partial pressure is shown in **bellow**.



Equimolar counter diffusion of A and B: Partial pressure distribution with position

2.2.3 Non-Equimolar counter diffusion

In some practical cases, A and B molecules diffuse in opposite directions at different molar velocities [1]. Let carbon monoxide is generated from the reaction between hot char and oxygen. The stoichiometry is as follows:

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When one mole oxygen molecule diffuses towards char, two moles carbon monoxide molecules diffuse in opposite direction. Here, $N_A = -N_B/2$ molar latent heats of vaporization are not equal.

$$N_A \Delta H_A^V = -N_B \Delta H_B^V \quad (2.22)$$

2.3 DIFFUSION COEFFICIENT: MEASUREMENT AND PREDICTION

The proportionality factor of Fick's law is called diffusivity or diffusion coefficient which can be defined as the ratio of the flux to its concentration gradient and its unit is m^2/s . It is a function of the temperature, pressure, nature and concentration of other constituents. Diffusivity decreases with increase in pressure ($D_{AB} \propto 1/p$ for moderate ranges of pressures, upto 25 atm) because number of collisions between species is less at lower pressure. But the diffusivity is hardly dependent on pressure in case of liquid. The diffusivity increases with increase in temperature ($D_{AB} \propto T^{1.5}$) because random thermal movement of molecules increases with increase in temperature. The diffusivity is generally higher for gases (in the range of 0.5×10^{-5} to $1.0 \times 10^{-5} m^2/s$) than for liquids (in the range of 10^{-10} to $10^{-9} m^2/s$). The diffusivity value reported for solids is higher in the range of 10^{-13} to $10^{-5} m^2/s$. Diffusion is almost impossible in solids because the particles are too closely packed and strongly held together with no 'empty space' for particles to move through. Solids diffuse much slower than liquids because intermolecular forces in solid are stronger enough to hold the solid molecules together.

2.3.1 Measurement of gas-phase diffusion coefficient

There are several methods of experimental determination of gas-phase diffusion coefficient. Two methods are (a) Twin-bulb method and (b) Stefan tube method. Predictive Equations are sometimes used to determine diffusivity. These may be empirical, theoretical or semi-empirical.

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(a) Twin-bulb method

Two large bulbs are connected by a narrow tube. The schematic diagram is shown in bellow. In the beginning two bulbs are evacuated and all the three valves [V1, V2 and V3] are kept closed. Then V2 is opened and bulb 1 is filled with pure A at a pressure P. After that V3 is opened and bulb 2 is filled with pure B at the same pressure P. At steady state

$$aN_A = \frac{aD_{AB}(p_{A1} - p_{A2})}{RTl} = -aN_B \quad (2.37)$$

where, a is cross sectional area of the connecting tube of length l . If p_{A1} and p_{A2} are partial pressures of A in two bulbs at any time,

$$-\frac{V1}{RT} \frac{dp_{A1}}{dt} = aN_A \quad (2.38)$$

$$\text{and } \frac{V2}{RT} \frac{dp_{A2}}{dt} = aN_A \quad (2.39)$$

From Equations (2.38) and (2.39) we have

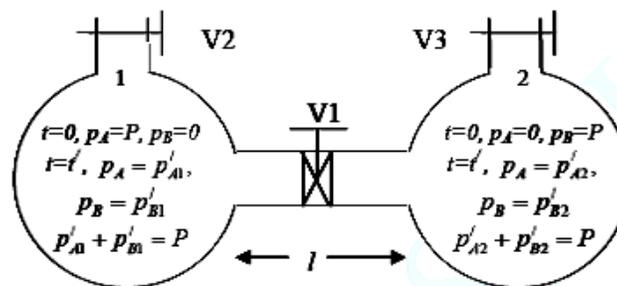
$$-\frac{d(p_{A1} - p_{A2})}{dt} = aN_A RT \left(\frac{1}{V1} - \frac{1}{V2} \right) \quad (2.40)$$

$$-\frac{d(p_{A1} - p_{A2})}{dt} = \frac{aD_{AB}(p_{A1} - p_{A2})}{l} \left(\frac{1}{V1} - \frac{1}{V2} \right) \quad (2.41)$$

Boundary conditions:

$$t=0; (p_{A1}-p_{A2}) = (P-0)=P$$

$$t=t', (p_{A1}-p_{A2}) = (p'_{A1} - p'_{A2})$$



Schematic of twin bulb apparatus.

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applying the above boundary conditions, Equation (2.41) is integrated to obtain the expression of D_{AB} as follows:

$$\ln \frac{P}{(p'_{A1} - p'_{A2})} = \frac{aD_{AB}}{l} \left(\frac{1}{V1} - \frac{1}{V2} \right) t' \quad (2.42)$$

(b) Stefan tube method

Stefan tube consists of a T tube made of glass, placed in a constant temperature water bath. Air pump is used to supply the air, passed through the T tube as shown below. So, Volatile component is filled in the T tube and air passed over it by the pump and change in the level is observed by the sliding microscope. Let, at any time t , partial pressure of A at the Z distance from the top of the vertical tube is p_{A1} and that at the top it is p_{A2} . The diffusional flux of A is given as:

$$N_A = \frac{D_{AB}P}{RTZ} \frac{(p_{A1} - p_{A2})}{p_{B,lm}} \quad (2.43)$$

The rate of evaporation is given by

$$N_A = \frac{\rho_A}{M_A} \frac{dZ}{dt} = \frac{D_{AB}P}{RTZ} \frac{(p_{A1} - p_{A2})}{p_{B,lm}} \quad (2.44)$$

Boundary conditions:

$$t=0; Z=Z_0$$

$$t=t'; Z=Z'$$

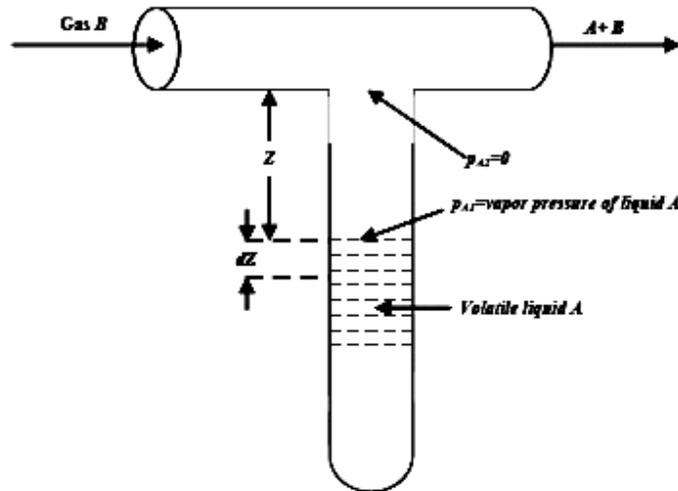
Integration of Equation (2.44) using the above boundary conditions gives,

$$D_{AB} = \frac{RTp_{B,lm}(Z'^2 - Z_0^2)}{2PM_A(p_{A1} - p_{A2})t'} \quad (2.45)$$

where, partial pressure of a at liquid surface, p_{A1} is equal to vapor pressure at the same temperature. The partial pressure of A at the top of the vertical tube, p_{A2} is zero due to high flow rate of B.

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where, partial pressure of a at liquid surface, p_{A1} is equal to vapor pressure at the same temperature. The partial pressure of A at the top of the vertical tube, p_{A2} is zero due to high flow rate of B.



Schematic representation of the Stefan tube

(c) Predictive Equations:

(I) Empirical: Fuller, Schettler and Giddings

$$D_{AB} = \frac{1.0133 \times 10^{-7} T^{1.75}}{P \left[(\sum v)_A^{1/2} + (\sum v)_B^{1/2} \right]^2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad (2.46)$$

where,

T is temperature in K

M_A, M_B are molecular weights of A and B

P is total pressure in bar

v_A, v_B are atomic diffusion volume in m^3 .

(II) Theoretical: Chapman-Enskog Equation

$$D_{AB} = \frac{1.858 \times 10^{-7} T^{1.5}}{P \sigma_{AB}^2 \Omega_D} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad (2.47)$$

where, σ_{AB} is characteristic length parameter of binary mixture in \AA , Ω_D is collision integral = $f(kT/\epsilon_{AB})$

$$\sigma_{AB} = \frac{(\sigma_A + \sigma_B)}{2} \text{ and } \epsilon_{AB} = (\epsilon_A + \epsilon_B)^{0.5} \quad (2.48)$$

2.4 MEASUREMENT OF LIQUID-PHASE DIFFUSION COEFFICIENT

There are few methods of determination of liquid-phase diffusivities. The most commonly used method is *Diaphragm cell method*.

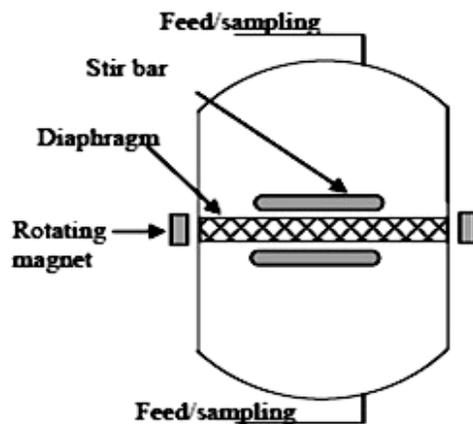
2.4.1 Diaphragm cell method

Diaphragm cell contains two compartments as shown in bellow. These are separated by diaphragm. Let the area of the diaphragm is 'a' and porosity is 'ε'.

Effective area for diffusion = $a \epsilon$

$$\tau = \frac{\text{average length of diffusion path}}{\text{diaphragm thickness}} \quad (2.49)$$

where τ is tortuosity. As the solute concentration is very low, bulk flow term can be taken as zero. Hence,



schematic diagram of **Diaphragm cell**

$$N_A = D_{AB} \frac{dC_A}{dZ} = D_{AB} \frac{(C_{A1} - C_{A2})}{l\tau} \quad (2.50)$$

$$-V_1 \frac{dC_{A1}}{dt} = a\epsilon N_A \quad (2.51)$$

$$\text{and } V_2 \frac{dC_{A2}}{dt} = a\epsilon N_A \quad (2.52)$$

Mass Transfer-I

Adding Equations (2.51) and (2.52) and substituting N_A from Equation (2.50) we have,

$$\frac{d(C_{A1} - C_{A2})}{dt} = \frac{a\epsilon D_{AB}(C_{A1} - C_{A2})}{l\tau} \left[\frac{1}{V_1} + \frac{1}{V_2} \right] \quad (2.53)$$

Boundary conditions

$$t=0, C_{A1}=C_{A1,0}, C_{A2}=C_{A2,0}$$

$$t=t_f, C_{A1}=C_{A1,f}, C_{A2}=C_{A2,f}$$

$$\text{Therefore, } D_{AB} = \frac{l\tau}{a\epsilon t_f} \left[\frac{1}{V_1} + \frac{1}{V_2} \right]^{-1} \ln \left(\frac{C_{A1,0} - C_{A2,0}}{C_{A1,f} - C_{A2,f}} \right) \quad (2.54)$$

2.4.2 Semi-empirical Equation: Wilke-Chang Equation

$$D_{AB}^0 = \frac{1.173 \times 10^{-16} (\phi M_B)^{0.5} T}{\mu_B \nu_A^{0.6}} \text{ m}^2/\text{s} \quad (2.55)$$

where, D_{AB}^0 is diffusivity of solute A in solvent B, m^2/s , ϕ is association factor [for $\text{H}_2\text{O}=2.26$; $\text{MeOH}=1.9$; $\text{EtOH}=1.5$; non-associated solvent=1.0]; M_B is molecular weight of B; T is absolute temperature in K; μ_B is solution viscosity, $\text{kg}/\text{m}\cdot\text{s}$; ν_A is solute molar volume at normal boiling point, m^3/kmol [$\nu_A=0.0756 \text{ m}^3/\text{kmol}$ for H_2O as solvent].

2.4.3 Stokes-Einstein Equation

Liquid diffusivity varies linearly with absolute temperature and inversely proportional to viscosity of the medium. Hence,

$$\frac{D_{AB}\mu}{T} = \text{Constant} \quad (2.56)$$

3.1 MASS TRANSFER COEFFICIENT

3.1.1 Concepts of mass transfer coefficients

Movement of the bulk fluid particles in the turbulent condition is not yet thoroughly understood. For gases it is fairly well known as a molecular diffusion since it is described in terms of kinetic theory. The rate of mass transfer from the interface to the turbulent zone in the same manner can be useful for molecular diffusion. Thus the term CD_{AB}/Z of Equation (2.13) which is a characteristic of molecular diffusion is replaced by F . For binary solution,

$$N_A = \frac{N_A}{(N_A + N_B)} F \ln \left[\frac{\frac{N_A}{(N_A + N_B)} - y_{A2}}{\frac{N_A}{(N_A + N_B)} - y_{A1}} \right] \quad (3.1)$$

The term F is called mass transfer coefficient. The value of F depends on the local nature of the fluid motion. It is a local mass transfer coefficient defined for a particular location on the interface. Its variation depends on the effect of variation in concentrations y_{A1} and y_{A2} on the flux. In case of equimolar counter diffusion and transfer of one substance through stagnant another substance, special mass transfer coefficients are generally used which are defined as:

$$\text{Flux} = (\text{a coefficient}) (\text{concentration difference}) \quad (3.2)$$

How mass transfer rate is calculated when there is bulk motion (turbulent) in the medium? The answer will be addressed in this study. Convective mass transfer is of two types, namely, forced convection mass transfer and free convection mass transfer. The concept of mass transfer coefficient is to develop a simple and practically helpful approach to convective mass transfer problems. Mass transfer rate (W_A) is proportional to: (i) concentration driving force (ΔC_A) (ii) area of the contact between phases (a)

Mass Transfer-I

$$\text{Hence, } W_A \propto (\alpha \cdot \Delta X_A) \quad (3.3)$$

$$W_A = k_c \times a \times \Delta C_A \quad (3.4)$$

where k_c is proportionality constant, called mass transfer coefficient.

Mass transfer rate, W_A can also be expressed in terms of molar flux, N_A as:

$$W_A = a \times N_A = k_c \times a \times \Delta C_A \quad (3.5)$$

$$k_c = \frac{N_A}{\Delta C_A} \quad (3.6)$$

3.1.2 Types of mass transfer coefficients

- Mass transfer occurs in gas/liquid phase
- Choice of driving force (concentration, partial pressure, mole fraction)
- Diffusion of "A" through non-diffusing "B"/equimolar counter diffusion of "A" and "B".

Diffusion of A through non-diffusion B ($N_B=0$)

$$N_A = k_G(p_{A1} - p_{A2}) = k_Y(y_{A1} - y_{A2}) = k_C(C_{A1} - C_{A2}) \rightarrow \text{Gas phase} \quad (3.7)$$

$$N_A = k_X(x_{A1} - x_{A2}) = k_L(C_{A1} - C_{A2}) \rightarrow \text{Liquid phase} \quad (3.8)$$

Subscripts (1 and 2) refer two positions in a medium.

For gas phase diffusion we know,

$$N_A = \frac{D_{AB} P (p_{A1} - p_{A2})}{RT \delta \times p_{BM}} \quad (3.9)$$

where, $p_{BM} = \frac{(p_{B2} - p_{B1})}{\ln \frac{p_{B2}}{p_{B1}}}$ and " δ " is film thickness.

Equating Equation (3.7) and Equation (3.9),

$$k_G = \frac{D_{AB} P}{RT \delta \times p_{BM}} \quad (3.10)$$

Mass Transfer-I

Again,

$$N_A = \frac{D_{AB}P(p_{A1} - p_{A2})}{RT\delta \times p_{BM}} = \frac{D_{AB}P \times P(y_{A1} - y_{A2})}{RT\delta \times p_{BM}} \quad (3.11)$$

Equating Equation (3.7) and Equation (3.11),

$$k_y = \frac{D_{AB}P^2}{RT\delta \times p_{BM}} \quad (3.12)$$

Also,

$$N_A = \frac{D_{AB}P(p_{A1} - p_{A2})}{RT\delta \times p_{BM}} = \frac{D_{AB}P(C_{A1} - C_{A2})}{\delta \times p_{BM}} \quad (3.13)$$

Equating Equation (3.7) and Equation (3.13),

$$k_c = \frac{D_{AB}P}{\delta \times p_{BM}} \quad (3.14)$$

For liquid phase diffusion,

$$N_A = \frac{D_{AB}}{\delta \times x_{BM}} \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2}) \quad (3.15)$$

where, $x_{BM} = \frac{(x_{B2} - x_{B1})}{\ln \frac{x_{B2}}{x_{B1}}}$ and $\left(\frac{\rho}{M} \right)_{av}$ is average molar concentration.

Equating Equation (3.8) and Equation (3.15),

$$k_x = \frac{D_{AB}}{\delta \times x_{BM}} \left(\frac{\rho}{M} \right)_{av} \quad (3.16)$$

Also,

$$N_A = \frac{D_{AB}}{\delta \times x_{BM}} \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2}) = \frac{D_{AB}}{\delta \times x_{BM}} (C_{A1} - C_{A2}) \quad (3.17)$$

Equating Equation (3.8) and Equation (3.17),

$$k_L = \frac{D_{AB}}{\delta \times x_{BM}} \quad (3.18)$$

Conversions: $k_c = RT \times k_G$; $k_y = P \times k_G$; $k_x = \left(\frac{\rho}{M} \right)_{av} k_L$

Mass Transfer-I

Equimolar counter-diffusion of A and B ($N_A = -N_B$)

$$N_A = k'_G(p_{A1} - p_{A2}) = k'_y(y_{A1} - y_{A2}) = k'_c(C_{A1} - C_{A2}) \rightarrow \text{Gas phase} \quad (3.19)$$

$$N_A = k'_x(x_{A1} - x_{A2}) = k'_L(C_{A1} - C_{A2}) \rightarrow \text{Liquid phase} \quad (3.20)$$

For gas phase diffusion we know,

$$N_A = \frac{D_{AB}(p_{A1} - p_{A2})}{RT\delta} \quad (3.21)$$

Equating Equation (3.19) and Equation (3.21),

$$k'_G = \frac{D_{AB}}{RT\delta} \quad (3.22)$$

Again,

$$N_A = \frac{D_{AB}(p_{A1} - p_{A2})}{RT\delta} = \frac{D_{AB}P(y_{A1} - y_{A2})}{RT\delta} \quad (3.23)$$

Equating Equation (3.19) and Equation (3.23),

$$k'_y = \frac{D_{AB}P}{RT\delta} \quad (3.24)$$

Also,

$$N_A = \frac{D_{AB}(p_{A1} - p_{A2})}{RT\delta} = \frac{D_{AB}(C_{A1} - C_{A2})}{\delta} \quad (3.25)$$

$$\text{Equating Equation (3.19) and Equation (3.25), } k'_c = \frac{D_{AB}}{\delta} \quad (3.26)$$

For liquid phase diffusion the flux can be written as

$$N_A = \frac{D_{AB}}{\delta} \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2}) \quad (3.27)$$

$$\text{Equating Equation (3.20) and Equation (3.27), } k'_x = \frac{D_{AB}}{\delta} \left(\frac{\rho}{M} \right)_{av} \quad (3.28)$$

Mass Transfer-I

Also,

$$N_A = \frac{D_{AB}}{\delta} \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2}) = \frac{D_{AB}}{\delta} (C_{A1} - C_{A2}) \quad (3.29)$$

$$k_L' = \frac{D_{AB}}{\delta} \quad (3.30)$$

Equating Equation (3.8) and Equation (3.17),

$$\text{Conversions: } k_c' = RT \times k_G'; \quad k_y' = P \times k_G'; \quad k_x' = \left(\frac{\rho}{M} \right)_{av} \times k_L'$$

3.2 Mass transfer under laminar flow condition

Mass transfer coefficient does not play a big role in laminar flow condition as molecular diffusion exists there. In laminar flow regime, the average liquid phase mass transfer coefficient, $k_{L,av}$ is correlated with Sherwood number (Sh) and D_{AB} as follows:

$$k_{L,av} = 3.41 \frac{D_{AB}}{\delta} \quad (3.31)$$

$$Sh_{av} = \frac{k_{L,av} \delta}{D_{AB}} = 3.41 \quad (3.32)$$

3.3 Mass transfer under turbulent flow past solids

Mass transfer under flow past solid is a practically useful situation. Several theories have attempted to clarify the behavior of mass transfer coefficients. All the theories have some assumptions and some drawbacks. Hence, these are revised frequently. In turbulent flow medium, small fluid an element of different sizes, called **eddies**, move randomly. These eddies form, interact among others and disappear in the flow path. The total molar flux of a solute 'A' due to molecular diffusion and eddy diffusion, J_A is as follows:

Mass Transfer-I

$$J_A = -(D_{AB} + D_E) \frac{dC_A}{dZ} \quad (3.33)$$

where D_E is eddy diffusivity. Eddy diffusivity depends on intensity of local turbulence.

3.4 Correlation for convective mass transfer coefficient

In this section various correlations that are used to estimate the convective mass transfer coefficients for various cases are presented. The various correlations are generally formed in terms of different dimensionless groups associated with the mass transfer. The definitions of mostly useful dimensionless groups associated with the mass transfer are given in the Table as follows:

Dimensionless groups for mass transfer:

Name of dimensionless groups	Definition of group	Significance of group
Reynolds number (Re)	$\frac{\rho ul}{\mu}$	Ratio of inertia force to viscous force
Schmidt number (Sc)	$\frac{\mu}{\rho D_{AB}}$	Ratio of molecular diffusivity of momentum to molecular diffusivity of mass transfer
Sherwood number (Sh)	$\frac{k_g P_{BM} RTl}{PD_{AB}}, \frac{k_c P_{BM} l}{PD_{AB}},$ $\frac{k_c l}{D_{AB}}, \frac{k_y P_{BM} RTl}{PD_{AB}},$ etc.	Ratio of total mass transfer rate to mass transfer by molecular diffusion
Grashof number (Gr _D)	$\frac{gl^3 \rho \Delta \rho}{\mu^2}$	Ratio of product of buoyancy forces and inertia forces to

Continued next page

Mass Transfer-I

		square of viscous force
Peclet number (Pe_D)	$Re \cdot Sc, \frac{ul}{D_{AB}}$	Ratio of inertia forces to mass transfer by molecular diffusion
Stanton number (St_D)	$Sh/(Re \cdot Sc), Sh/Pe_D$	Ratio of total mass transfer rate to inertia forces

Correlations for mass transfer coefficient for different cases

Cases	Correlations for mass transfer coefficient
For a single sphere (natural convection)	<ul style="list-style-type: none"> • $Sh = Sh_{nc} + 0.347(Re Sc^{0.5})^{0.62}$ where $1 \leq Re \leq 3 \times 10^4$ and $0.6 \leq Sc \leq 3200$ • $Sh_{nc} = 2.0 + 0.569(Gr_D Sc)^{1/4}$ where $Gr_D Sc < 10^8$ • $Sh_{nc} = 2.0 + 0.0254(Gr_D Sc)^{1/3} Sc^{0.244}$ where $Gr_D Sc > 10^8$
For a single sphere (forced convection)	$Sh = 2.0 + 0.552 Re^{1/7} Sc^{1/3}$ Where $2 < Re < 12000$ and $0.6 < Sc < 2.7$
For flat plates	at laminar condition and $Re < 3 \times 10^5$ $Sh = 0.664 Re^{1/2} Sc^{1/3}$ at turbulent condition and $Re \geq 3 \times 10^5$ $Sh = 0.036 Re^{4/5} Sc^{1/3}$ For both laminar and turbulent condition $0.6 < Sc < 2500$

Continued in next page

Mass Transfer-I

For single cylinder	$\frac{k_G P}{G_m} = 0.281 \text{Re}^{-0.4} \text{Sc}^{-0.56}$ <p>where $400 < \text{Re} < 25000$ and $0.6 < \text{Sc} < 2.6$.</p>
Circular pipes	$\text{Sh} = 0.023 \text{Re}^{0.83} \text{Sc}^{0.44}$ <p>where $2.0 \times 10^3 < \text{Re} < 3.50 \times 10^3$ and $0.6 < \text{Sc} < 2.5$</p> $\text{Sh} = 0.023 \text{Re}^{0.83} \text{Sc}^{1/3}$ <p>where $0.4 \times 10^4 < \text{Re} < 7.0 \times 10^4$ and $0.6 < \text{Sc} < 3.0 \times 10^3$</p>
Packed and fluidized beds	$\text{St}_D \text{Sc}^{2/3} = \frac{0.010}{\varepsilon} + \frac{0.863 / \varepsilon}{\text{Re}^{0.58} - 0.483}$ <p>where $1 < \text{Re} < 2100$</p> $\text{St}_D = 1.17 \text{Re}^{-0.415} \text{Sc}^{-2/3}$ <p>where $10 < \text{Re} < 2500$.</p>
Hollow-fiber membrane module	$\text{Sh} = 1.62 \left(\text{Pe}_D \frac{d_i}{L} \right)^{1/3}$ <p>Where $\text{Re} (= d_i v \rho / \mu) < 2100$</p>

3.5 THEORIES OF MASS TRANSFER

Many theories are available to explain the behavior of mass transfer coefficient such as the film, penetration, surface renewal and others. The theories are based on both molecular and turbulent diffusion. The theories are explained in details in the following sections.

3.5.1 Film theory

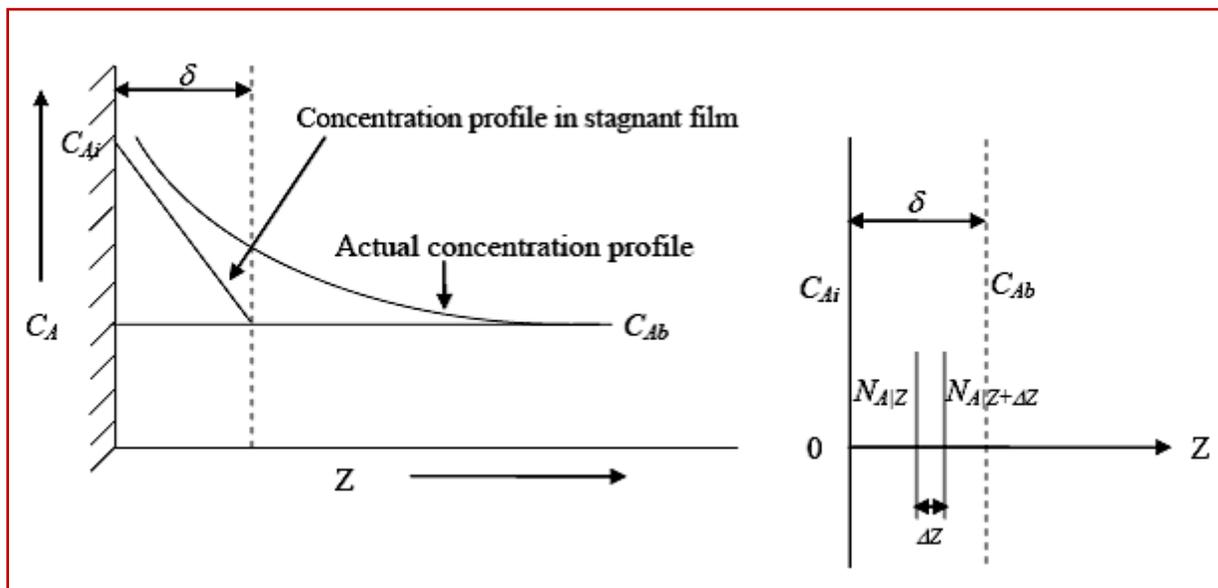
In case of one dimensional convective mass transfer, the concentration distribution is linear. The coefficient of mass transfer in this special case is proportional to the diffusion coefficient and inversely proportional to the film. This phenomenon is commonly known as the film theory. The schematic diagram of concentration

Mass Transfer-I

profile with stagnant film is shown in Figure below. The expression of mass transfer coefficient is developed theoretically by visualizing the mechanism. This is done by film theory. Film theory is based on the following assumptions:

- Mass transfer occurs by molecular diffusion through a fluid layer at phase boundary (solid wall). Beyond this film, concentration is homogeneous and is C_{Ab} .
- Mass transfer through the film occurs at steady state.
- Flux is low and mass transfer occurs at low concentration.

$$\text{Hence, } N_A = \frac{-D_{AB}dC_A}{dZ} \quad (3.51)$$



Schematic diagram of concentration profile with stagnant film.

Steady-state mass balance is done over an elementary volume of thickness ΔZ .

Rate of input of solute at $Z=N_A|z$

Rate of output of solute at $Z+\Delta Z=N_A|z+\Delta Z$

Rate of accumulation = 0 = (rate of input - rate of output)

Therefore, at steady state, $N_A|z - N_A|z+\Delta Z = 0$

Mass Transfer-I

$$\lim_{\Delta Z \rightarrow 0} \frac{N_A|_Z - N_A|_{Z+\Delta Z}}{\Delta Z} = 0 \quad (3.52)$$

$$\frac{dN_A}{dZ} = 0 \quad (3.53)$$

$$\frac{d}{dZ} \left(\frac{-D_{AB} dC_A}{dZ} \right) = 0 \quad (3.54)$$

$$\frac{-D_{AB} d^2 C_A}{dZ^2} = 0 \quad (3.55)$$

$$\frac{d^2 C_A}{dZ^2} = 0 \quad (3.56)$$

Integrating Equation (3.55) for the following boundary conditions:

$$C_A = C_{Ai} \text{ when } Z=0$$

$$C_A = C_{Ab} \text{ when } Z=\delta$$

We have now,

$$C_A = C_{Ai} - (C_{Ai} - C_{Ab}) \frac{Z}{\delta} \quad (3.57)$$

Hence, according to film theory, concentration profile in stagnant film is linear

Molar flux through film, N_A :

$$N_A = \left. \frac{-D_{AB} dC_A}{dZ} \right|_{Z=0}$$

$$N_A = \frac{D_{AB}(C_{Ai} - C_{Ab})}{\delta} \quad (3.58)$$

Now comparing Equation (3.58) with Equation (3.8),

$$k_L = \frac{D_{AB}}{\delta} \quad (3.59)$$

Film theory is useful in the analysis of mass transfer with chemical reaction. For turbulent flow, the mass transfer coefficient has much smaller dependency compared to laminar flow. In the turbulent flow, the mass transfer coefficient is proportional to D_{AB}^n where n may be zero to 0.9, depending upon the operating conditions. Although the film theory offers some explanation of the mechanism of

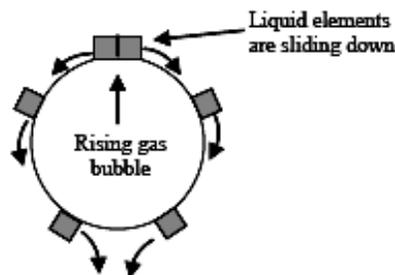
Mass Transfer-I

mass transfer in fluid media, it does not explain the estimation thickness of the film. Due to this disadvantage, application of the model is restricted to mass transfer in a diffusion cell.

3.5.2 Penetration theory

Most of the industrial processes of mass transfer is unsteady state process. In such cases, the contact time between phases is too short to achieve a stationary state. This non stationary phenomenon is not generally taken into account by the film model. In the absorption of gases from bubbles or absorption by wetted-wall columns, the mass transfer surface is formed instantaneously and transient diffusion of the material takes place. Figure shown below demonstrates the schematic of penetration model. *Basic assumptions of the penetration theory are as follows:*

- 1) Unsteady state mass transfer occurs to a liquid element so long it is in contact with the bubbles or other phase
- 2) Equilibrium exists at gas-liquid interface
- 3) Each of liquid elements stays in contact with the gas for same period of time



Schematic of penetration model.

Mass Transfer-I

Under these circumstances, the convective terms in the diffusion can be neglected and the unsteady state mass transfer of gas (penetration) to the liquid element can be written as:

$$\frac{\partial c}{\partial t} = D_{AB} \frac{\partial^2 c}{\partial Z^2} \quad (3.60)$$

The boundary conditions are: $t = 0, Z > 0 : c = c_{Ab}$ and $t > 0, Z = 0 : c = c_{Ai}$.

The term c_{Ab} is the concentration of solute at infinite distance from the surface and c_{Ai} is the concentration of solute at the surface. The solution of the partial differential equation for the above boundary conditions is given by the following equation:

$$\frac{c_{Ai} - c}{c_{Ai} - c_{Ab}} = \text{erf}\left(\frac{Z}{2\sqrt{D_{AB}t}}\right) \quad (3.61)$$

Where erf(x) is the error function defined by

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-Z^2) dZ \quad (3.62)$$

If the process of mass transfer is a unidirectional diffusion and the surface concentration is very low ($c_{Ab} \sim 0$), the mass flux of component A, N_A [$\text{kg m}^{-2} \text{s}^{-1}$], can be estimated by the following equation:

$$N_A = \frac{-\rho D_{AB}}{1 - c_{Ab}} \left(\frac{\partial c}{\partial Z}\right)_{Z=0} \approx -\rho \left(\frac{\partial c}{\partial Z}\right)_{Z=0} \quad (3.63)$$

Substituting Equation (3.61) into Equation (3.63), the rate of mass transfer at time t is given by the following equation:

$$N_A(t) = \rho \sqrt{\frac{D_{AB}}{\pi t}} (c_{Ai} - c_{Ab}) \quad (3.64)$$

Then the mass transfer coefficient is given by

$$k_L(t) = \sqrt{\frac{D_{AB}}{\pi t}} \quad (3.65)$$

The average mass transfer coefficient during a time interval t_c is then obtained by integrating Equation (3.61) as

Mass Transfer-I

$$\bar{k}_{L,av} = \frac{1}{t_c} \int_0^{t_c} k(t) dt = 2 \sqrt{\frac{D_{AB}}{\pi t_c}} \quad (3.66)$$

So from the above equation, the mass transfer coefficient is proportional to the square root of the diffusivity. This was first proposed by R. Higbie in 1935 and the theory is called Higbie's penetration theory.

3.5.3 Surface Renewal Theory

For the mass transfer in liquid phase, Danckwert (1951) modified the Higbie's penetration theory. He stated that a portion of the mass transfer surface is replaced with a new surface by the motion of eddies near the surface and proposed the following assumptions:

- 1) The liquid elements at the interface are being randomly swapped by fresh elements from bulk
- 2) At any moment, each of the liquid elements at the surface has the same probability of being substituted by fresh element
- 3) Unsteady state mass transfer takes place to an element during its stay at the interface.

Hence, average molar flux, $N_{A,av}$

$$N_{A,av} = (C_{A,i} - C_{A,b}) \sqrt{s \times D_{AB}} \quad (3.67)$$

Comparing Equation (3.67) with Equation (3.8) we get

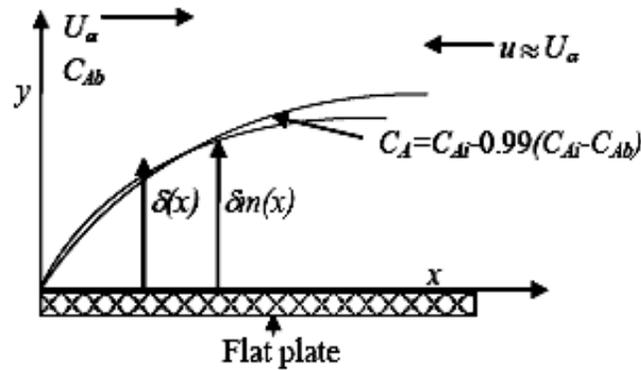
$$k_{L,av} = \sqrt{s \times D_{AB}} \quad (3.68)$$

where s is fraction of the surface renewed in unit time, i.e., the rate of surface renewal [s^{-1}].

3.5.4 Boundary Layer Theory

Boundary layer theory takes into account the hydrodynamics/flow field that characterizes a system and gives a realistic picture of the way mass transfer at a phase boundary. A schematic of concentration boundary layer is shown in Figure below.

Mass Transfer-I



Schematic of concentration boundary layer.

When $\delta = \delta(x) \rightarrow u = U_\alpha$ and when $\delta = \delta_m(x) \rightarrow u = 0.99U_\alpha$ distance over which solute concentration drops by 99% of $(C_{Ai} - C_{Ab})$.

$$Sh_x = \frac{x k_{L,x}}{D_{AB}} = 0.332(Re)^{0.5} (Sc)^{0.33} \quad (3.69)$$

where, x is the distance of a point from the leading edge of the plate; $k_{L,x}$ is the local mass transfer coefficient.

$$Sh_{av} = \frac{l k_{L,x}}{D_{AB}} = 0.664(Re)^{0.5} (Sc)^{0.33} \quad (3.70)$$

where, l is the length of the plate.

3.6.1 Overall mass transfer coefficients:

Experimentally the mass transfer film coefficients k_y and k_x are difficult to measure except for cases where the concentration difference across one phase is small and can be neglected. Under these circumstances, the overall mass transfer coefficients K_y and K_x are measured on the basis of the gas phase or the liquid phase. The entire two-phase mass transfer effect can then be measured in terms of gas phase molar fraction driving force as:

Mass Transfer-I

$$N_A = K_y(y_{AG} - y_A^*) \quad (3.76)$$

where, K_y is based on the overall driving force for the gas phase, in mole/m².s and y_A^* is the value of concentration in the gas phase that would be in the equilibrium with x_{AL} . Similarly, the entire two-phase mass transfer effect can then be measured in terms of liquid phase molar fraction driving force as:

$$N_A = K_x(x_A^* - x_{AL}) \quad (3.77)$$

where K_x is based on the overall driving force for the liquid phase, in mole/m².s and x_A^* is the value of concentration in the liquid phase that would be in the equilibrium with y_{AG} . A relation between the overall coefficients and the individual mass transfer film coefficients can be obtained when the equilibrium relation is linear as $y_{Ai} = mx_{Ai}$. The linear equilibrium condition can be obtained at the low concentrations, where Henry's law is applicable. Here the proportionality constant m is defined as $m = H/P$. Utilizing the relationship, $y_{Ai} = mx_{Ai}$, gas and liquid phase concentrations can be related by

Mass Transfer-I

$$y_A^* = mx_{AL} \quad (3.78)$$

and

$$y_{AG} = mx_A^* \quad (3.79)$$

Rearranging Equation (3.76), one can get

$$\frac{1}{K_y} = \frac{y_{AG} - y_A^*}{N_A} \quad (3.80)$$

From geometry, $y_{AG} - y_A^*$ can be written as

$$y_{AG} - y_A^* = (y_{AG} - y_{Ai}) + (y_{Ai} - y_A^*) \quad (3.81)$$

Substituting Equation (3.81) in Equation (3.80)

$$\frac{1}{K_y} = \frac{y_{AG} - y_A^*}{N_A} = \frac{(y_{AG} - y_{Ai})}{N_A} + \frac{(y_{Ai} - y_A^*)}{N_A} = \frac{(y_{AG} - y_{Ai})}{N_A} + \frac{m(x_{Ai} - x_{AL})}{N_A} \quad (3.82)$$

The substitution of Equation (3.76) into the Equation (3.82) relates overall gas phase mass transfer coefficient (K_y) to the individual film coefficients by

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{m}{k_x} \quad (3.83)$$

Similarly the relation of overall liquid phase mass transfer coefficient (K_x) to the individual film coefficients can be derived as follows:

$$\frac{1}{K_x} = \frac{x_A^* - x_{AL}}{N_A} = \frac{y_{AG} - y_{Ai}}{mN_A} + \frac{x_{Ai} - x_{AL}}{N_A} \quad (3.84)$$

Or

$$\frac{1}{K_x} = \frac{1}{mk_y} + \frac{1}{k_x} \quad (3.85)$$

The following relationships between the mass transfer resistances can be made from the Equations (3.83) and (3.85):

$$\frac{\text{Resistance in gas phase}}{\text{Total resistance in both phases}} = \frac{1/k_y}{1/K_y} \quad (3.86)$$

$$\frac{\text{Resistance in liquid phase}}{\text{Total resistance in both phases}} = \frac{1/k_x}{1/K_x} \quad (3.87)$$

Mass Transfer-I

If solute A is very soluble in the liquid, m is very small. Then the term m/k_x in Equation (3.83) becomes minor and consequently the major resistance is represented by $1/k_y$. In this case, it is said that the rate of mass transfer is gas phase controlled. In the extreme it becomes:

$$\frac{1}{K_y} \approx \frac{1}{k_y} \quad (3.88)$$

The total resistance equals the gas film resistance. The absorption of a very soluble gas, such as ammonia in water is an example of this kind. Conversely when solute A is relatively insoluble in the liquid, m is very large. Consequently the first term of Equation (3.85) becomes minor and the major resistance to the mass transfer resides within the liquid. The system becomes liquid film controlling. Finally this becomes:

$$\frac{1}{K_x} \approx \frac{1}{k_x} \quad (3.89)$$

The total resistance equals the liquid film resistance. The absorption of a gas of low solubility, such as carbon dioxide or oxygen in water is of this type of system.

3.7 ANALOGIES AMONG MASS, HEAT AND MOMENTUM TRANSFER

Analogies among mass, heat and momentum transfer have their origin either in the mathematical description of the effects or in the physical parameters used for quantitative description. To explore those analogies, it could be understood that the diffusion of mass and conduction of heat obey very similar equations. In particular, diffusion in one dimension is described by the Fick's Law as

$$J_A = -D_{AB} \frac{dC_A}{dz} \quad \text{-----} \quad (3.90)$$

Similarly, heat conduction is described by Fourier's law as

Mass Transfer-I

$$q = -k \frac{dT}{dz} \text{----- (3.91)}$$

Where k is the thermal conductivity.

The similar equation describing momentum transfer as given by Newton's law is

$$\tau = -\mu \frac{dv}{dz} \text{----- (3.92)}$$

Where τ is the momentum flux (or shear stress) and μ is the viscosity of fluid.

At this point it has become conventional to draw an analogy among mass, heat and momentum transfer. Each process uses a simple law combined with a mass or energy or momentum balance.

In this section, we will consider several analogies among transfer phenomenon which has been proposed because of the similarity in their mechanisms. The analogies are useful in understanding the transfer phenomena and as a satisfactory means for predicting behavior of systems for which limited quantitative data are available.

The similarity among the transfer phenomena and accordingly the existence of the analogies require that the following five conditions exist within the system

1. The physical properties are constant
2. There is no mass or energy produced within the system. This implies that there is no chemical reaction within the system
3. There is no emission or absorption of radiant energy.
4. There is no viscous dissipation of energy.
5. The velocity profile is not affected by the mass transfer. This implies there should be a low rate of mass transfer.

Mass Transfer-I

3.7.1 Reynolds Analogy

The first recognition of the analogous behaviour of mass, heat and momentum transfer was reported by Osborne Reynolds in 1874. Although his analogy is limited in application, it served as the base for seeking better analogies.

Reynolds postulated that the mechanisms for transfer of momentum, energy and mass are identical. Accordingly,

$$\frac{k_c}{v_\infty} = \frac{h}{\rho v_\infty C_p} = \frac{f}{2} \text{----- (3.93)}$$

Here h is heat transfer coefficient

f is friction factor

v_∞ is velocity of free stream

The Reynolds analogy is interesting because it suggests a very simple relation between different transport phenomena. This relation is found to be accurate when Prandtl and Schmidt numbers are equal to one. This is applicable for mass transfer by means of turbulent eddies in gases. In this situation, we can estimate mass transfer coefficients from heat transfer coefficients or from friction factors.

3.7.2 Chilton – Colburn Analogy

Because the Reynold's analogy was practically useful, many authors tried to extend it to liquids. Chilton and Colburn, using experimental data, sought modifications to the Reynold's analogy that would not have the restrictions that Prandtl and Schmidt numbers must be equal to one. They defined for the j factor for mass transfer as

$$j_D = \frac{k_c}{v_\infty} (Sc)^{2/3} \text{----- (3.94)}$$

The analogous j factor for heat transfer is

Mass Transfer-I

$$j_H = St Pr^{2/3} \text{ ----- (3.95)}$$

$$\text{where St is Stanton number} = \frac{Nu}{Re Pr} = \frac{h}{\rho g_\infty C_p}$$

Based on data collected in both laminar and turbulent flow regimes, they found

$$j_D = j_H = \frac{f}{2} \text{ ----- (3.96)}$$

This analogy is valid for gases and liquids within the range of $0.6 < Sc < 2500$ and $0.6 < Pr < 100$.

The Chilton-Colburn analogy has been observed to hold for much different geometry for example, flow over flat plates, flow in pipes, and flow around cylinders.

EXAMPLE.

A stream of air at 100 kPa pressure and 300 K is flowing on the top surface of a thin flat sheet of solid naphthalene of length 0.2 m with a velocity of 20 m/sec. The other data are: Mass diffusivity of naphthalene vapor in air = $6 * 10^{-6} \text{ m}^2/\text{sec}$

Kinematic viscosity of air = $1.5 * 10^{-5} \text{ m}^2/\text{sec}$ Concentration of naphthalene at the air-solid naphthalene interface = $1 * 10^{-5} \text{ kmol/m}^3$

Calculate:

- (a) The overage mass transfer coefficient over the flat plate?
- (b) The rate of loss of naphthalene from the surface per unit width?

Note: For heat transfer over a flat plate, convective heat transfer coefficient for laminar flow can be calculated by the equation.

$$Nu = 0.664 Re_L^{1/2} Pr^{1/3}$$

You may use analogy between mass and heat transfer.

Mass Transfer-I

Solution:

Given: Correlation for heat transfer

$$Nu = 0.664 Re_L^{1/2} Pr^{1/3}$$

The analogous relation for mass transfer is

$$Sh = 0.664 Re_L^{1/2} Sc^{1/3} \text{ ----- (1)}$$

Where

Sh = Sherwood number = kL/D_{AB}

Re_L = Reynolds number = $Lv\rho/\mu$

Sc = Schmidt number = $\mu / (\rho D_{AB})$

k = overall mass transfer coefficient

L = length of sheet

D_{AB} = diffusivity of A in B

v = velocity of air

μ = viscosity of air

ρ = density of air, and

μ/ρ = kinematic viscosity of air.

Substituting for the known quantities in equation (1)

$$\frac{k(0.2)}{6 * 10^{-6}} = 0.664 \left(\frac{(0.2)(20)}{1.5 * 10^{-5}} \right)^{1/2} \left(\frac{1.5 * 10^{-5}}{6 * 10^{-6}} \right)^{1/3}$$

$$k = 0.014 \text{ m/sec}$$

Rate of loss of naphthalene = $k (C_{Ai} - C_{A\infty})$

$$= 0.014 (1 * 10^{-5} - 0) = 1.4024 * 10^{-7} \text{ kmol/m}^2 \text{ sec}$$

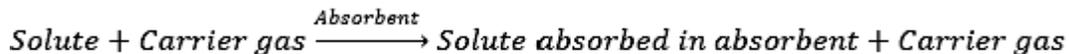
Rate of loss per meter width = $(1.4024 * 10^{-7}) (0.2) = 2.8048 * 10^{-8} \text{ kmol/m.sec}$

$$= 0.101 \text{ gmol/m.hr.}$$

Mass Transfer-I

MODULE: II **ABSORPTION**

GAS ABSORPTION: It is a mass transfer operation in which one or more gas solutes is removed by dissolution in a liquid. The inert gas in the gas mixture is called “carrier gas”. In the absorption process of ammonia from air-ammonia mixture by water, air is carrier gas, ammonia is “solute” and water is absorbent. An intimate contact between solute gas and absorbent liquid is achieved in suitable absorption equipment, namely, tray tower, packed column, spray tower, venture scrubber, etc. Desorption or stripping operation is the reverse of absorption. Absorption operation is of two types; physical and chemical.



1.1 EQUILIBRIUM SOLUBILITY OF GASES IN LIQUIDS

For the determination of driving force in any mass transfer operation, the solubility of a species in a solvent, i.e., equilibrium distribution between phases is important. With the increase in temperature, solubility of a gas in liquid decreases. Hence, absorption is done at lower temperature. On the contrary, desorption is done at higher temperature.

1.2 Selection of solvent for absorption and stripping

If the objective of absorption is separation of a particular component from a mixture, selection of absorbent plays a great role and when absorption operation is used to prepare a solution, solvent is selected according to final product. Few criteria for the selection of an absorbent are as follows:

(A) Gas Solubility: High solubility of a gas in the solvent is preferred, utilizing low quantity of solvent. Absorbent should not dissolve carrier gas. Similar chemical nature of solute and absorbent (solvent) gives a good solubility. If chemical reaction takes place between solute and solvent, rate of absorption is extremely high. But the reaction should be reversible to recover solvent during desorption.

(B) Volatility: Low volatility or low vapor pressure of the solvent enhances the adsorption operation as solvent loss with carrier gas is very small. Sometimes, a second less volatile solvent is used to recover the first solvent.

Mass Transfer-I

(C) Viscosity: For better absorption, a solvent of low viscosity is required. In mechanically agitated absorber, greater amount of power is required for high viscous solvent and flooding is also caused at lower liquid and gas flow rates.

(D) Corrosiveness: Non-corrosive or less corrosive solvent reduces equipment construction cost as well as maintenance cost.

(E) Cost: The solvent should be cheap so that losses will be insignificant and should be easily available.

(F) Toxicity and Hazard: The solvent should be non-toxic, non-flammable, non-hazardous and should be chemically stable.

1.3 Design of single stage counter-current flow absorption tower (packed tower)

Two common gas absorption equipments are packed tower and plate tower. Other absorption equipments are, namely, spray column, agitated contactor, venture scrubber, etc. The gas and the liquid phases come in contact in several discrete stages. Thus, a stage wise contact is there in a plate column. But in packed tower, the up-flowing gas remains in contact with down-flowing liquid throughout the packing, at every point of the tower. Therefore, packed tower is known as “continuous” differential contact equipment. It is different from the stage-wise distillation column. In the stage distillation column the equilibrium in each stage will vary not in a continuous fashion whereas in the packed column the equilibrium is changed point wise in each axial location.

Steps for the design of packed tower

- (A) Selection of solvent
- (B) Selection of packing
- (C) Calculation of minimum solvent flow rate as well as actual solvent flow rate
- (D) Column diameter
- (E) Height of column
- (F) Design of solvent distributors and redistributors (if needed)
- (G) Design of gas distributor, packing support, shell, nozzles, column support

(a) Equilibrium data; (b) gas and liquid flow rates; (c) solute concentration in two terminals; (d) individual and overall volumetric mass transfer coefficients should be known for the design of a packed absorption tower.

Mass Transfer-I

Packing Materials: Packing materials are utilized to provide large interfacial area of contact between two phases. These are made from either of ceramics, metals or plastics. A number of packing materials with various size, shape and performance are available. These are classified into three types, namely, **dumped or random, structured** and **grid**.

The packing materials have following characteristics:

(a) Cost: The cost of the packing materials should be very low.

(b) Surface area: A large interfacial area of contact is always recommended. In that case, pressure drop will be more.

(c) Void volume: A high void volume is needed to maintain low pressure drop.

(d) Fouling resistance: Packing materials should not trap suspended solids present in liquid. Bigger packing materials generally give low fouling resistance.

(e) Mechanical strength: Good mechanical strength is desired for choosing packing materials as this will not break or deform during filling or operation.

(f) Uniform flow of streams: Stack of packing materials should have uniform void spaces through which both the streams (gas and liquid) can flow uniformly. Non-uniform flow of streams leads to stagnant liquid pool which in turn gives low mass transfer.

(A) Dumped or random packing materials: Dumped or random packing materials are classified into three categories as first generation (1907 to mid 1950); second generation (mid 1950 to mid 1970) and third generation (mid 1970 to till date). The first generation random packing materials are of three categories, such as, (a) Raschig rings; (b) Lessing rings and modified Raschig rings and (c) Berl saddles. These are shown in Figure below.



(a) Raschig rings;



(b) Lessing rings and modified Raschig rings (Cross-partition rings)



(c) Berl saddle

First generation dumped or random packing materials

The second generation random packing materials are mainly (a) Intalox saddle and modification; (b) Pall ring and modification. Intalox saddle is the modified version of Berl saddle and offers less friction resistance due to particular shape (two saddles

Mass Transfer-I

will never nest). Pall rings are modified version of Raschig rings. These are shown in Figure below.



(a) Intalox saddle and modification (b) Pall ring and modification

Second generation dumped or random packing materials.

The third generation random packing materials are numeral; (a) Intalox Metal Tower Packing (IMTP); (b) Nutter ring; (c) Cascade Mini-Ring (CMR); (d) Jaeger Tripac; (e) Koch Flexisaddle; (f) Nor-Pac; (g) Hiflow ring, etc. These are shown in Figure below.



(a) Intalox Metal Tower Packing (IMTP)



(b) Nutter ring



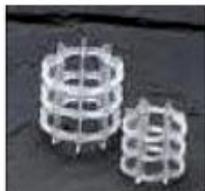
(c) Cascade Mini-Ring (CMR)



(d) Jaeger Tripac



(e) Koch Flexisaddle



(f) Nor-Pac



(g) Hiflow ring

Third generation dumped or random packing materials.

(B) Structured packing materials: These materials are used widely as packing materials in packed tower due to low gas pressure drop and improved efficiency. Corrugated metal sheet structured packing and Wire mesh structured packing

Mass Transfer-I

materials are widely used in the industries. These include Mellapak, Flexipak, Gempak, Montz and MaxPak. These are shown in Figure below.

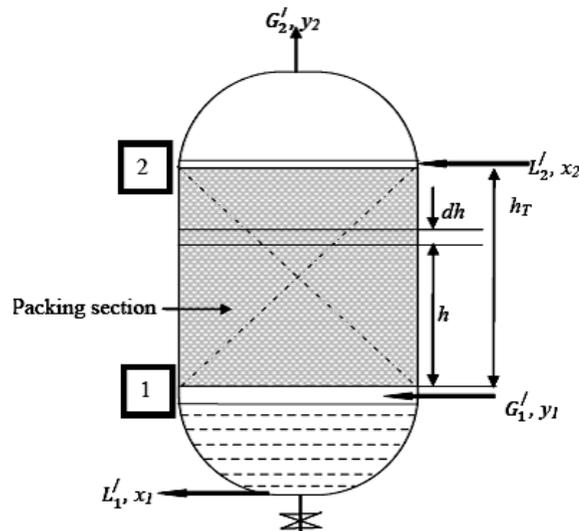


Snapshots of some structured packing materials.

(C) Grid packing materials: This packing material is used for high gas or vapor capacities at low pressure drop. Mellagrid series; Flexigrid series; Snap grid series are among these grids.

1.4 DESIGN OF PACKED TOWER:

The cross sectional view of the packed tower is shown in Figure below.



Cross sectional view of packed tower.

Design of packed tower may be

- (I) On the basis of individual mass transfer coefficients or
- (II) On the basis of overall mass transfer coefficient.

Mass Transfer-I

Let, G' and L' are gas and liquid flow rate per unit area basis, mol/h.m². \bar{a} is specific interfacial contact area between gas and liquid, m²/m³. The mole fraction of solute in gas is y .

Hence, solute flow rate in gas = $G'y$ mol/h.m²

The decrease in solute flow rate over the thickness

$$dh = d(G'y) \dots\dots\dots (4.1)$$

For a unit cross-sectional area (1m²), volume of differential section = $1 \times dh$ m³ and interfacial area of contact in differential section = $\bar{a} \times 1 \times dh$ m²

If N_A is solute flux and k_y is individual gas-phase mass transfer coefficient, solute transfer through differential section = $\bar{a} \times dh \times N_A$.

Therefore,

$$-[G'dy + y dG'] = \bar{a} \times dh \times N_A \dots\dots\dots (4.2)$$

$$-G'dy - y dG' = \bar{a} \times dh \times N_A \dots\dots\dots (4.3)$$

The change in total gas flow rate (dG') is equal to rate of solute transfer ($\bar{a} \times dh \times N_A$) as carrier gas is not soluble, i.e.,

$$-dG' = \bar{a} \times dh \times N_A \dots\dots\dots (4.4)$$

Putting the value of $-dG'$ in Equation -4.3, we have,

$$-G'dy + \bar{a} \times dh \times N_A y = \bar{a} \times dh \times N_A \dots\dots\dots (4.5)$$

Mass Transfer-I

$$-G'dy = \bar{a} \times dh \times N_A(1-y)$$

$$dh = -\frac{G'dy}{\bar{a}(1-y)N_A} = -\frac{G'dy}{\bar{a}(1-y)k_y(y-y_i)} \dots\dots\dots (4.6)$$

Boundary conditions: $h=0$; $y=y_1$ $h=h_T$; $y=y_2$ Integration of Equation -4.6 gives the height of packed column as follows:

$$h_T = \int_0^{h_T} dh = -\int_{y_1}^{y_2} \frac{G'dy}{\bar{a}(1-y)k_y(y-y_i)} = \int_{y_2}^{y_1} \frac{G'dy}{\bar{a}(1-y)k_y(y-y_i)} \dots\dots\dots (4.7)$$

Interfacial solute concentration, y_i is not known; hence the integration of the right hand side of Equation-4.7 is complicated.

STEP-BY-STEP PROCEDURE

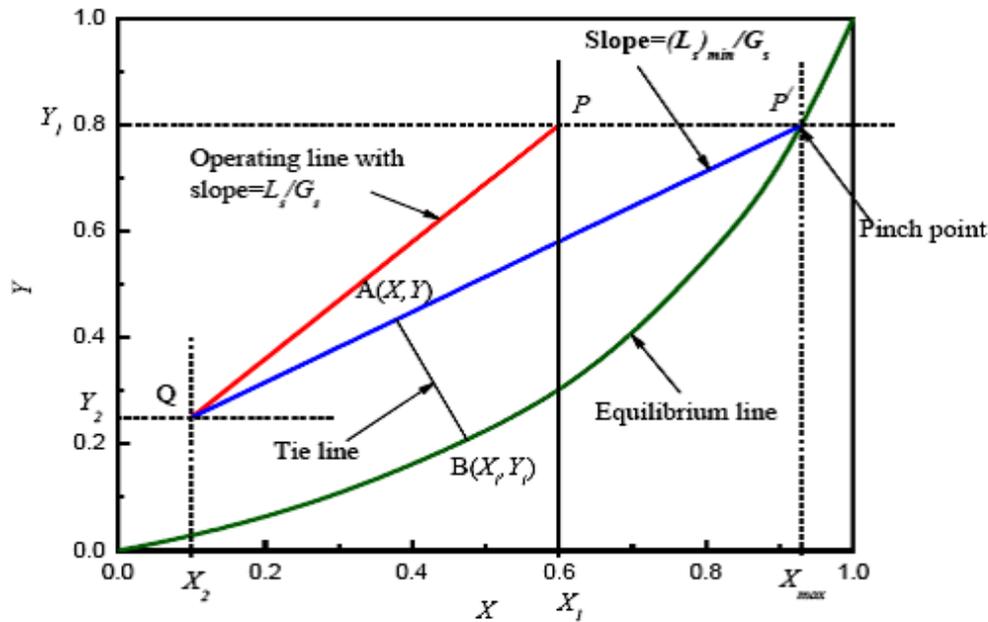
- (1) For a particular gas-liquid system, draw equilibrium curve on X-Y plane.
- (2) Draw operating line in X-Y plane (PQ) using material balance Equation. Lower terminal Q (X_2, Y_2) and upper terminal P (X_1, Y_1) are placed in x-y plane. Overall mass balance Equation for the absorption tower is as follows:

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

$$G_s \left(\frac{y_1}{1-y_1} - \frac{y_2}{1-y_2} \right) = L_s \left(\frac{x_1}{1-x_1} - \frac{x_2}{1-x_2} \right) \dots\dots\dots (4.8)$$

If liquid mass flow rate, L_s is not known, minimum liquid mass flow rate $(L_s)_{min}$ is to be determined. L_s is generally 1.2 to 2 times the $(L_s)_{min}$.

Mass Transfer-I



Graphical determination of $(L_s)_{min}$ for absorption.

In the above figure, lower terminal of absorption tower is represented by Q (X_2, Y_2); i.e., bottom of the tower. Operating line is PQ. If liquid rate is decreased, slope of operating line (L_s/G_s) also decreases and operating line shifts from PQ to P'Q when touches equilibrium line. This operating line is tangent to equilibrium line.

$$\text{Slope of } P'Q = \frac{(L_s)_{min}}{G_s}$$

The driving force for absorption is zero at P' and is called "PINCH POINT".

(3) A point A (x, y) is taken on the operating line. From the known value of k_x and k_y or $k_x\bar{a}$ and $k_y\bar{a}$, a line is drawn with slope of k_x/k_y to equilibrium line, B(x_i, y_i). Line AB is called "TIE LINE" and x_i and y_i are known for a set of values of x and y .

(4) Step (3) is repeated for other points in the operating line to get several (x_i, y_i) sets for $y_1 \geq y \geq y_2$.

(5) Calculate flow rate of gas G (kg/h) at each point as $G = G_s(1+y)$.

(6) Calculate height of the packing h_T of Equation-4.7 graphically or numerically. The height of the „stripping column“ is also obtained in a similar way. For stripping, $y_2 > y_1$ and driving force is $(y_i - y)$. The corresponding design Equation will be

Mass Transfer-I

$$h_T = \int_{y_1}^{y_2} \frac{G' dy}{\bar{a}(1-y)k_y(y_i - y)} \dots\dots\dots(4.9)$$

1.5. Design of packed tower based on overall mass transfer coefficient

From overall mass transfer equation, $N_A = K_y(y_{AG} - y_A^*)$ one can write for packed tower as

$$N_A = K_y(y - y^*)$$

Then,

$$dh = - \frac{G' dy}{K_y \bar{a}(1-y)(y - y^*)} \tag{4.10}$$

where, y^* is solute concentration in gas phase that is capable of remaining in equilibrium with a liquid having a bulk concentration of x .

Therefore,

where, y^* is solute concentration in gas phase that is capable of remaining in equilibrium with a liquid having a bulk concentration of x .

Therefore,

$$\begin{aligned} h_T &= \int_0^{h_T} dh = \int_{y_2}^{y_1} \frac{G' dy}{K_y \bar{a}(1-y)(y - y^*)} \\ &= \int_{y_2}^{y_1} \frac{G' dy}{k_G \bar{a} P(1-y)(y - y_i)} \\ &= \int_{x_2}^{x_1} \frac{L' dx}{k_L \bar{a}(C_{av})(1-x)(x_i - x)} \end{aligned} \tag{4.11}$$

Graphical integration of right hand side of Equation (4.11):

Operating line AB is drawn in xy plane. Any point (x,y) is taken in operating line.

A vertical line is drawn upto equilibrium line to get y^* .

$$h_T = \int_{x_2}^{x_1} \frac{L' dx}{K_x \bar{a}(1-x)(x^* - x)} = \int_{y_2}^{y_1} \frac{G' dy}{K_G \bar{a} P(1-y)(y - y^*)} = \int_{x_2}^{x_1} \frac{L' dx}{k_L \bar{a}(C_{av})(1-x)(x^* - x)} \tag{4.12}$$

Mass Transfer-I

1.6. Design based on height of a transfer unit (HTU)

Equation 4.7 can be written as

$$h_T = \int_0^{h_T} dh = \int_{y_2}^{y_1} \frac{G' y_{iBM} dy}{k_y \bar{a} y_{iBM} (1-y)(y-y_i)} = \int_{y_2}^{y_1} \frac{G' (1-y)_{iM} dy}{k_y \bar{a} (1-y)_{iM} (1-y)(y-y_i)} \quad (4.13)$$

$$\text{where, } y_{iBM} = (1-y)_{iM} = \frac{(1-y_i)-(1-y)}{\ln \frac{(1-y_i)}{(1-y)}}$$

$$h_T = \frac{G'}{k_y \bar{a} (1-y)_{iM}} \int_{y_2}^{y_1} \frac{(1-y)_{iM} dy}{(1-y)(y-y_i)} \quad (4.14)$$

As, $\frac{G'}{k_y \bar{a} (1-y)_{iM}}$ remains constant at the packing section though G' varies. This quantity is called 'height if transfer units' (HTU) and designated as H_{tG} . It is important to measure the separation effectiveness of the particular packings for a particular separation process. It also describes the mass transfer coefficient. Larger mass transfer coefficient leads to the smaller value of HTU.

Hence,

$$H_{tG} = \frac{G'}{k_y \bar{a} (1-y)_{iM}} = \frac{G'}{k_y' \bar{a}} \quad (4.15)$$

The integral part of Equation (4.14) is called number of gas phase transfer units as N_{tG} .

$$h_T = H_{tG} \times N_{tG}$$

When overall gas phase mass transfer coefficients are used, the height of the packing is as follows:

$$h_T = \int_{y_2}^{y_1} \frac{G' dy}{K_y \bar{a} y_{BM}^* (1-y)(y-y^*)} = \frac{G'}{K_y \bar{a} y_{BM}^*} \int_{y_2}^{y_1} \frac{dy}{(1-y)(y-y^*)} = H_{tOG} \times N_{tOG} \quad (4.16)$$

$$\text{where, } H_{tOG} = \frac{G'}{K_y \bar{a} y_{BM}^*}, N_{tOG} = \int_{y_2}^{y_1} \frac{dy}{(1-y)(y-y^*)} \text{ and } y_{BM}^* = (1-y)_{BM}^* = \frac{(1-y^*)-(1-y)}{\ln \frac{(1-y^*)}{(1-y)}}$$

Mass Transfer-I

1.7. Design Equations based concentration in mole ratio unit

If k_x , k_y are individual gas phase mass transfer coefficients and K_Y is overall gas phase mass transfer coefficient, height of packed tower is expressed as:

$$h_T = \int_{Y_2}^{Y_1} \frac{G'_s dy}{k_y \bar{a} (Y - Y_i)} = \int_{Y_2}^{Y_1} \frac{G'_s dy}{K_y \bar{a} (Y - Y^*)} = \frac{G'_s}{K_y \bar{a}} \int_{Y_2}^{Y_1} \frac{dy}{(Y - Y^*)} = H_{toG} \times N_{toG} \quad (4.17)$$

$$H_{toG} = \frac{G'_s}{K_y \bar{a}}$$

$$N_{toG} = \int_{Y_2}^{Y_1} \frac{dy}{(Y - Y^*)}$$

$$\text{Slope of operating line} = \frac{L'_s}{G'_s}$$

Overall gas-phase mass transfer coefficient, K_Y is correlated with individual mass transfer coefficients as follows:

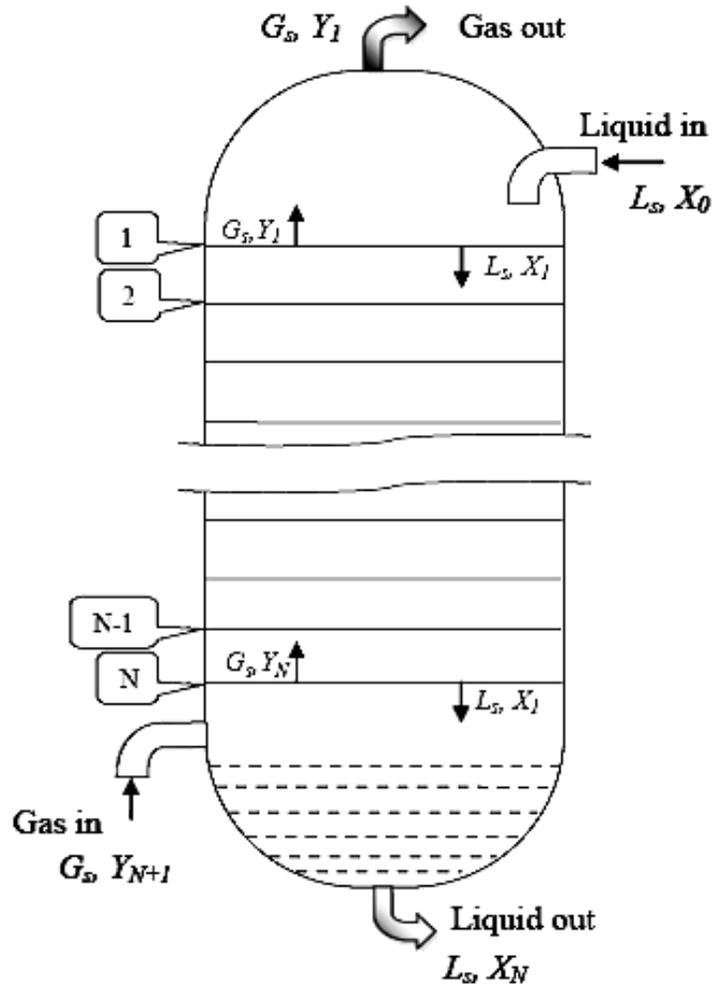
$$\frac{1}{K_Y} = \frac{1}{k_Y} + \frac{\alpha}{k_x}$$

1.8. Counter-current multi-stage absorption (Tray absorber)

In tray absorption tower, multi-stage contact between gas and liquid takes place. In each tray, the liquid is brought into intimate contact of gas and equilibrium is reached thus making an ideal stage. In ideal stage, average composition of liquid leaving the tray is in equilibrium with liquid leaving that tray. The most important step in design of tray absorber is the determination of number of trays. The schematic of tray tower is presented in figure below. The liquid enters from top of the column whereas gas is added from the bottom. The efficiency of the stages can be calculated as:

$$\text{Stage efficiency} = \text{Number of ideal stages} / \text{Number of real stages} \dots\dots\dots(4.8)$$

Mass Transfer-I



Schematic of tray tower.

The following parameters should be known for the determination of “number of stages” (1) Gas feed rate, (2) Concentration of gas at inlet and outlet of the tower, (3) Minimum liquid rate; actual liquid rate is 1.2 to 2 times the minimum liquid rate, (4) Equilibrium data for construction of equilibrium curve now, the number of theoretic stages can be obtained graphically or algebraically.

Mass Transfer-I

(A) Graphical Method for the Determination of Number of Ideal Stages

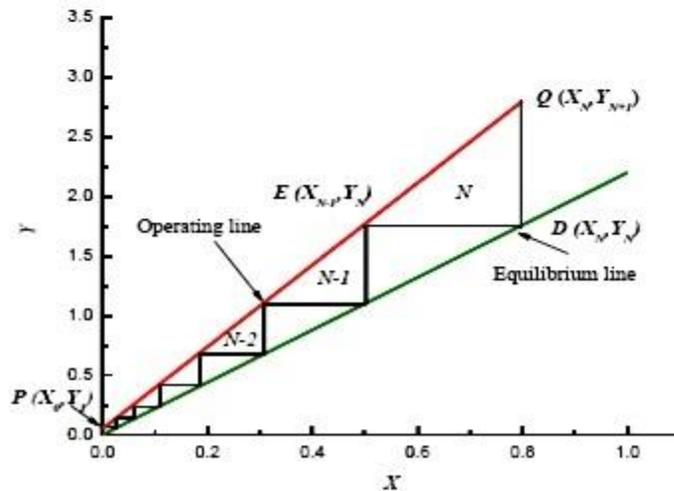
Overall material balance on tray tower

$$G_s(Y_{N+1} - Y_1) = L_s(X_N - X_0) \quad (4.19)$$

This is the operating line for tray tower.

If the stage (plate) is ideal, (X_n, Y_n) must lie on the equilibrium line, $Y^* = f(X)$

Top plate is located at $P(X_0, Y_1)$ and bottom plate is marked as $Q(X_N, Y_{N+1})$ in X - Y plane. A vertical line is drawn from Q point to D point in equilibrium line at (X_N, Y_N) . From point D in equilibrium line, a horizontal line is extended up to operating line at $E(X_{N-1}, Y_N)$. The region QDE stands for N -th plate (refer Figure below). We may get fraction of plates. In that situation, the next whole number will be the actual number of ideal plates. If the overall stage efficiency is known, the number of real plates can be obtained from Equation (4.18).



Graphical determination of number of ideal stages.

(B) Algebraic Determination of Number of Ideal Stages

If both operating line and equilibrium lines are straight, number of ideal stages can be calculated algebraically.

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Let solute transfers from gas to liquid (Absorption)

Equilibrium line, $Y=aX$

Point (X_N, Y_N) lies on the equilibrium line: $Y_N=aX_N$

(4.20)

Operating line:

$$(Y_{N+1} - Y_1) = \frac{L_g}{G_g}(X_N - X_0) \quad (4.21)$$

$$(Y_{N+1} - Y_1) = \frac{L_g}{G_g} \left(\frac{Y_N}{\alpha} - X_0 \right)$$

$$(Y_{N+1} - Y_1) = \frac{L_g}{G_g \alpha} (Y_N - \alpha X_0)$$

$$(Y_{N+1} - Y_1) = \bar{A} (Y_N - \alpha X_0) \quad (4.22)$$

where $\bar{A} = \frac{L_g}{G_g \alpha} = \frac{\text{Slope of operating line}}{\text{slope of equilibrium line}} = \text{absorption factor}$

Now Equation 4.22 becomes,

$$(Y_{N+1} - Y_1) = (\bar{A} Y_N - \bar{A} \alpha X_0)$$

$$(Y_{N+1} - \bar{A} Y_N) = (Y_1 - \bar{A} \alpha X_0) \quad (4.23)$$

This Equation is linear first order "difference Equation" (non-homogeneous).

Solution by finite difference method

$$\text{Corresponding homogeneous Equation: } Y_{N+1} - \bar{A} Y_N = 0 \quad (4.24)$$

$$\text{Solution is } Y_N = K_1 Z^n \quad (4.25)$$

$$K_1 Z^{N+1} - \bar{A} K_1 Z^N = 0 \quad (4.26)$$

$$Z = \bar{A} \quad (4.27)$$

Non-homogeneous Equation has a particular solution, which is constant.

Assuming $Y_N = Y_{N+1}$, we have, $Y = K_2$

$$K_2 - \bar{A} K_2 = Y_1 - \alpha \bar{A} X_0$$

$$K_2 = \frac{Y_1 - \alpha \bar{A} X_0}{1 - \bar{A}} \quad (4.28)$$

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The complete solution is as follows:

$$Y_N = K_1(\bar{A})^N + K_2 = K_1(\bar{A})^N + \frac{Y_1 - \alpha \bar{A} X_0}{1 - \bar{A}} \quad (4.29)$$

Initial conditions:

$$N=0; Y_0 = \alpha X_0$$

$$\alpha X_0 = K_1(\bar{A})^0 + \frac{Y_1 - \alpha \bar{A} X_0}{1 - \bar{A}}$$

$$K_1 = \frac{\alpha X_0 - \alpha \bar{A} X_0 - Y_1 + \alpha \bar{A} X_0}{1 - \bar{A}}$$

$$K_1 = \frac{\alpha X_0 - Y_1}{1 - \bar{A}} \quad (4.30)$$

$$Y_N = \frac{\alpha X_0 - Y_1}{1 - \bar{A}} (\bar{A})^N + \frac{Y_1 - \alpha \bar{A} X_0}{1 - \bar{A}} \quad (4.31)$$

When $N=N+1$;

$$Y_{N+1} = \frac{\alpha X_0 - Y_1}{1 - \bar{A}} (\bar{A})^{N+1} + \frac{Y_1 - \alpha \bar{A} X_0}{1 - \bar{A}}$$

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

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

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

$$(\bar{A})^N = \frac{\left(\frac{1}{\bar{A}} - 1\right) Y_{N+1} - \left(\frac{Y_1}{\bar{A}} - \alpha X_0\right)}{(\alpha X_0 - Y_1)} = \left(\frac{Y_{N+1} - \alpha X_0}{Y_1 - \alpha X_0}\right) \left(1 - \frac{1}{\bar{A}}\right) + \frac{1}{\bar{A}} \quad (4.32)$$

Taking logarithm in both the sides we get:

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

$$N = \frac{\ln \left[\left(\frac{Y_{N+1} - \alpha X_0}{Y_1 - \alpha X_0} \right) \left(1 - \frac{1}{\bar{A}} \right) + \frac{1}{\bar{A}} \right]}{\ln \bar{A}} \quad \text{when } \bar{A} \neq 1 \quad (4.33)$$

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When $\bar{A} = 1$, Equation (4.23) becomes

$$(Y_{N+1} - Y_N) = (Y_1 - \alpha X_0) \rightarrow \text{Operating line Equation} \quad (4.34)$$

Put $N=N, N-1, N-2, \dots, 3, 2, 1$ and add to get

$$(Y_{N+1} - Y_1) = N(Y_1 - \alpha X_0)$$

$$N = \frac{(Y_{N+1} - Y_1)}{(Y_1 - \alpha X_0)} \quad (4.35)$$

Let solute is transferred from liquid to gas (stripping).

$$N = \frac{\ln \left[\frac{(X_0 - Y_{N+1}/\alpha)(1 - \bar{A}) + \bar{A}}{(X_N - Y_{N+1}/\alpha)(1 - \bar{A}) + \bar{A}} \right]}{\ln \frac{1}{\bar{A}}} \quad \text{when } \bar{A} \neq 1 \quad (4.36)$$

When $\bar{A} = 1$, Equation (4.23) becomes

$$N = \frac{(X_0 - X_N)}{(X_N - Y_{N+1}/\alpha)} \quad (4.37)$$

These four Equations (4.33, 4.35-4.37) are called "**Kremser Equations**".

1.9. Continuous contact equipment

The liquid and gas compositions in a packed tower changes continuously throughout the height. The composition of solute from entry to exit of the packed tower is represented by operating line and every point indicates some location in the packed tower. On the other hand, in tray tower, few points (number of trays) in the operating line represents the conditions in the trays.

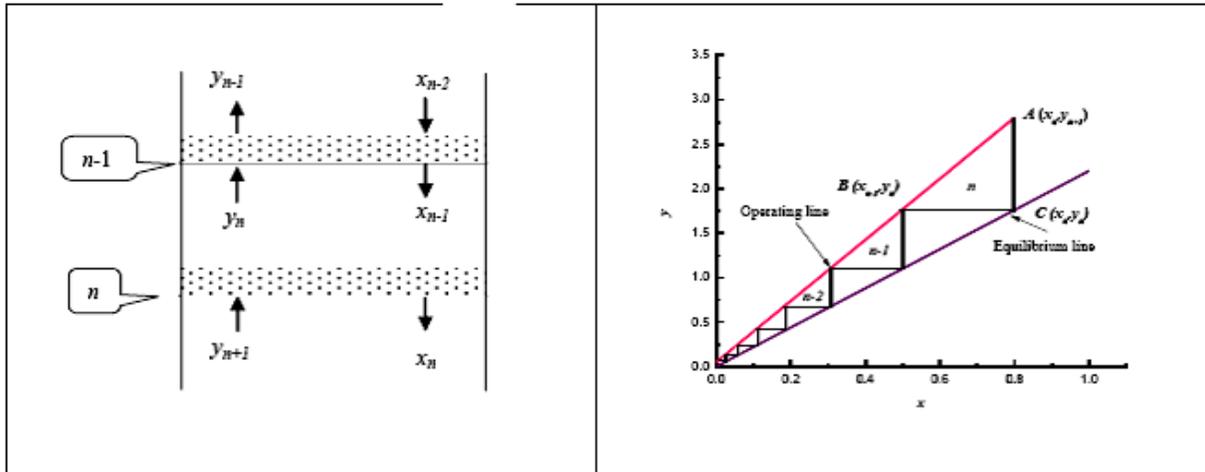
Height Equivalent to Theoretical Plate (HETP)

For a specified separation job, in packed tower, the height of packing is to be determined and in tray tower, numbers of ideal trays are determined. The ratio between packing height to number of trays required for the same separation is called height equivalent to theoretical plate (HETP).

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$$HETP = \frac{h_T}{N_T} = \frac{\text{Height of packing}}{\text{Number of ideal trays}}$$

HETP varies with size and type of packing, flow rate of gas and liquid, concentration of solute, physical and transport properties as well as equilibrium relationship and uniformity of liquid and gas distribution. The concept of HETP is presented in Figure below.



Model diagram of HETP.

$$G'(y_{n+1} - y_n) = L'(x_n - x_{n-1}) = \text{Mass transfer rate} \quad (4.38)$$

The mass transfer rate for h height can be expressed as

$$\text{Mass transfer rate} = K_G \bar{a} P \cdot h (y - y^*)_{av} \quad (4.39)$$

$$G'(y_{n+1} - y_n) = K_G \bar{a} P \cdot h (y - y^*)_{av}$$

$$h = \frac{G'(y_{n+1} - y_n)}{K_G \bar{a} P (y - y^*)_{av}} \quad (4.40)$$

where,

$$(y - y^*)_{av} = \frac{(y - y^*)_A - (y - y^*)_B}{\ln \frac{(y - y^*)_A}{(y - y^*)_B}} = \frac{(y_{n+1} - y_n) - (y_n - y_{n-1})}{\ln \frac{(y_{n+1} - y_n)}{(y_n - y_{n-1})}} \quad (4.41)$$

as $(y - y^*)_{av}$ is taken as log mean gas phase driving force from A to B across n th tray.

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It is observed from Figure of HETP

$$\frac{(y_n - y_{n-1})}{(y_{n+1} - y_n)} = \frac{\frac{(y_n - y_{n-1})}{(x_n - x_{n-1})}}{\frac{(y_{n+1} - y_n)}{(x_n - x_{n-1})}} = \frac{\text{slope of equilibrium line}}{\text{slope of operating line}} = \frac{m}{\frac{L'}{G'}} = \frac{mG'}{L'} \quad (4.42)$$

$$\left(1 - \frac{mG'}{L'}\right) = \left[1 - \frac{(y_n - y_{n-1})}{(y_{n+1} - y_n)}\right] = \frac{(y_{n+1} - y_n) - (y_n - y_{n-1})}{(y_{n+1} - y_n)} \quad (4.43)$$

From Equations (4.41- 4.43) we have,

$$(y - y^*)_{av} = \frac{(y_{n+1} - y_n) \left(1 - \frac{mG'}{L'}\right)}{\ln \frac{L'}{mG'}} = \frac{(y_{n+1} - y_n) \left(\frac{mG'}{L'} - 1\right)}{\ln \frac{mG'}{L'}} \quad (4.44)$$

From Equation (4.40) we can get the value of h as:

$$h = \frac{G'(y_{n+1} - y_n)}{K_G \bar{a} P \frac{(y_{n+1} - y_n) \left(\frac{mG'}{L'} - 1\right)}{\ln \frac{mG'}{L'}}} = \frac{G' \ln \frac{mG'}{L'}}{K_G \bar{a} P \left(\frac{mG'}{L'} - 1\right)} = H_{toG} \frac{\ln \frac{mG'}{L'}}{\left(\frac{mG'}{L'} - 1\right)} \quad (4.45)$$

Hence, the same separation is achieved for h height in packed tower and in the n th tray which is =HETP.

$$HETP = H_{toG} \frac{\ln \left(\frac{mG'}{L'}\right)}{\left(\frac{mG'}{L'} - 1\right)} = H_{toG} \frac{\ln \bar{S}}{(\bar{S} - 1)} \quad (4.46)$$

where, H_{toG} is height of overall gas phase transfer unit. \bar{S} is stripping factor $= \frac{mG'}{L'} = \frac{1}{A}$ and m is Henry's law constant. HETP is used to characterize packing. A good packing has small HETP.

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MODULE: III **DISTILLATION**

Introduction

Distillation is method of separation of components from a liquid mixture which depends on the differences in boiling points of the individual components and the distributions of the components between a liquid and gas phase in the mixture. The liquid mixture may have different boiling point characteristics depending on the concentrations of the components present in it. Therefore, distillation processes depends on the vapor pressure characteristics of liquid mixtures. The vapor pressure is created by supplying heat as separating agent. In the distillation, the new phases differ from the original by their heat content. During most of the century, distillation was by far the most widely used method for separating liquid mixtures of chemical components (Seader and Henley, 1998). This is a very energy intensive technique, especially when the relative volatility of the components is low. It is mostly carried out in multi tray columns. Packed column with efficient structured packing has also led to increased use in distillation.

1.1 Vapor Pressure

Vapor Pressure: The vaporization process changes liquid to gaseous state. The opposite process of this vaporization is called condensation. At equilibrium, the rates of these two processes are same. The pressure exerted by the vapor at this equilibrium state is termed as the vapor pressure of the liquid. It depends on the temperature and the quantity of the liquid and vapor. From the following Clausius-Clapeyron Equation or by using Antoine Equation, the vapor pressure can be calculated.

Clausius-Clapeyron Equation:

$$\ln\left(\frac{p^v}{p_1^v}\right) = \left(\frac{\lambda}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T}\right) \quad (5.1)$$

where p^v and p_1^v are the vapor pressures in Pascal at absolute temperature T and T_1 in K. λ is the molar latent heat of vaporization which is independent of temperature.

Antoine Equation:

$$\ln p^v (\text{Pascal}) = A - \frac{B}{T + C} \quad (5.2)$$

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Typical representative values of the constants A, B and C are given in the following Table ; (Ghosal et al., 1993)

Typical representative values of the constants A, B and C

Components	Range of Temperature (T), K	A	B	C
Acetone	241-350	21.5439	2940.46	-35.93
Ammonia	179-261	21.8407	2132.50	-32.98
Benzene	280-377	20.7934	2788.51	-52.36
Ethanol	270-369	21.8045	3803.98	-41.68
Methanol	257-364	23.4801	3626.55	-34.29
Toluene	280-410	20.9063	3096.52	-53.67
Water	284-441	23.1962	3816.44	-46.13

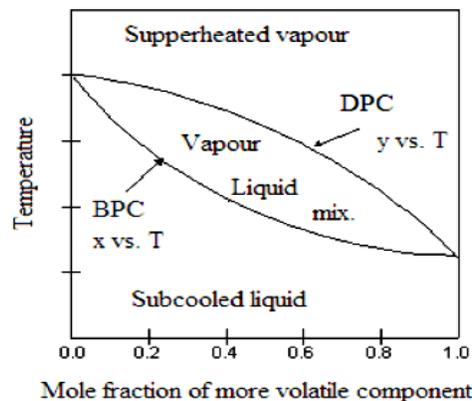
Readers are suggested to revise the thermodynamics for more about vapor pressure and boiling point.

1.2. Phase Diagram

For binary mixture phase diagram only two-component mixture, (e.g. A (more volatile) and B (less volatile)) are considered. There are two types of phase diagram: constant pressure and constant temperature.

1.3. Constant Pressure Phase Diagram

The Figure below shows a constant pressure phase diagram for an ideal solution (one that obeys Raoult's Law). At constant pressure, depending on relative



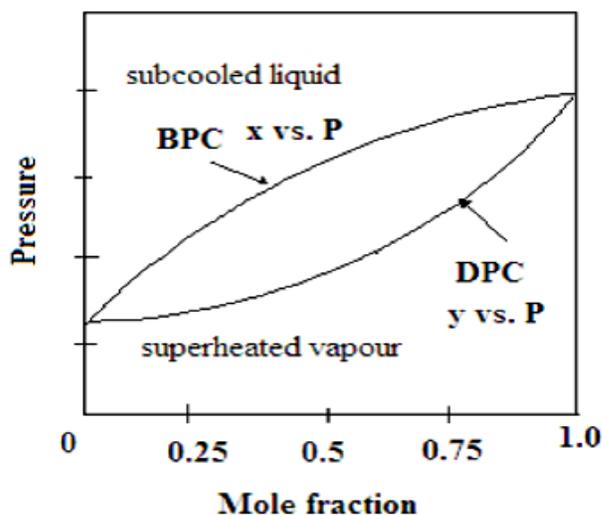
Phase diagram of binary system at constant pressure

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concentrations of each component in the liquid, many boiling point temperatures are possible for mixture of liquids (solutions) as shown in phase diagram (Figure above). For mixture, the temperature is called bubble point temperature when the liquid starts to boil and dew point when the vapor starts to condense. Boiling of a liquid mixture takes place over a range of boiling points. Likewise, condensation of a vapor mixture takes place over a range of condensation points. The upper curve in the boiling point diagram is called the dew-point curve (DPC) while the lower one is called the bubble-point curve (BPC). At each temperature, the vapor and the liquid are in equilibrium. The constant pressure phase diagram is more commonly used in the analysis of vapor-liquid equilibrium.

1.3 Constant temperature (isothermal) phase diagram

The constant temperature phase diagram is shown in Figure below. The constant temperature phase diagram is useful in the analysis of solution behaviour. The more volatile liquid will have a higher vapor pressure (i.e. p_A at $x_A = 1.0$)



Binary Phase diagram at constant temperature

1.5. Relative volatility

Relative volatility is a measure of the differences in volatility between two components, and hence their boiling points. It indicates how easy or difficult a particular separation will be. The relative volatility of component 'A' with respect to component 'B' in a binary mixture is defined as

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$$\alpha_{AB} = \frac{y_A / x_A}{y_B / x_B} \quad (5.3)$$

where, y_A = mole fraction of component 'A' in the vapor, x_A = mole fraction of component 'A' in the liquid. In general, relative volatility of a mixture changes with the mixture composition. For binary mixture, $x_B = 1-x_A$. So Equation (5.3) can be rearranged, simplifying and expressed by dropping subscript 'A' for more volatile component as:

$$y = \frac{\alpha_{ave} x}{1 - (\alpha_{ave} - 1)x} \quad (5.4)$$

The Equation (5.4) is a non-linear relationships between x and y. This Equation can be used to determine the equilibrium relationship (y vs. x) provided the average relative volatility, α_{ave} is known. If the system obeys Raoult's law, i.e. $p_A = P y_A$, $p_B = P y_B$, the relative volatility can be expressed as:

$$\alpha_{AB} = \frac{p_A / x_A}{p_B / x_B} \quad (5.5)$$

where p_A is the partial pressure of component A in the vapor, p_B is the partial pressure of component B in the vapor and P is the total pressure of the system. Thus if the relative volatility between two components is equal to one, separation is not possible by distillation. The larger the value of α , above 1.0, the greater the degree of separability, i.e. the easier the separation. Some examples of optimal relative volatility that are used for distillation process design are given in Table below.

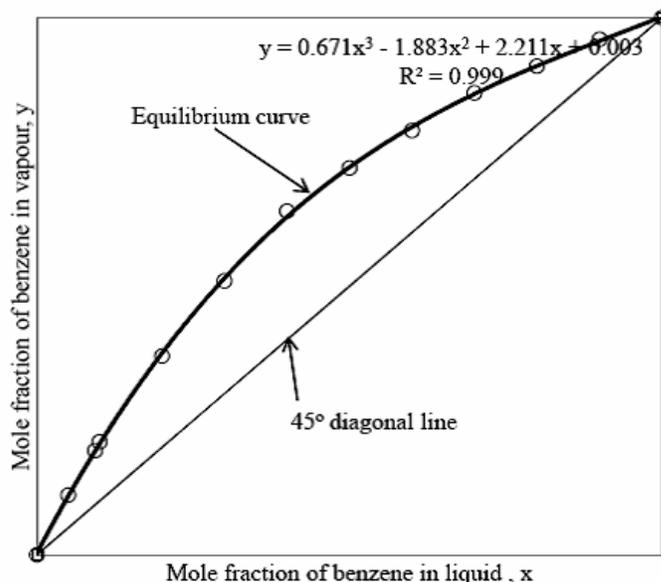
Some optimal relative volatility that are used for distillation process design

More volatile component (normal boiling point °C)	Less boiling component (normal boiling point, °C)	Optimal Relative volatility
Benzene (80.1)	Toluene (110.6)	2.34
Toluene (110.6)	p-Xylene (138.3)	2.31
Benzene (80.6)	p-Xylene (138.3)	4.82
m-Xylene (139.1)	p-Xylene (138.3)	1.02
Pentane (36.0)	Hexane (68.7)	2.59
Hexane (68.7)	Heptane (98.5)	2.45
Hexane (68.7)	p-Xylene (138.3)	7.0
Ethanol (78.4)	iso-Propanol (82.3)	1.17
iso-Propanol (82.3)	n-Propanol (97.3)	1.78
Ethanol (78.4)	n-Propanol (97.3)	2.10
Methanol (64.6)	Ethanol (78.4)	1.56
Methanol (64.6)	iso-Propanol (82.3)	2.26
Chloroform (61.2)	Acetic acid (118.1)	6.15

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1.6. Vapor-Liquid Equilibrium (VLE)

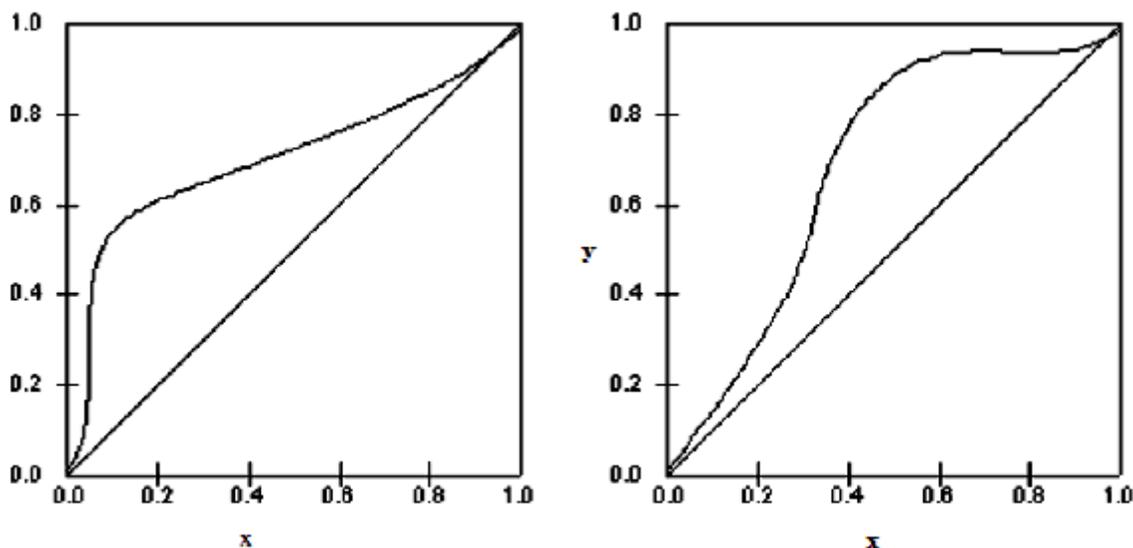
It is useful for graphical design in determining the number of theoretical stages required for a distillation column. A typical equilibrium curve for a binary mixture on x-y plot is shown in Figure below. It can be plotted by the Equations (5.4) or (5.5) as discussed earlier section. It contains less information than the phase diagram (i.e. temperature is not included), but it is most commonly used. The VLE plot expresses the bubble-point and the dew-point of a binary mixture at constant pressure. The curved line in Figure is called the equilibrium line and it describes the compositions of the liquid and vapor in equilibrium at some fixed pressure. The equilibrium line can be obtained from the Equation (5.4) once the relative volatility is known.



Equilibrium diagram for a benzene-toluene mixture at 1 atmosphere

This particular VLE plot (Figure above) shows a binary ideal mixture that has a uniform vapor-liquid equilibrium that is relatively easy to separate. On the other hand, the VLE plots shown in Figure below represented for non-ideal systems. These non-ideal VLE systems will present more difficult separation.

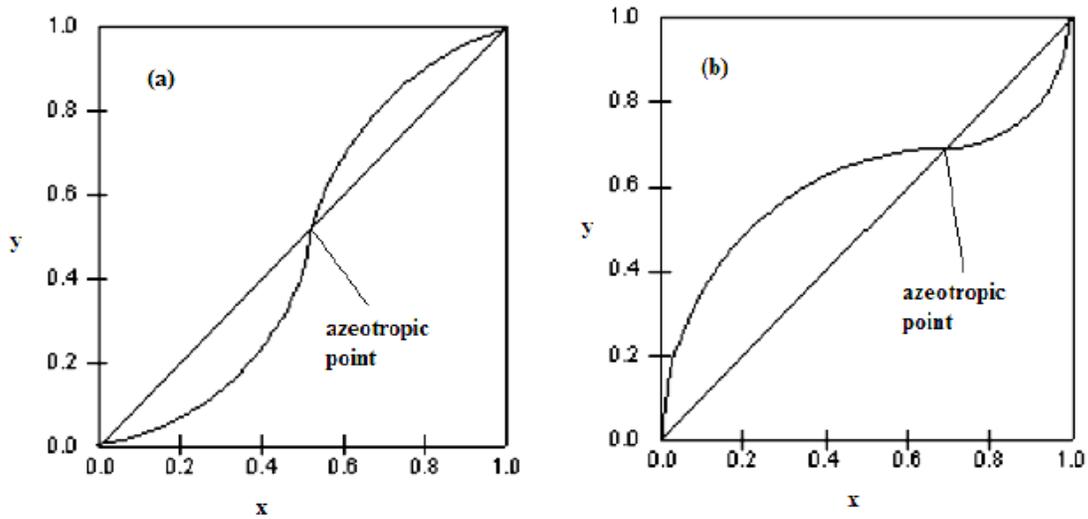
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Vapor-liquid equilibrium curve for non-ideal systems

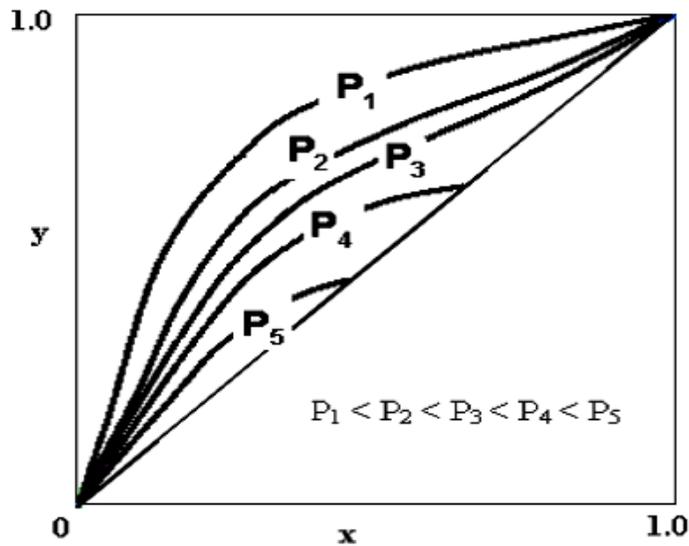
The most challenging VLE curves are generated by azeotropic systems. An azeotrope is a liquid mixture which when vaporized, produces the same composition as the liquid. Two types of azeotropes are known: minimum-boiling and maximum-boiling (less common). Ethanol-water system (at 1 atm, 89.4 mole %, 78.2°C; Carbon-disulfide - acetone (61.0 mole% CS₂, 39.25°C, 1 atm) and Benzene - water (29.6 mole% H₂O, 69.25°C, 1 atm) are minimum-boiling azeotropes. Hydrochloric acid - water (11.1 mole% HCl, 110°C, 1 atm); Acetone - chloroform (65.5 mole% chloroform, 64.5°C, 1 atm) are the examples of Maximum-boiling azeotropes. The Figure below (a and b) shows two different azeotropic systems, one with a minimum boiling point (Figure. a) and one with a maximum boiling point (Figure b). The points of intersections of the equilibrium curves with the diagonal lines are called azeotropic points. An azeotrope cannot be separated by conventional distillation. However, vacuum distillation may be used as the lower pressures which can shift the azeotropic point.

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VLE curves for azeotropic systems: (a) for maximum boiling point, (b) for minimum boiling point

Although most distillations are carried out at atmospheric or near atmospheric pressure, it is not uncommon to distill at other pressures. High pressure distillation (typically 3 - 20 atm) usually occurs in thermally integrated processes. In those cases the equilibrium curve becomes narrower at higher pressures as shown in Figure below. Separability becomes less at higher pressures.



Variation of equilibrium curve with pressure

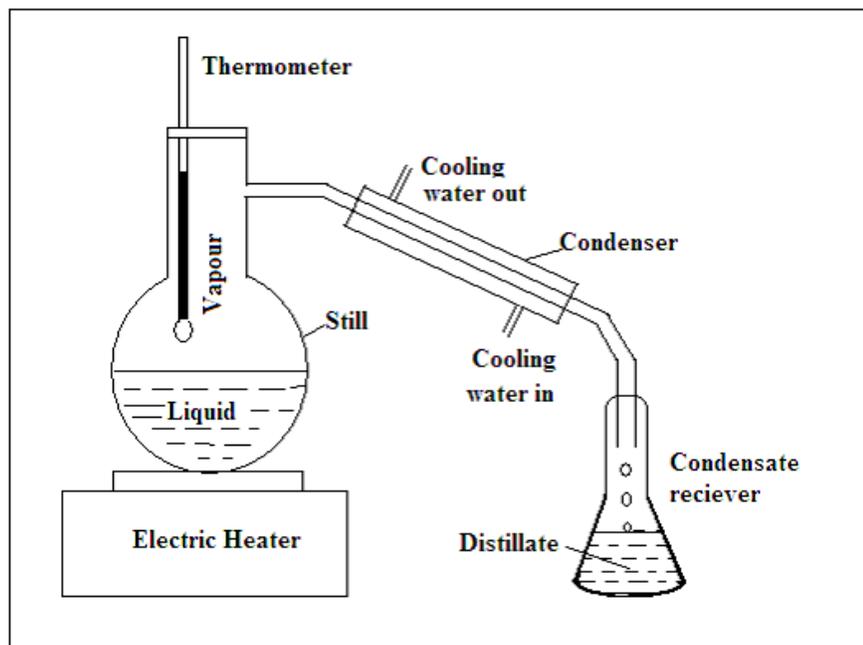
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1.7 Distillation columns and their process calculations

There are many types of distillation columns each of which is designed to perform specific types of separations. One way of classifying distillation column type is to look at how they are operated. Based on operation, they are of two types: batch or differential and continuous columns.

1.7.1 Batch or differential distillation columns and their process calculation

In batch operation, the feed is introduced batch-wise to the column. That is, the column is charged with a 'batch' and then the distillation process is carried out. When the desired task is achieved, a next batch of feed is introduced. Consider a binary mixture of components A (more volatile) and B (less volatile). The system consists of a batch of liquid (fixed quantity) inside a kettle (or still) fitted with heating element and a condenser to condense the vapor produced as shown in Figure below. The condensed vapor is known as the distillate. The distillate is collected in a condensate receiver. The liquid remaining in the still is known as the residual. The process is unsteady state.



Simple batch or differential distillation process

The concentration changes can be analyzed using the phase diagram, and detailed mathematical calculations carried out using the Rayleigh Equation.

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Readers are suggested to follow chapter 9 (Page 369) of text book “Mass-transfer operations” by **R. E Treybal**, third edition. As the process is unsteady state, the derivation is based on a differential approach to changes in concentration with time. Let L_1 = initial moles of liquid

originally in still, L_2 = final moles of liquid remained in still, x_1 = initial liquid composition in still (mole fraction of A), x_2 = final liquid composition in still (mole fraction A). At any time t , the amount of liquid in the still is L , with mole fraction of A in the liquid being x . After a small differential time ($t + dt$), a small amount of vapor dL is produced, and the composition of A in the vapor is y (mole fraction). The vapor is assumed to be in equilibrium with the residue liquid. The amount of liquid in the still is thus reduced from L to $(L - dL)$, while the liquid composition changed from x to $(x - dx)$. Then the material balance on A can be written as:

Initial amount in still = Amount left in still + Amount vaporized

$$xL = (x - dx)(L - dL) + ydL \quad (5.6)$$

or

$$xL = xL - xdL - Ldx + dx dL + ydL \quad (5.7)$$

Neglecting the term $(dx)(dL)$, the Equation (5.7) may be written as:

$$Ldx = ydL - xdL \quad (5.8)$$

Re-arranging and Integrating from L_1 to L_2 , and from x_1 to x_2 , one can obtain the following Equation which is called Rayleigh Equation:

$$\ln\left(\frac{L_1}{L_2}\right) = \int_{x_2}^{x_1} \frac{1}{(y-x)} dx \quad (5.9)$$

The integration of Equation (5.9) can be obtained graphically from the equilibrium curve, by plotting $1/(y-x)$ versus x .

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1.7.2. Continuous distillation columns

In contrast, continuous columns process a continuous feed stream. No interruptions occur unless there is a problem with the column or surrounding process units. They are capable of handling high throughputs. Continuous column is the more common of the two types.

Types of Continuous Columns

Continuous columns can be further classified according to the nature of the feed that they are processing:

Binary distillation column: feed contains only two components

Multi-component distillation column: feed contains more than two components the number of product streams they have

Multi-product distillation column:

Column has more than two product streams where the extra feed exits when it is used to help with the separation,

Extractive distillation: where the extra feed appears in the bottom product stream

Azeotropic distillation: where the extra feed appears at the top product stream the type of column internals.

Tray distillation column: where trays of various designs are used to hold up the liquid to provide better contact between vapor and liquid, hence better separation. The details of the tray column are given in Module-2.

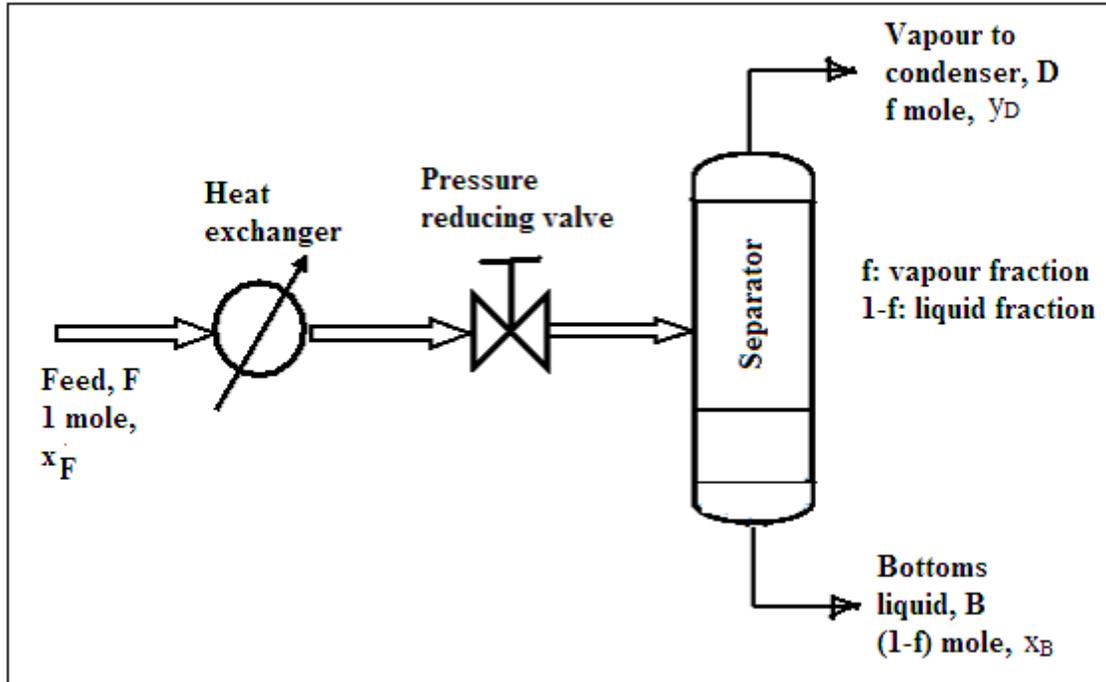
Packed distillation column: where instead of trays, 'packings' are used to enhance contact between vapor and liquid. The details of the packed column are given in Module-2.

1.7.2.1. A single-stage continuous distillation (Flash distillation):

A single-stage continuous operation occurs where a liquid mixture is partially vaporized. The vapor produced and the residual liquids are in equilibrium in the process are separated and removed as shown in Figure below. Consider a binary mixture of A (more volatile component) and B (less volatile component). The feed is preheated before entering the separator. As such, part of the feed may be vaporized. The heated mixture then flows through a pressure-reducing valve to the separator. In the separator, separation between the vapor and liquid takes place. The amount of vaporization affects the concentration (distribution) of A in vapor phase and liquid phase. The relationship between the scale of vaporization and mole fraction of A in vapor and liquid (y and x) is known as the Operating Line Equation. Define f as molal fraction of the feed that is vaporized and withdrawn continuously as vapor. Therefore, for 1 mole of binary feed mixture, $(1 - f)$ is the molal fraction of the feed that leaves continuously as liquid. Assume, y_D = mole fraction of A in vapor leaving, x_B = mole fraction of A in liquid leaving, x_F = mole

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fraction of A in feed entering. Based on the definition for f , the greater the heating is, the larger the value of f . If the feed is completely vaporized, then $f = 1.0$. Thus, the value of f can vary from 0 (no vaporization) to 1 (total vaporization). From material balance for the more volatile component (A) one can write



Flash distillation process

$$1 \cdot x_F = f y_D + (1-f)x_B \quad (5.10)$$

Or,

$$f y_D = x_F - (1-f)x_B \quad (5.11)$$

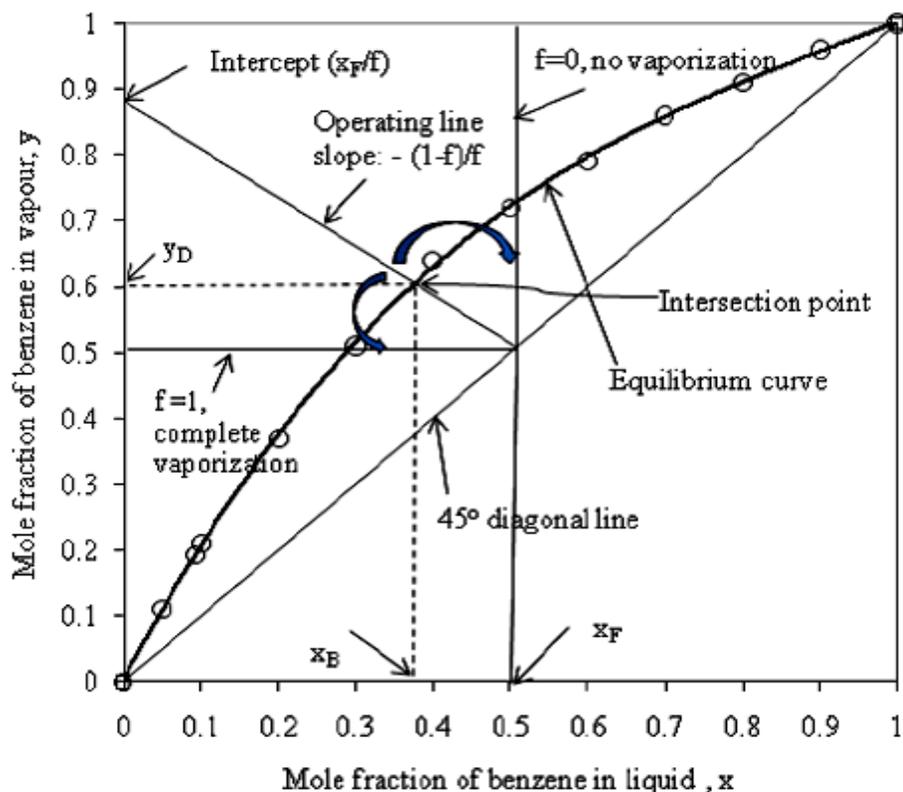
The Equation (5.11) on rearranging becomes:

$$y_D = \left(\frac{1-f}{f} \right) x_B + \frac{x_F}{f} \quad (5.12)$$

The fraction f depends on the enthalpy of the liquid feed, the enthalpies of the vapor and liquid leaving the separator. For a given feed condition, and hence the

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known value of f and x_F , the Equation (5.12) is a straight line Equation with slope $-(1-f)/f$ and intercept x_F/f as shown in Figure below. It will intersect the equilibrium line at the point (x_B, y_D) . From this value, the composition of the vapor and liquid leaving the separator can be obtained.

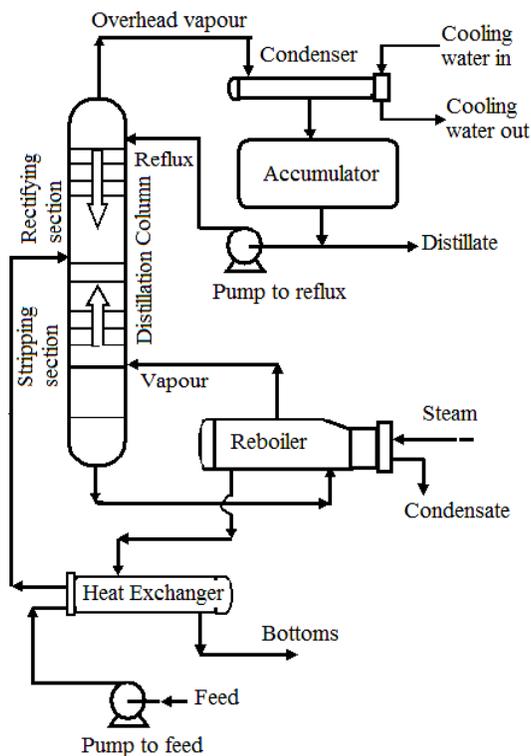


1.7.2.2. Multi-stage Continuous distillation-Binary system

A general schematic diagram of a multistage counter-current binary distillation operation is shown in Figure below. The operation consists of a column containing the equivalent N number of theoretical stages arranged in a two-section cascade; a condenser in which the overhead vapor leaving the top stage is condensed to give a liquid distillate product and liquid reflux that is returned to the top stage; a reboiler in which liquid from the bottom stage is vaporized to give a liquid bottom products and the vapor boil off returned to the bottom stage; accumulator is a horizontal (usually) pressure vessel whereby the condensed vapor is collected; Heat exchanger where the hot bottoms stream is used to heat up the feed stream before it enters the distillation column. The feed enters the column at feed stage contains more volatile components (called light key, LK) and less volatile

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components (called heavy key, HK). At the feed stage feed may be liquid, vapor or mixture of liquid and vapor. The section above the feed where vapor is washed with the reflux to remove or absorb the heavy key is called enriching or rectifying section. The section below the feed stage where liquid is stripped of the light key by the rising vapor is called stripping section.



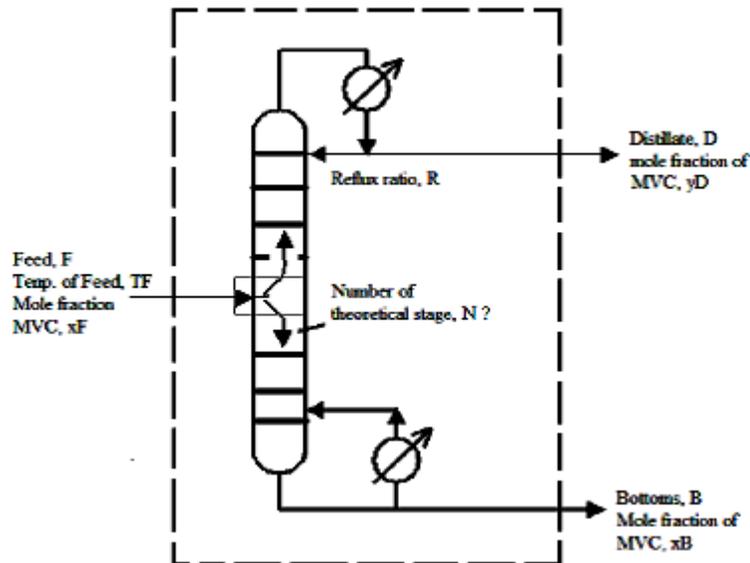
Multi-stage binary distillation column

1.7.2.3. Analysis of binary distillation in tray towers: McCabe-Thiele Method

McCabe and Thiele (1925) developed a graphical method to determine the theoretical number of stages required to effect the separation of a binary mixture (McCabe and Smith, 1976). This method uses the equilibrium curve diagram to determine the number of theoretical stages (trays) required to achieve a desired degree of separation. It assumes constant molar overflow and this implies that: (i) molar heats of vaporization of the components are roughly the same; (ii) heat effects are negligible. The information required for the systematic calculation are the VLE data, feed condition (temperature, composition), distillate and bottom compositions; and the reflux ratio, which is defined as the ratio of reflux liquid over the distillate product. For example, a column is to be designed for the separation of a binary mixture as shown in Figure below. The feed has a concentration of x_F

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(mole fraction) of the more volatile component, and a distillate having a concentration of x_D of the more volatile component and a bottoms having a concentration of x_B is desired. In its essence, the method involves the plotting on the equilibrium diagram three straight lines: the rectifying section operating line (ROL), the feed line (also known as the q-line) and the stripping section operating line (SOL).



Schematic of column for separation of binary mixture

An important parameter in the analysis of continuous distillation is the Reflux Ratio, defined as the quantity of liquid returned to the distillation column over the quantity of liquid withdrawn as product from the column, i.e. $R = L / D$. The reflux ratio R is important because the concentration of the more volatile component in the distillate (in mole fraction x_D) can be changed by changing the value of R . The steps to be followed to determine the number of theoretical stages by McCabe-Thiele Method:

1. Determination of the Rectifying section operating line (ROL).
2. Determination the feed condition (q).
3. Determination of the feed section operating line (q -line).
4. Determination of required reflux ratio (R).
5. Determination of the stripping section operating line (SOL).
6. Determination of number of theoretical stage.

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Determination of the Rectifying section operating line (ROL)

Consider the rectifying section as shown in the Figure below. Material balance can be written around the envelope as shown below.

Overall or total balance:

$$V_{n+1} = L_n + D \quad (5.13)$$

Component balance for more volatile component:

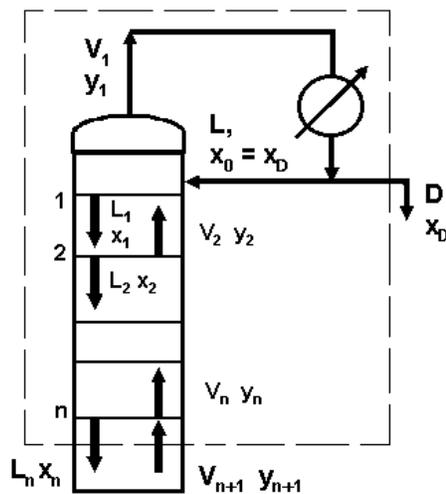
$$V_{n+1}y_{n+1} = L_nx_n + Dx_D \quad (5.14)$$

From Equations (4.13) and (4.14), it can be written as

$$(L_n + D)y_{n+1} = L_nx_n + Dx_D \quad (5.15)$$

Consider the constant molal flow in the column, and then one can write: $L_1 = L_2 = \dots\dots\dots L_{n-1} = L_n = L_{n+1} = L = \text{constant}$ and $V_1 = V_2 = \dots\dots\dots V_{n-1} = V_n = V_{n+1} = V = \text{constant}$. Thus, the Equation (5.15) becomes:

$$(L + D)y_{n+1} = Lx_n + Dx_D \quad (5.16)$$



Outline graph of rectifying section

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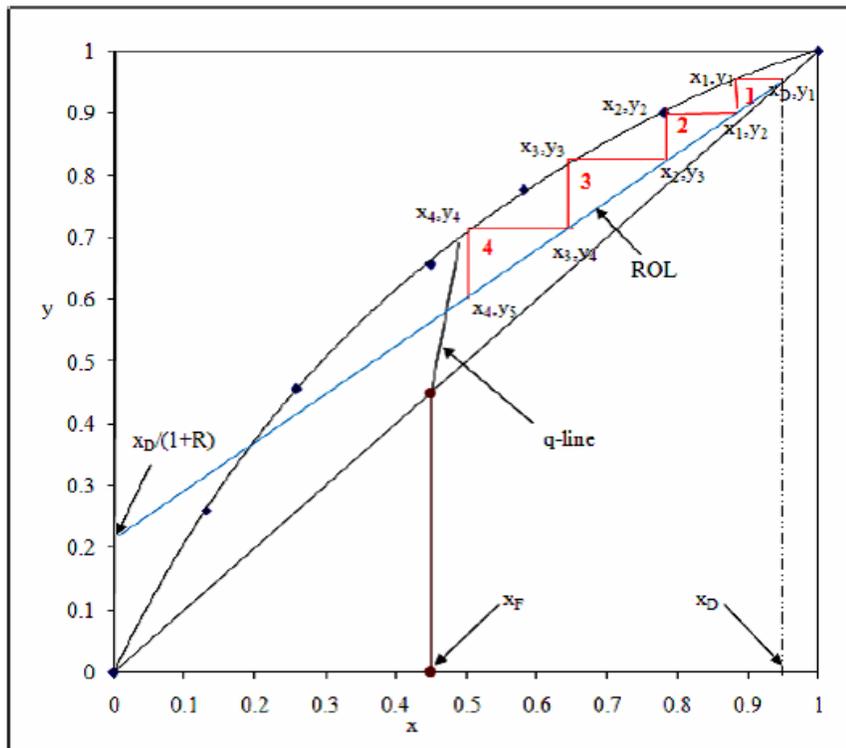
After rearranging, one gets from Equation (5.16) as:

$$y_{n+1} = \left(\frac{L}{L+D}\right)x_n + \left(\frac{D}{L+D}\right)x_D \quad (5.17)$$

Introducing reflux ratio defined as: $R = L/D$, the Equation (5.17) can be expressed as:

$$y_{n+1} = \left(\frac{R}{R+1}\right)x_n + \left(\frac{1}{R+1}\right)x_D \quad (5.18)$$

The Equation (5.18) is the rectifying section operating line (ROL) Equation having slope $R/(R+1)$ and intercept, $x_D/(R+1)$ as shown in Figure 5.13. If $x_n = x_D$, then $y_{n+1} = x_D$, the operating line passed through the point (x_D, x_D) on the 45° diagonal line. When the reflux ratio R changed, the ROL will change. Generally the



Representation of the rectifying operating line

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rectifying operating line is expressed without subscript of n or n+1. Without subscript the ROL is expressed as:

$$y = \left(\frac{R}{R+1} \right) x + \left(\frac{1}{R+1} \right) x_D \quad (5.19)$$

Determination the feed condition (q):

The feed enters the distillation column may consists of liquid, vapor or a mixture of both. Some portions of the feed go as the liquid and vapor stream to the rectifying and stripping sections. The moles of liquid flow in the stripping section that result from the introduction of each mole of feed, denoted as 'q'. The limitations of the q-value as per feed conditions are shown in Table below.

Limitations of q-value as per feed conditions

Feed condition	Limit of q-value
cold feed (below bubble point)	$q > 1$
feed at bubble point (saturated liquid)	$q = 1$
feed as partially vaporized	$0 < q < 1$
feed at dew point (saturated vapor)	$q = 0$
feed as superheated vapor	$q < 0$
feed is a mixture of liquid and vapor	q is the fraction of the feed that is liquid

Calculation of q-value *when feed is partially vaporized:*

Other than saturated liquid ($q = 1$) and saturated vapor ($q = 0$), the feed condition is uncertain. In that case one must calculate the value of q. The q-value can be obtained from enthalpy balance around the feed plate. By enthalpy balance one can obtain the q-value from the following form of Equation:

$$q = \frac{H_V - H_F}{H_V - H_L} \quad (5.20)$$

where H_F , H_V and H_L are enthalpies of feed, vapor and liquid respectively which can be obtained from enthalpy-concentration diagram for the mixture.

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When feed is cold liquid or superheated vapor:

q can be alternatively defined as the heat required to convert 1 mole of feed from its entering condition to a saturated vapor; divided by the molal latent heat of vaporization. Based on this definition, one can calculate the q-value from the following Equations for the case whereby $q > 1$ (cold liquid feed) and $q < 0$ (superheated vapor feed) as:

For cold liquid feed:

$$q = \frac{C_{p,L}(T_{bp} - T_F) + \lambda}{\lambda} \quad (5.21)$$

For superheated vapor feed:

$$q = \frac{C_{p,V}(T_{dp} - T_F)}{\lambda} \quad (5.22)$$

where T_{bp} is the bubble point, λ is the latent heat of vaporization and T_{dp} is the dew point of the feed respectively.

Determination of the feed section operating line (q-line):

Consider the section of the distillation column (as shown in Figure below) at the tray (called feed tray) where the feed is introduced. In the feed tray the feed is introduced at F moles/hr with liquid of q fraction of feed and vapor of $(1-q)$ fraction of feed as shown in Figure below. Overall material balance around the feed tray:

$$L' = L + qF \quad \text{and} \quad V = V' + (1 - q)F \quad (5.23)$$

Component balances for the more volatile component in the rectifying and stripping sections are:

For rectifying section:

$$V_y = Lx + Dx_D \quad (5.24)$$

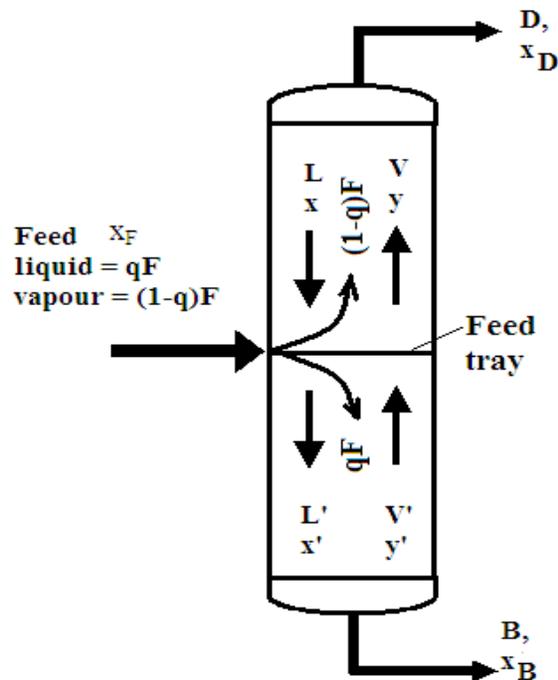
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For stripping section:

$$V'y = L'x - Bx_B \quad (5.25)$$

At the feed point where the two operating lines (Equations (5.24) and (5.25)) intersect can be written as:

$$(V - V')y = (L - L')x + Dx_D + Bx_B \quad (5.26)$$



Feed tray with fraction of liquid and vapor of feed

From component balance around the entire column, it can be written as

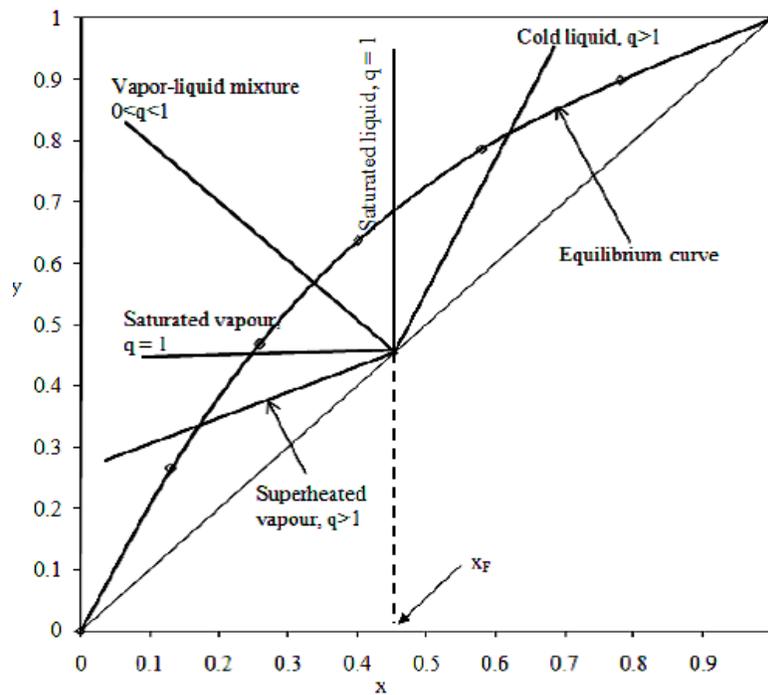
$$Fx_F = Dx_D + Bx_B \quad (5.27)$$

Substituting $L-L'$ and $V-V'$ from Equations (5.23) and (5.24) into Equation (5.26) and with Equation (5.27) one can get the q-line Equation after rearranging as:

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$$y = -\left(\frac{q}{1-q}\right)x + \left(\frac{1}{1-q}\right)x_F \quad (5.28)$$

For a given feed condition, x_F and q are fixed, therefore the q -line is a straight line with slope $-q / (1-q)$ and intercept $x_F/(1-q)$. If $x = x_F$, then from Equation (5.28) $y = x_F$. At this condition the q -line passes through the point (x_F, x_F) on the 45° diagonal. Different values of q will result in different slope of the q -line. Different q -lines for different feed conditions are shown in Figure below.

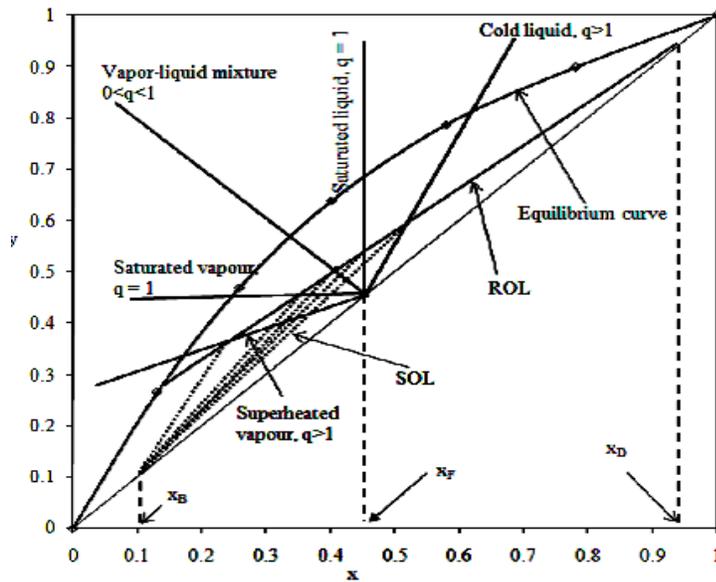


Different q -lines for different feed conditions

Determination of the stripping section operating line (SOL):

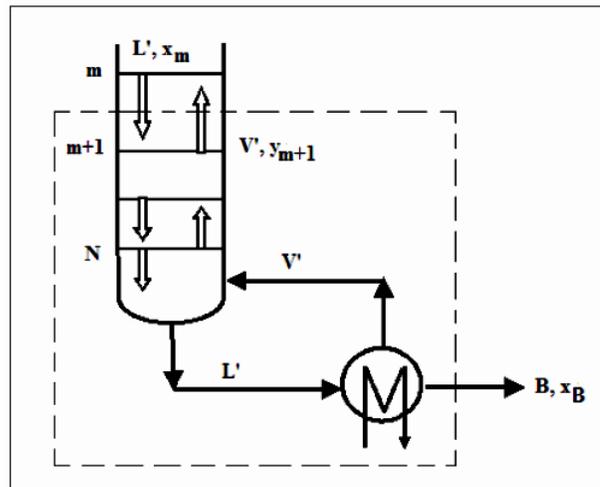
The stripping section operating line (SOL) can be obtained from the ROL and q -line without doing any material balance. The SOL can be drawn by connecting point x_B on the diagonal to the point of intersection between the ROL and q -line. The SOL will change if q -line is changed at fixed ROL. The change of SOL with different q -lines for a given ROL at constant R and x_D is shown in Figure below.

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Stripping section operating line with different q-lines

The stripping section operating line can be derived from the material balance around the stripping section of the distillation column. The stripping section of a distillation column is shown in Figure below. The reboiled vapor is in equilibrium with bottoms liquid which is leaving the column.



Schematic of the stripping section

Consider the constant molal overflow in the column. Thus $L'_m = L'_{m+1} = \dots = L' =$ constant and $V'_m = V'_{m+1} = \dots = V' =$ constant. Overall material balance gives

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$$L' = V' + B \quad (5.29)$$

More volatile component balance gives:

$$L'x_m = V'y_{m+1} + Bx_B \quad (5.30)$$

Substituting and re-arranging the Equation (5.30) yields

$$y_{m+1} = \left(\frac{L'}{V'}\right)x_m - \left(\frac{B}{V'}\right)x_B \quad (5.31)$$

Dropping the subscripts "m+1" and "m" it becomes:

$$y = \left(\frac{L'}{V'}\right)x - \left(\frac{B}{V'}\right)x_B \quad (5.32)$$

Substituting $V' = L' - B$ from Equation (5.29), the Equation (5.32) can be written as:

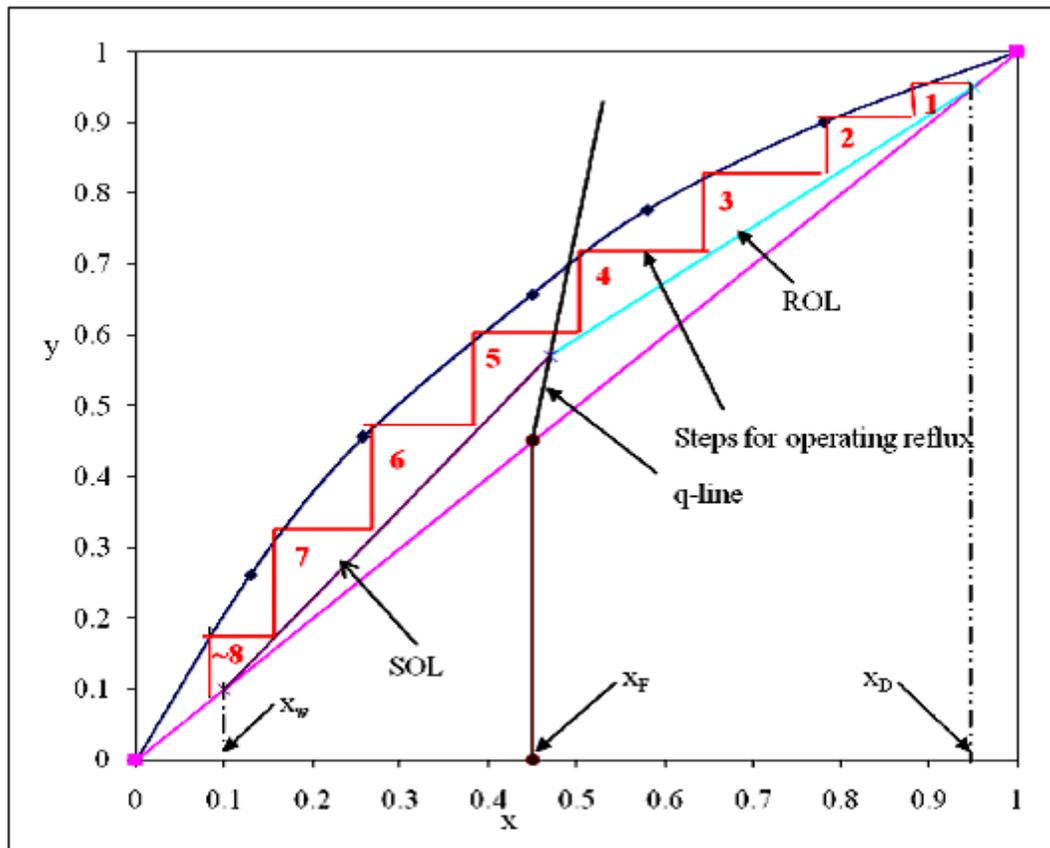
$$y = \left(\frac{L'}{L' - B}\right)x - \left(\frac{B}{L' - B}\right)x_B \quad (5.33)$$

The Equation (5.33) is called the stripping operating line (SOL) which is a straight line with slope $(L' / L' - B)$ and intercept $(Bx_B / L' - B)$. When $x = x_B$, $y = x_B$, the SOL passes through (x_B, x_B) on the 45° diagonal line.

Determination of number of theoretical stage

Suppose a column is to be designed for the separation of a binary mixture where the feed has a concentration of x_F (mole fraction) of the more volatile component and a distillate having a concentration of x_D of the more volatile component whereas the bottoms having a desired concentration of x_B . Once the three lines (ROL, SOL and q-line) are drawn, the number of theoretical stages required for a given separation is then the number of triangles that can be drawn between these operating lines and the equilibrium curve. The last triangle on the diagram represents the reboiler. A typical representation is given in Figure below.

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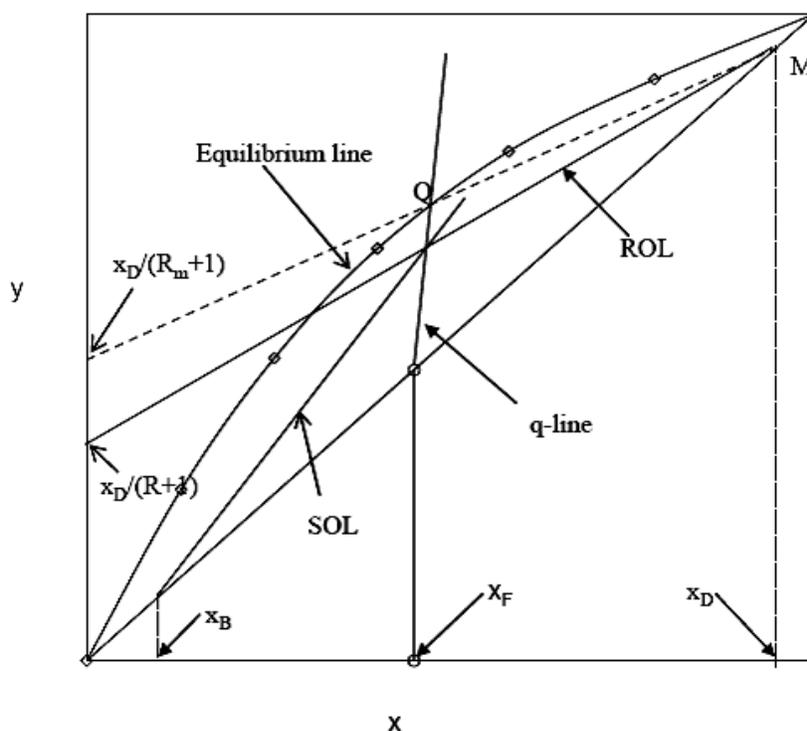
A typical representation of identifying number of theoretical stages

Reflux Ratio, R

The separation efficiency by distillation depends on the reflux ratio. For a given separation (i.e. constant x_D and x_B) from a given feed condition (x_F and q), higher reflux ratio (R) results in lesser number of required theoretical trays (N) and vice versa. So there is an inverse relationship between the reflux ratio and the number of theoretical stages. At a specified distillate concentration, x_D , when R changes, the slope and intercept of the ROL changes (Equation (5.19)). From the Equation (5.19), when R increases (with x_D constant), the slope of ROL becomes steeper, i.e. $(R/R+1)$ and the intercept $(x_D/R+1)$ decreases. The ROL therefore rotates around the point (x_D, x_D) . The reflux ratio may be any value between a minimum value and an infinite value. The limit is the minimum reflux ratio (result in infinite stages) and the total reflux or infinite reflux ratio (result in minimum stages). With x_D constant, as R decreases, the slope $(R/R+1)$ of ROL (Equation (5.19)) decreases, while its intercept $(x_D/R+1)$ increases and rotates upwards around (x_D, x_D) as shown in Figure below. The ROL moves closer to the equilibrium curve as R

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decreases until point Q is reached. Point Q is the point of intersection between the q-line and the equilibrium curve.



Representation of minimum reflux ratio

At this point of intersection the driving force for mass transfer is zero. This is also called as Pinch Point. At this point separation is not possible. The R cannot be reduced beyond this point. The value of R at this point is known as the minimum reflux ratio and is denoted by R_{min} . For non-ideal mixture it is quite common to exhibit inflections in their equilibrium curves as shown in Figure below (a, b). In those cases, the operating lines where it becomes tangent to the equilibrium curve (called tangent pinch) is the condition for minimum reflux. The ROL cannot move beyond point P, e.g. to point K. The condition for zero driving force first occurs at point P, before point K which is the intersection point between the q-line and equilibrium curve. Similarly it is the condition SOL also. At the total reflux ratio, the ROL and SOL coincide with the 45° diagonal line. At this condition, total number of triangles formed with the equilibrium curve is equal minimum number of theoretical stages. The reflux ratio will be infinite.

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tray and the trays are operating at 100% efficiency. In practice, the trays are not perfect. There are deviations from ideal conditions. The equilibrium with temperature is sometimes reasonable for exothermic chemical reaction but the equilibrium with respect to mass transfer is not often valid. The deviation from the ideal condition is due to: (1) Insufficient time of contact (2) Insufficient degree of mixing. To achieve the same degree of desired separation, more trays will have to be added to compensate for the lack of perfect separability. The concept of tray efficiency may be used to adjust the the actual number of trays required. **Overall Efficiency** The overall tray efficiency, E_o is defined as:

$$E_o = \frac{\text{No. of theoretical trays}}{\text{No. of actual trays}} \quad (5.34)$$

It is applied for the whole column. Every tray is assumed to have the same efficiency. The overall efficiency depends on the (i) geometry and design of the contacting trays, (ii) flow rates and flow paths of vapor and liquid streams, (iii) Compositions and properties of vapor and liquid streams (Treybal, 1981; Seader and Henley, 1998). The overall efficiency can be calculated from the following correlations: The Drickamer-Bradford empirical correlation:

$$E_o = 13.3 - 66.8 \log(\mu) \quad (5.35)$$

The correlation is valid for hydrocarbon mixtures in the range of $342 \text{ K} < T < 488.5 \text{ K}$, $1 \text{ atm} < P < 25 \text{ atm}$ and $0.066 < \mu < 0.355 \text{ cP}$

The O'Connell correlation:

$$E_o = 50.3(\alpha\mu)^{-0.226} \quad (5.36)$$

Murphree Efficiency

The efficiency of the tray can also be calculated based on semi-theoretical models which can be interpreted by the Murphree Tray Efficiency E_M . In this case it is assumed that the vapor and liquid between trays are well-mixed and have uniform composition. It is defined for each tray according to the separation achieved on each tray based on either the liquid phase or the vapor phase. For a given component, it can be expressed as: Based on vapor phase:

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$$E_{MV} = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} \quad (5.37)$$

Based on liquid phase:

$$E_{ML} = \frac{x_n - x_{n-1}}{x_n^* - x_{n-1}} \quad (5.38)$$

1.7.2.4. Analysis of binary distillation by Ponchon-Savarit Method

Background Principle:

The method is concerned with the graphical analysis of calculating the theoretical stages by enthalpy balance required for desired separation by distillation process (Hines and Maddox, 1984). In this method, the enthalpy balances are incorporated as an integral part of the calculation however it is not considered in the analysis separation by distillation process by McCabe-Thele method. This procedure combines the material balance calculations with enthalpy balance calculations. This method also provides the information on the condenser and reboiler duties. The overall material balance for the distillation column is as below

$$F = D + B \quad (5.39)$$

For any component the material balance around the column can be written as:

$$Fx_F = Dx_D + Bx_B \quad (5.40)$$

Overall enthalpy balance for the column yields

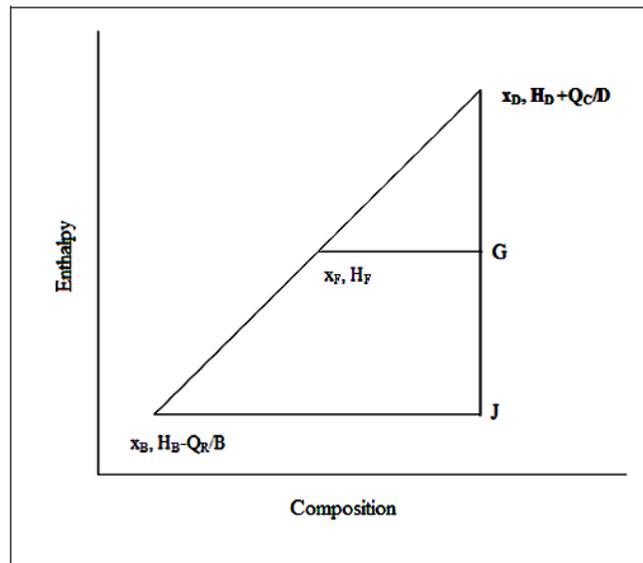
$$FH_F + Q_R = DH_D + BH_B + Q_C \quad (5.41)$$

where H is the enthalpy of the liquid stream, energy/mol, Q_R is the heat input to the reboiler, J/s and Q_C is the heat removed from condenser, J/s. The heat balance on rearrangement of Equation (5.41) gives

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$$FH_F = D\left(H_D + \frac{Q_C}{D}\right) + B\left(H_B - \frac{Q_R}{R}\right) \quad (5.42)$$

The Equation (5.41) is rearranged as Equation (5.42) for the convenience to plot it on the enthalpy-concentration diagram. The points represented by the feed, distillate and bottom streams can be plotted on the enthalpy-concentration diagram as shown in Figure below.



Representation of feed, distillate and bottom streams on the enthalpy-concentration

Substituting the Equation (5.39) into the Equation (5.40) and (5.42) we get

$$(D + B)x_F = Dx_D + Bx_B \quad (5.43)$$

$$(D + B)H_F = D\left(H_D + \frac{Q_C}{D}\right) + B\left(H_B - \frac{Q_R}{R}\right) \quad (5.44)$$

From the Equations (5.43) and (5.44) one can write

$$\frac{D}{B} = \frac{x_F - x_B}{x_D - x_F} = \frac{H_F - \left(H_B - \frac{Q_R}{R}\right)}{\left(H_D + \frac{Q_C}{D}\right) - H_F} \quad (5.45)$$

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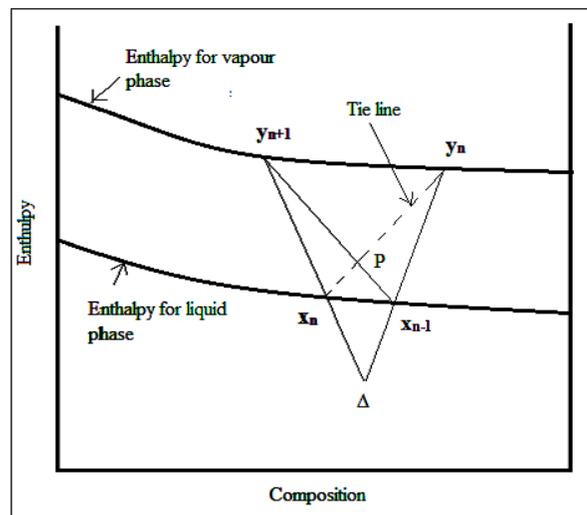
The Equation (5.45) can also be written on rearrangement as:

$$\frac{x_F - x_B}{H_F - (H_B - \frac{Q_R}{R})} = \frac{x_D - x_F}{(H_D + \frac{Q_C}{D}) - H_F} \quad (5.46)$$

Comparing the Equation (5.46) with the points plotted on Figure above, it is found that the left hand side of the Equation (5.46) represents the slope of the straight line between the points $(x_B, H_B - Q_R/B)$ and (x_F, H_F) . The right hand side of the Equation (5.46) represents the slope of the straight line passing through the points (x_F, H_F) and $(x_D, H_D - Q_C/D)$. From this it can be said that all three points are on a same straight line. The amount of distillate as per Equation (5.45) is proportional to the horizontal distance $\underline{x_F x_B}$ and the amount of bottoms is proportional to the horizontal distance $\underline{x_D x_F}$, then from the overall material balance it can be interpreted that the amount of feed is proportional to the horizontal distance $\underline{x_D x_B}$. This leads to the inverse lever rule. Based on this principle, the analysis of distillation column is called Enthalpy-composition analysis or Ponchon-Savarit analysis of distillation column.

Analysis of tray column

Consider the theoretical stage (Follow the outline graph of rectifying section) and the principle by which it operates is described in the enthalpy-composition diagram as shown in Figure below.



Operation principle of stage-wise binary distillation on enthalpy-concentration diagram

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The vapor entering to the tray (n), V_{n+1} is a saturated vapor of composition y_{n+1} where as the liquid entering to the tray is L_{n-1} of composition x_{n-1} . The point P in the above Figure represents the total flow to the tray. The point P lies in a straight line joining x_{n-1} and y_{n+1} . The distance $\underline{y_{n+1}P}$ is proportional to the quantity L_{n-1} and the distance $\underline{x_{n-1}P}$ is proportional to the quantity V_{n+1} as per lever rule. So

$$\frac{(y_{n+1}P) \text{ distance}}{(x_{n-1}P) \text{ distance}} = \frac{L_{n-1}}{V_{n+1}} \dots\dots\dots (5.47)$$

The sum of the liquid and vapor leaving the plate must equal the total flow to the plate. So the tie line must pass through the point P which represents the addition point of the vapor V_n and liquid L_n leaving the tray. The intersection of the tie line with the enthalpy-composition curves will represent the compositions of these streams. Around the tray n, the material balances can be written as:

$$V_{n+1} - L_n = V_n - L_{n-1} \tag{5.48}$$

$$V_{n+1}y_{n+1} - L_nx_n = V_ny_n - L_{n-1}x_{n-1} \tag{5.49}$$

The enthalpy balance around the tray gives

$$V_{n+1}H_{V,n+1} - L_nH_{L,n} = V_nH_{V,n} - L_{n-1}H_{L,n-1} \tag{5.50}$$

Where H_V is the enthalpy of the vapor and H_L is the enthalpy of the liquid. From the material and enthalpy balance Equations above mean that the stream that added to V_{n+1} to generate L_n is same to the stream that must be added to V_n to generate L_{n-1} . In the Figure (Operation principle of stage-wise binary distillation on enthalpy-concentration diagram), Δ represents the difference point above and below the tray. This point of a common difference point can be extended to a section of a column that contains any number of theoretical trays.

STEPWISE PROCEDURE TO DETERMINE THE NUMBER OF THEORETICAL TRAYS:

Step 1: Draw the equilibrium curve and the enthalpy concentration diagram for the mixture to be separated

Step 2: Calculate the compositions of the feed, distillate and bottom products. Locate these compositions on the enthalpy-concentration diagram.

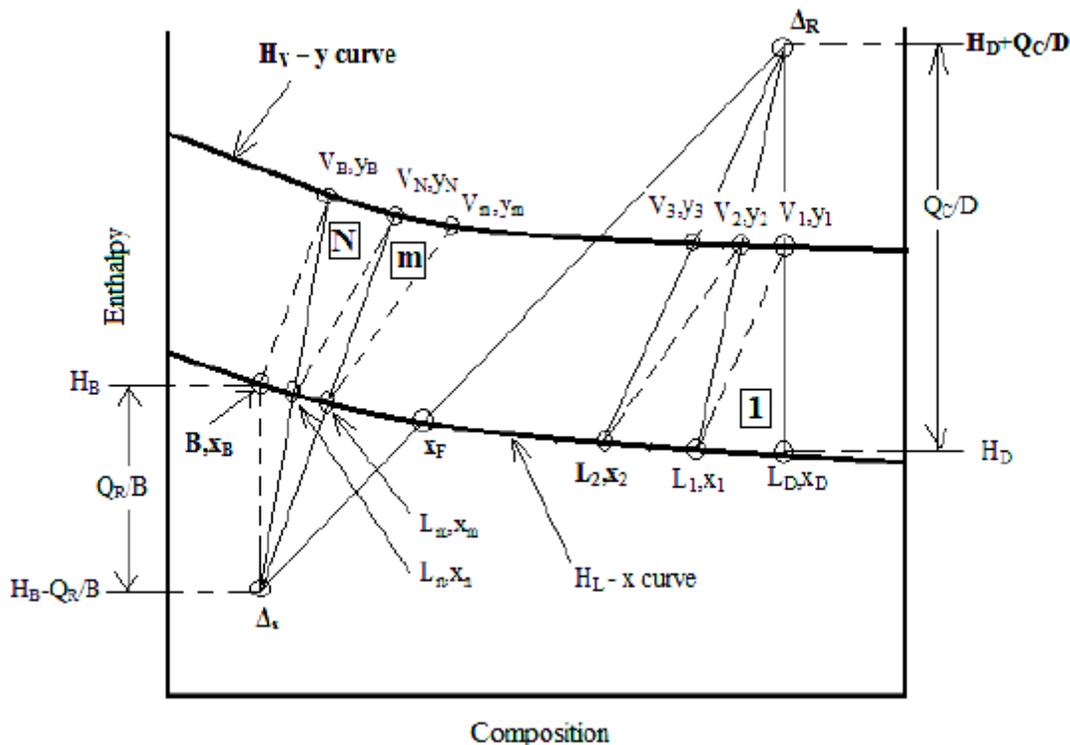
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Step 3: Estimate the reflux rate for the separation and locate the rectifying section difference point as Δ_R as shown in Figure below. Point y_1 is the intersection point of line joining point x_D and Δ_R and H_{V-y} curve.

Step 4: Locate the stripping section difference point Δ_s . The point Δ_s is to be located at a point where the line from Δ_R through x_F intersects the x_B composition coordinate as shown in Figure below.

Step 5: Step off the trays graphically for the rectifying section. Then the point of composition x_1 of liquid of top tray is to be determined from the equilibrium relation with y_1 of vapor which is leaving the tray and locate it to the H_{L-x} curve. Then the composition y_2 is to be located at the point where the line of points Δ_R and x_1 intersects H_{V-y} curve. This procedure is to be continued until the feed plate is reached.

Step 6: Similarly follow the same rule for stripping section. In the stripping section, the vapor composition y_B leaving the reboiler is to be estimated from the equilibrium relation. Then join the y_B and Δ_s to find the x_N . The vapor composition y_N is to be determined by extending a tie line to saturated vapor curve H_{V-y} . The procedure is to be continued until the feed tray is attained.



Representation of estimation of no of stages by Ponchon-Savarit Method

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Determination of the reflux rate:

The reflux rate can be calculated from the energy balance around the condenser as:

$$V_1 H_{V,1} = L_D H_D + D H_D + Q_C \quad (5.51)$$

By substituting $V_1 = L_D + D$ into Equation (5.51) and rearranging, it can be written as:

$$\frac{L_D}{D} = \frac{(H_D + Q_C / D) - H_{V,1}}{H_{V,1} - H_D} = \frac{\overline{\Delta_R H_{V,1}}}{\overline{H_{V,1} H_D}} \quad (5.52)$$

Where $\overline{\Delta_R H_{V,1}}$ and $\overline{H_{V,1} H_D}$ are the lengths of lines between points Δ_R and $H_{V,1}$ and $H_{V,1}$ and H_D . The internal reflux ratio between any two stages in rectifying section can be expressed as:

$$\frac{L_n}{V_{n+1}} = \frac{(H_D + Q_C / D) - H_{V,n+1}}{(H_D + Q_C / D) - H_{L,n}} = \frac{\overline{\Delta_R H_{V,n+1}}}{\overline{\Delta_R H_{L,n}}} \quad (5.53)$$

Whereas in the stripping section it can be expressed as:

$$\frac{L_{m-1}}{V_m} = \frac{H_{V,m} - (H_B - Q_R / B)}{H_{L,m-1} - (H_B - Q_R / B)} \quad (5.54)$$

The relationship between the distillate and bottom products in terms of compositions and enthalpies can be made from the material balance around the overall column which can be written as:

The relationship between the distillate and bottom products in terms of compositions and enthalpies can be made from the material balance around the overall column which can be written as:

Mass Transfer-I

$$FH_F + Q_R = DH_D + BH_B + Q_C \quad (5.55)$$

Overall material balance $F = D + B$ combining with Equation (5.55) yields

$$\frac{D}{B} = \frac{H_F - (H_B - Q_R / B)}{(H_D + Q_C / D) - H_F} = \frac{x_F \Delta_S}{x_F \Delta_R} \quad (5.56)$$

Minimum number of trays

In this method, if D approaches zero, the enthalpy coordinate $(H_D + Q_C/D)$ of the difference point approaches infinity. Other way it can be said that Q_C becomes large if L becomes very large with respect to D . Similarly enthalpy coordinate for stripping section becomes negative infinity as B approaches zero or liquid loading in the column becomes very large with respect to B . Then the difference points will locate at infinity. In such conditions, the trays required for the desired separation is referred as minimum number of trays. The thermal state of the feed has no effect on the minimum number of trays required for desired separation.

Minimum reflux

The minimum reflux for the process normally occurs at the feed tray. The minimum reflux rate for a specified separation can be obtained by extending the tie line through the feed composition to intersect a vertical line drawn through x_D . Extend the line to intersect the x_B composition line determines the boilup rate and the reboiler heat duty at minimum reflux.

MODULE -IV

HUMIDIFICATION AND AIR CONDITIONING

1.1 Basic concepts

Humidification is the process of constituting the water-vapor content in a gas. The reverse of the operation is called dehumidification. Both are important for many industrial operations such as air conditioning, gas cooling, controlled drying of wet solids, comfort heating etc. When a gas is brought in contact with a pure liquid in which it is essentially insoluble, interphase mass and heat transfer takes place.

Four major applications of humidification operations are as follows:

- a) Humidification of gases for controlled drying of wet solids
- b) Dehumidification and cooling of gas in air conditioning
- c) Gas cooling with the help of water
- d) Cooling of liquid (e.g. water) before reuse

1.1.1 Terminologies and definitions Three most important quantities, namely, 'temperature', 'humidity' and 'enthalpy', are essential terminologies in dealing humidification.

1) Dry-bulb temperature: It is true temperature of air measured (or, any non-condensable and condensable mixture) by a thermometer whose bulb is dry.

2) Wet-bulb temperature: It is the steady-state temperature attained by a small amount of evaporating water in a manner such that the sensible heat transferred from the air to the liquid is equal to the latent heat required for evaporation.

3) Relative humidity: It is the ratio of partial pressure of water vapor (p_A) in air at a given temperature to the vapor pressure of water (p_A^0) at the same temperature.

$$\% \text{relative humidity} = \frac{p_A}{p_A^0} \times 100 \quad (6.1)$$

"Relative humidity does not 'explicitly' give the moisture content of a gas, but gives the 'degree of saturation' of the gas at a given temperature.

4) Absolute humidity (simply humidity): It is the direct measurement of moisture content in a gas. The mass of water vapor per unit mass of dry gas is called absolute humidity, Y .

Mass Transfer-I

$$Y' = \left(\frac{p_A}{P - p_A} \right) \frac{18.02}{28.97} \quad (6.2)$$

It is occasionally called '**Grosvenor humidity**' after the name of the inventor.

5) Percent humidity or percent saturation: It is the relation between absolute humidity to that of saturation humidity at the same temperature and pressure.

$$\%Humidity = \frac{Y'}{Y'_s} \times 100 \quad (6.3)$$

where, Y' is absolute humidity of sample of air and Y'_s is humidity at same temperature and pressure if saturated with water vapor.

$$Y'_s = \left(\frac{p_A^v}{P - p_A^v} \right) \frac{18.02}{28.97} \quad (6.4)$$

and vapor pressure of water can be calculated by Antoine Equation:

$$\ln p_A^v = 11.96481 - \frac{3984.923}{(T - 39.97)} \text{ where, pressure is in bar and temperature is in K.}$$

6) Dew point: Dew point is a temperature at which a vapor-gas mixture must be cooled (at constant humidity) to become saturated. The dew point of a saturated gas equals the gas temperature. If a vapor-gas mixture is gradually cooled at a constant pressure, the temperature at which it just becomes saturated is also called its dew point.

7) Humid volume: The humid volume, V_H , is defined as the volume of unit mass of dry air with accompanying water vapor at a given temperature and pressure.

$$V_H = \left(\frac{1}{28.97} + \frac{1}{18.02} \right) \times 22.4 \times \left(\frac{T_G + 273}{273} \right) \text{ m}^3/\text{kg dry air} \quad (6.5)$$

assuming ideal gas behavior. T_G is gas temperature in °C.

8) Humid heat: The humid heat, c_H , is the heat energy required to raise the temperature of unit mass of dry air with the accompanying water vapor by one (1) degree. $c_H = 1.005 + 1.88Y'$ kJ/(kg dry air)(K); first part of right hand side is heat capacity of dry air in kJ/kg.K and second part is heat capacity of water vapor in kJ/kg.K.

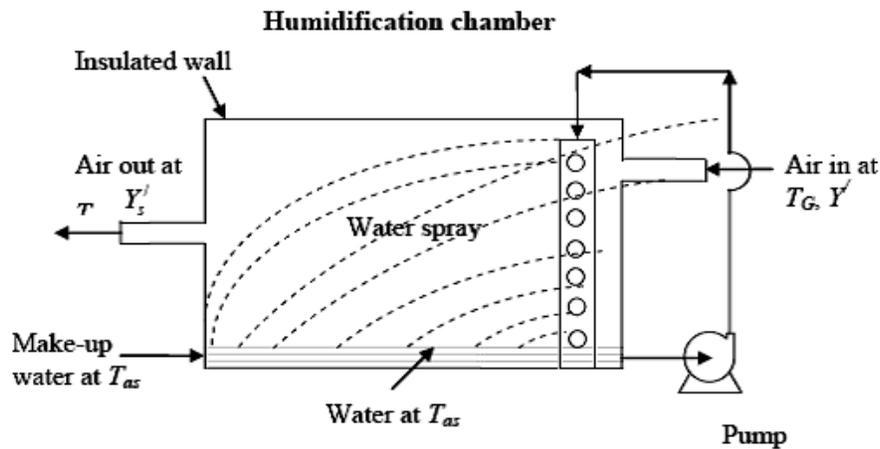
Mass Transfer-I

9) Enthalpy: The enthalpy of a vapor-gas mixture is the sum of the relative enthalpies of gas and vapor content.

$$H' = c_H(T_G - T_0) + Y' \lambda_0 = (1.005 + 1.88Y')(T_G - T_0) + 2500Y' \text{ kJ/kg} \quad (6.6)$$

where λ_0 is latent heat of vaporization of water, 2500 kJ/Kg.

1.1.2 Adiabatic saturation temperature:



Schematic representation of adiabatic saturation of air

The schematic of the adiabatic saturation of air by water is shown in Figure above. The air stream attains thermal equilibrium with water at temperature T_{as} and also gets saturated with water vapor at that temperature before it leaves. A small quantity of water at the temperature T_{as} is fed to the humidification chamber continuously in order to compensate for the vaporization loss of water. The chamber operates adiabatically, wall is well-insulated. The temperature T_{as} attained by air (same as water) is called "**adiabatic saturation temperature, T_{as}** ".

$$\text{Enthalpy of inlet air, } H'_i = c_H(T_G - T_{as}) + \lambda_2 Y'_i \quad (6.7)$$

$$\text{Enthalpy of exit air, } H'_o = c_H(T_{as} - T_{as}) + \lambda_2 Y'_o = \lambda_2 Y'_o \quad (6.8)$$

At steady state, $H'_i = H'_o$;

Hence,

$$c_H(T_G - T_{as}) + \lambda_2 Y'_i = \lambda_2 Y'_o \quad (6.9)$$

$$(T_G - T_{as}) = \frac{\lambda_2}{c_H} (Y'_o - Y'_i) \quad (6.10)$$

Mass Transfer-I

1.1.3 Wet bulb temperature

When evaporation of water occurs?

If the vapor pressure of water is higher than the partial pressure of water vapor in the ambient air, evaporation occurs. The latent heat for evaporation will be supplied by (i) surrounding air and (ii) water drop itself. Now, consider a drop of water at the tip of thin wire. As temperature of water drop decreases with time, vapor pressure decreases causing a reduction in partial pressure driving force. Temperature driving force for heat transfer from ambient air to water increases. If sufficient time is allowed, a steady state temperature will be attained by drop. This is wet bulb temperature.

Factors that have influence on wet-bulb temperature

- (i) Dry bulb temperature of air T_G
- (ii) Humidity, Y'
- (iii) Air velocity
- (iv) Shape of the thermometer bulb

The combination of a dry-bulb and wet-bulb thermometer is called a “psychrometer”.

Determination of relationship between wet-bulb and dry-bulb temperature

$$\text{Heat flux, } q = h_G(T_G - T_w) \quad (6.11)$$

$$\text{Molar flux, } N_A = k_G(p_w - p_A) \quad (6.12)$$

Since, heat flux is sufficient to meet requirement of latent heat of vaporization at steady state.

$$\text{Hence, } h_G(T_G - T_w) = \lambda_w M_w k_G (p_w - p_A) = \lambda_w K_Y' (Y_w' - Y') \quad (6.13)$$

$$(T_G - T_w) = \frac{\lambda_w (Y_w' - Y')}{\left(\frac{h_G}{K_Y'} \right)} \quad (6.14)$$

$$\frac{h_G}{K_Y'} \approx c_H; \quad \frac{h_G}{c_H K_Y'} \approx 1 \rightarrow \text{Lewis relation}$$

Mass Transfer-I

For any system,

$$\frac{h_G}{K_Y'} = 1.231Sc^{0.56} \text{ kJ/kg.K}$$

Now Equation (6.14) becomes, $(T_G - T_w) = \frac{\lambda_w(Y_w' - Y')}{c_H}$ (6.15)

Equations (6.10) and (6.15) are identical and $T_{as} = T_w$.

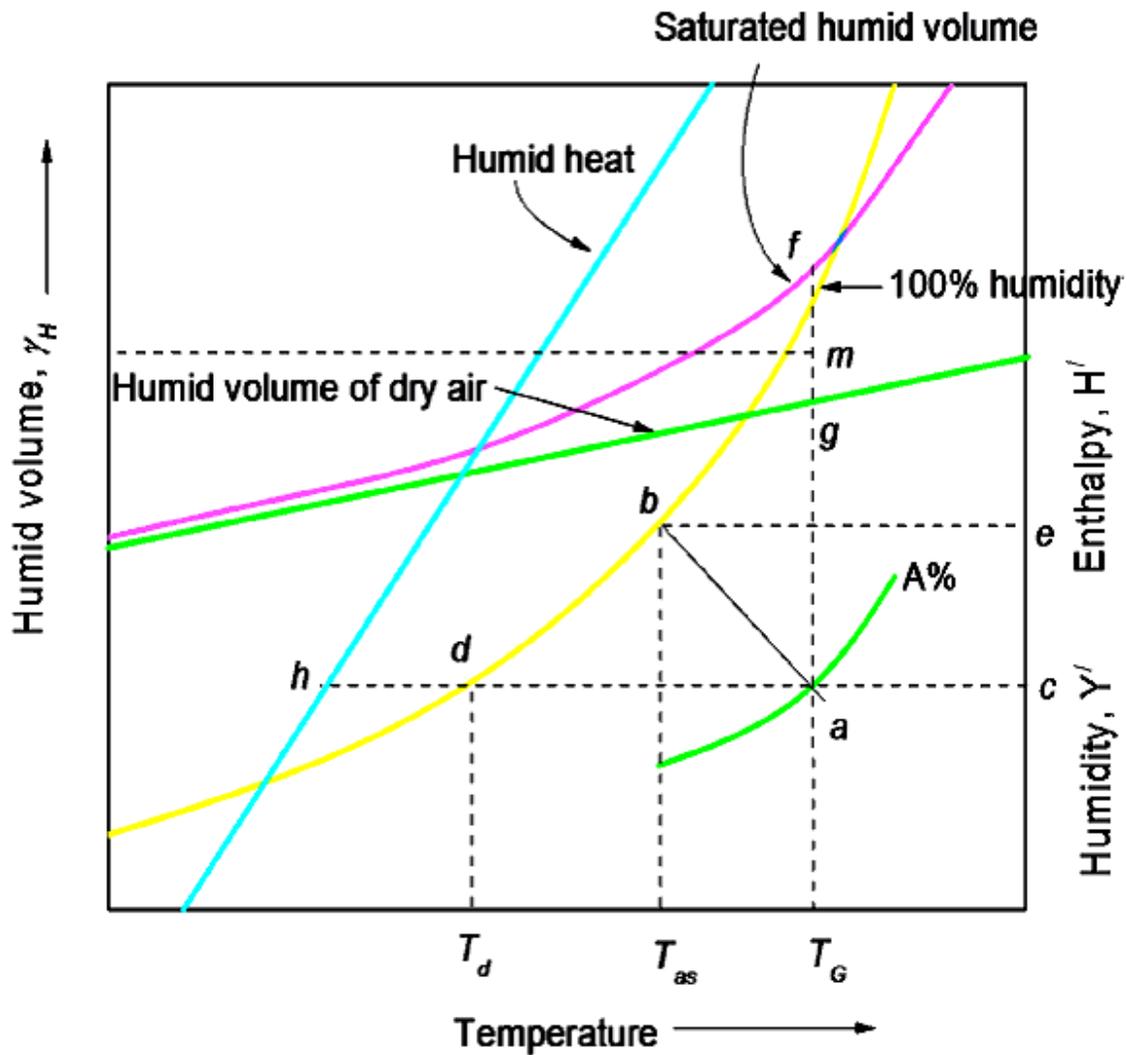
Adiabatic saturation temperature and wet-bulb temperature are nearly equal for air-water system.

$(T_G - T_w)$ is called wet-bulb depression.

1.2 The Psychrometric chart construction and its use

Seven important quantities, namely, dry-bulb temperature, wet-bulb temperature, relative humidity, absolute humidity, dew point, enthalpy and specific volume, are all inter-related. The psychrometric chart characterizes this interdependence. If any two of these quantities are known, the other five quantities can be readily obtained from the Psychrometric chart. The Psychrometric chart can be obtained from the link: <http://en.wikipedia.org/wiki/Psychrometrics>.

The interdependency of these seven properties is presented in Figure below. If T_G is the dry-bulb temperature of air and Y' is its humidity, its state is denoted by point a. It falls on the constant humidity line, A%. The adiabatic saturation line through a is ab. c point indicates its humidity, Y' . The adiabatic saturation temperature, T_{as} is obtained by drawing the vertical line through b. For air-water system, wet-bulb temperature T_w is practically same as T_{as} . The humidity of the adiabatically saturated air is given by the point e. The dew point T_d is given by the point „d“ that can be reached by moving horizontally from the point a to 100% humidity line and then moving vertically down to the temperature axis. The humid volume of saturated air at T_G corresponds to the point „f“ and that of dry air at T_G given by point „g“. The point m gives the humid volume if the humidity is Y' and it is reached by interpolation between q and f. Enthalpy of a sample of air can also be obtained from humidity chart.



Determination of properties from the psychrometric chart.

1.2 Humidification and dehumidification operations and design calculations

Humidification operations:

In this operation, water transfers from liquid phase to gas phase. Hence, moisture content of air increases. Air with particular moisture content is useful for drying of a solid under controlled condition.

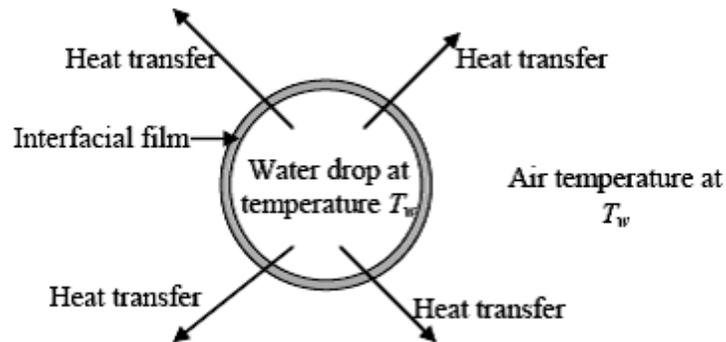
Dehumidification operations:

It is the reverse phenomena of humidification. A portion of water vapor from moist warm air is condensed by contacting cold water in air conditioning.

1.3 Cooling tower principle and operation

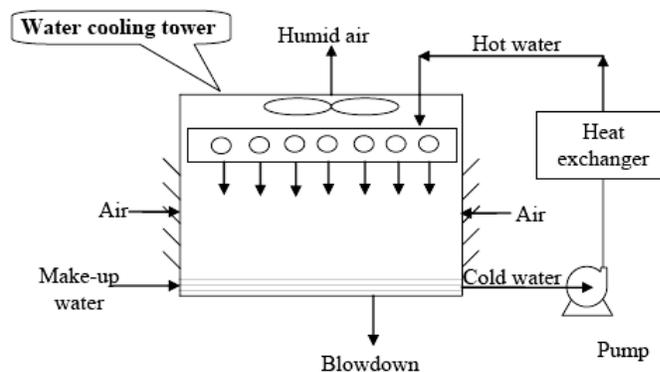
Mass Transfer-I

A cooling tower is a special type of heat exchanger in which the warm water and the air are brought in direct contact for '**evaporative cooling**'. It provides a very good contact of air and water in terms of the contact area and mass transfer coefficient of water vapor while keeping air pressure drop low. Enthalpy of air is lower than enthalpy of water. Sensible heat and latent heat transfer take place from water drop to surrounding air. Schematic of heat transfer from water drop to surrounding air is presented in Figure below.



Schematic of heat transfer from water drop to surrounding air

Thus, cooling is accomplished by sensible heat transfer from water to air and evaporation of a small portion of water. A generalized cooling tower system is shown in Figure below. The hot water which is coming from heat exchanger is sprayed at the top of the cooling tower. Air enters through the louvers at the two opposite walls of the cooling tower. During cooling process of water, around 2% water is evaporated. Make up water is used to compensate the water loss due to evaporation. Blowdown is there to drain a part of water containing solid deposit. The exit cold water from the cooling tower is used in the heat exchanger or other unit operation.



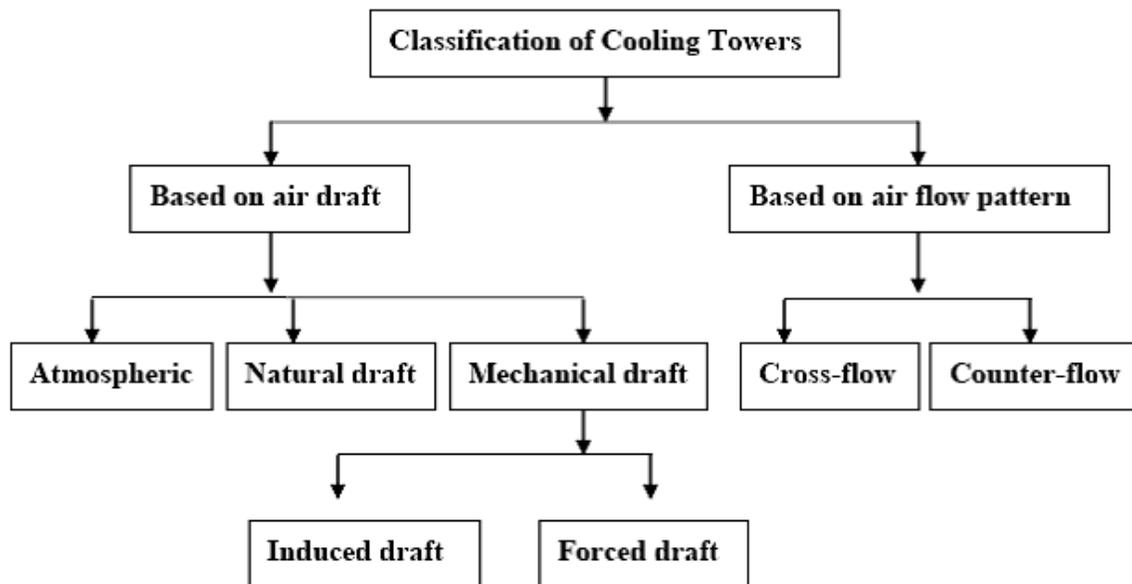
Generalized cooling tower system.

Mass Transfer-I

Factors govern the operation of cooling tower

- i. The dry-bulb and wet-bulb temperatures of air
- ii. Temperature of warm water
- iii. The efficiency of contact between air and water in terms of volumetric mass transfer coefficient. ($k'_y a$)
- iv. Contact time between air and water
- v. The uniformity of the distribution of the phases within the tower
- vi. Air pressure drop
- vii. Desired temperature of cooled water

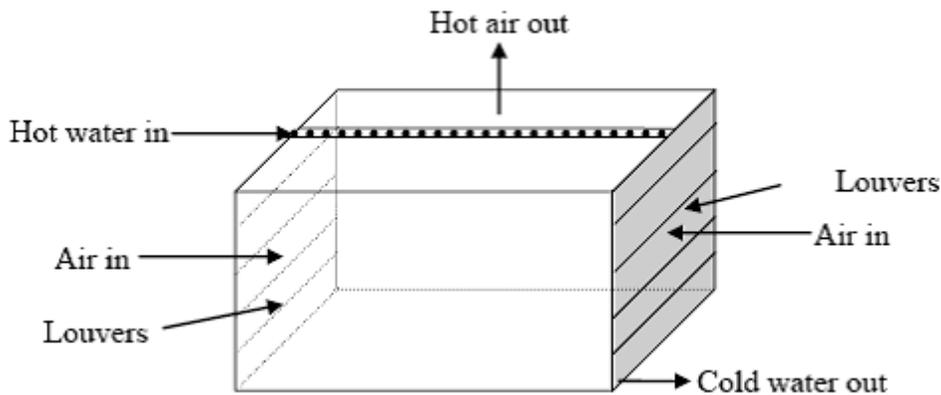
1.5 Types of equipment



(A) Atmospheric Towers

It is a big rectangular chamber with two opposite 'louvered' walls. Tower is packed with a suitable 'tower fill'. Atmospheric air enters the tower through louvers driven by its own velocity. Direction and velocity of wind greatly influence its performance. Figure below shows the schematic of the atmospheric cooling tower.

Mass Transfer-I



Schematic of atmospheric cooling tower.

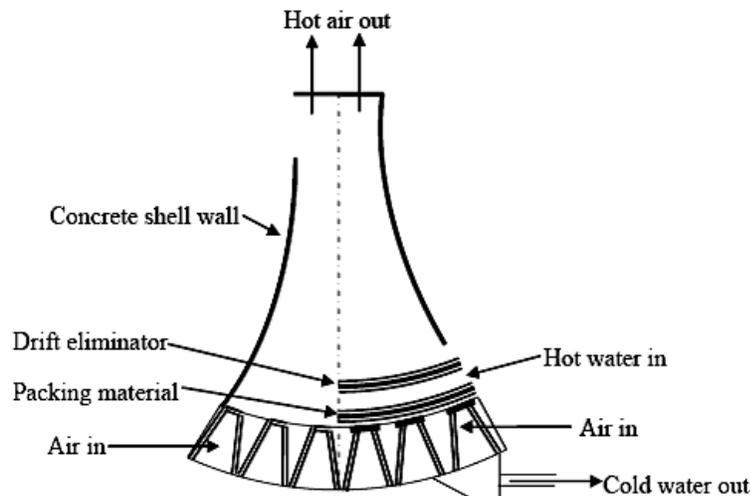
(B) Natural Draft Towers

A natural draft cooling tower has a large reinforced concrete shell of hyperbolic shape (also called 'hyperbolic tower'). Natural flow of air occurs through the tower; hence it is called natural draft (refer Figure below).

Factors responsible for creating natural draft

- (a) A rise in temperature and humidity of air in the column reduces its density
- (b) Wind velocity at the tower bottom

Fan is used to enhance the air flow rate in fan assisted natural draft tower. The typical diameter of tower is 150 m and capacity is 5,00,000 gallon/minute.



Mass Transfer-I

Schematic of natural draft tower.

Why hyperbolic shape?

- (i) More packing materials can be placed at the bottom
- (ii) The entering air gets smoothly directed towards the centre
- (iii) Greater structural strength and stability

(A) Mechanical Draft Towers: forced draft towers and induced draft towers

Fans are used to move air through the tower in mechanical draft cooling towers. Two types of mechanical draft towers are there, namely, forced draft tower and induced draft tower.

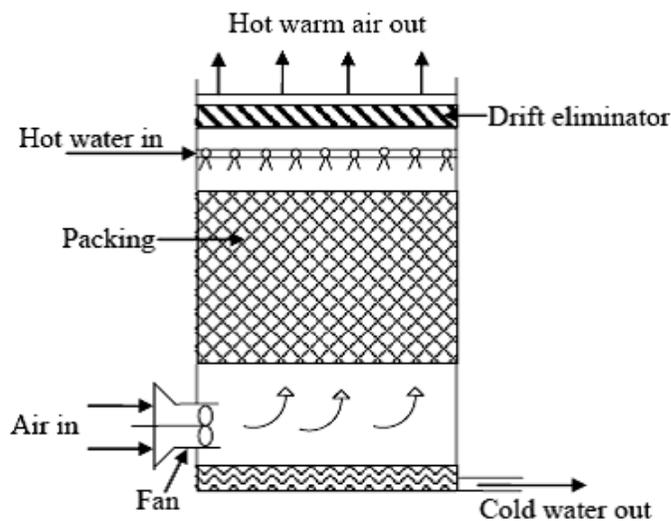
Forced draft towers: It can be seen from Figure below; that it has one or more fans located at the tower bottom to push air into tower.

Advantages:

- (a) A part of the velocity head of air thrown by the blower is converted to pressure head on entering into the tower. It makes energy efficient than induced draft.
- (b) Less susceptible to vibrations as fans are installed near the ground.

Disadvantages:

- (a) Air flow through the packing may not be uniform
- (b) Some of the warm and humid air may be recirculated back. Recirculation rate becomes low if the wind velocity is high. It is not popular except for small capacities.



Schematic of forced draft towers.

Mass Transfer-I

Induced draft towers:

One or more fans are installed at the top of the tower. Depending on the air inlet and flow pattern, induced draft towers are of two types, cross-flow and counter flow towers.

Major advantages of countercurrent induced draft cooling tower

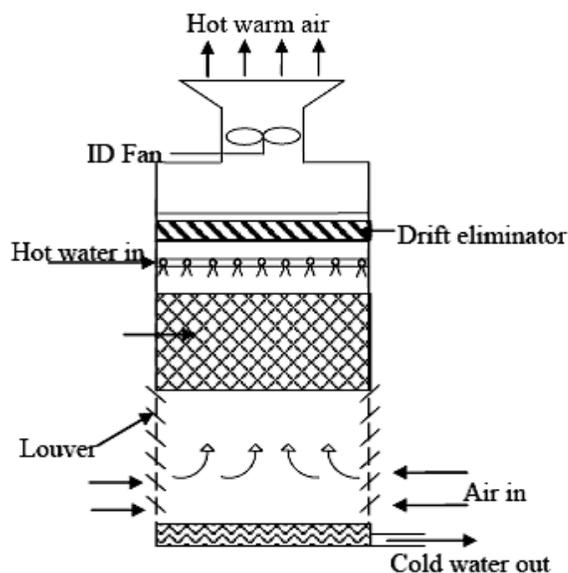
- (a) Relatively dry air contacts the coldest water at the bottom of the cooling tower
- (b) Humid air is in contact with the warm water and hence maximum average driving force prevails for both heat and mass transfer.

Disadvantage of induced draft towers compared to forced draft towers

It consumes more horse power. Cross-flow induced draft cooling tower requires less motor horse power than countercurrent induced draft cooling towers.

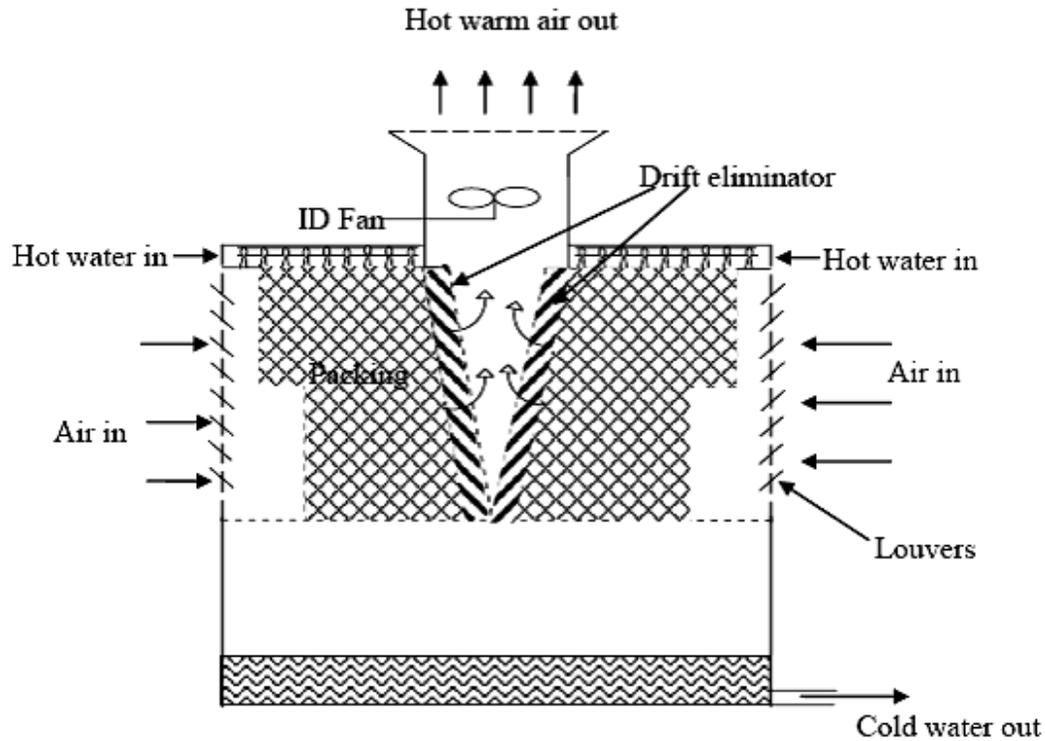
(B) Cross-current and counter-current

Cross-flow induced draft cooling tower supplies horizontal air flow along the packed height and requires less motor horse power than the counter-flow type. Additional 'cells' may be added to raise the capacity. The schematic of induced draft counter-flow and cross-flow cooling towers are presented in Figures below.



Mass Transfer-I

Schematic of mechanical draft counter-flow tower.



Schematic of mechanical draft cross-flow tower.

SPRAY POND:

A **spray pond** is a reservoir in which warmed water is cooled for reuse by evaporation of water discharged from nozzles in spray or mist form over the pond. A comprehensive image is shown below.



Image of industrial spray pond.

Mass Transfer-I

The warm water is sprayed into cooler air, cooling down as it reaches the water. The spray pond is the predecessor to the natural draft cooling tower, which is much more efficient and takes up less space but has a much higher construction cost. A spray pond requires between 25 to 50 times the area of a cooling tower. However, some spray ponds are still in use today.

SPRAY TOWER:

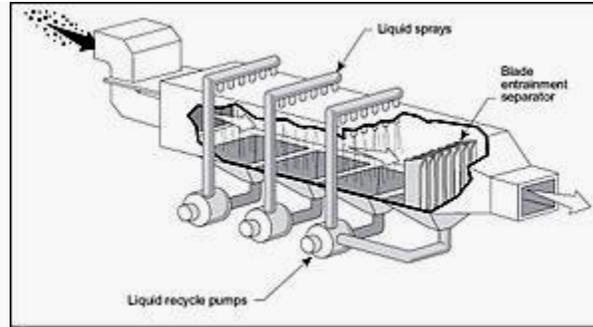
A **spray tower** (or **spray column** or **spray chamber**) is gas-liquid contactor used to achieve the mass and heat transfer between a continuous gas phase (that can contain dispersed solid particles) and a dispersed liquid phase. It consists of empty cylindrical vessel made of steel or plastic and nozzles that spray liquid into the vessel. The inlet gas stream usually enters the bottom of the tower and moves upward, while liquid is sprayed downward from one or more levels. This flow of inlet gas and liquid in the opposite direction is called countercurrent flow.

This type of technology can be used for example as a wet scrubber for air pollution control. Countercurrent flow exposes the outlet gas with the lowest pollutant concentration to the freshest scrubbing liquid. Many nozzles are placed across the tower at different heights to spray all of the gas as it moves up through the tower. The reason for using many nozzles is to maximize the number of fine droplets impacting the pollutant particles and to provide a large surface area for absorbing gas.

Theoretically, the smaller the droplets formed, the higher the collection efficiency achieved for both gaseous and particulate pollutants. However, the liquid droplets must be large enough to not be carried out of the scrubber by the scrubbed outlet gas stream. Therefore, spray towers use nozzles to produce droplets that are usually 500–1000 μm in diameter. Although small in size, these droplets are large compared to those created in the venturi scrubbers that are 10–50 μm in size. The gas velocity is kept low, from 0.3 to 1.2 m/s (1–4 ft/s) to prevent excess droplets from being carried out of the tower.

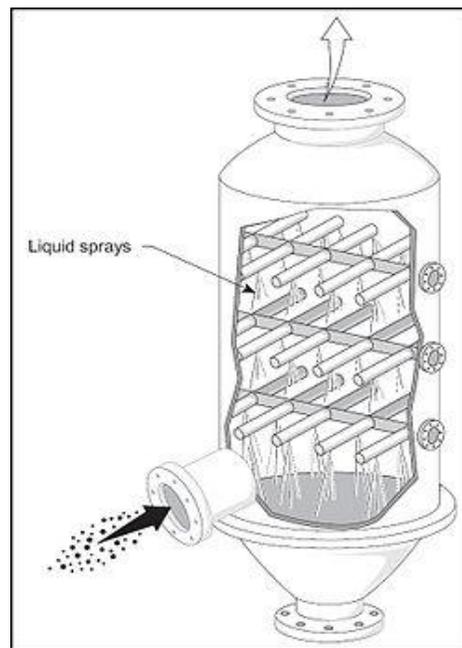
In order to maintain low gas velocities, spray towers must be larger than other scrubbers that handle similar gas stream flow rates. Another problem occurring in spray towers is that after the droplets fall short distances, they tend to agglomerate or hit the walls of the tower. Consequently, the total liquid surface area for contact is reduced, reducing the collection efficiency of the scrubber.

Mass Transfer-I



Crosscurrent-flow spray tower

In addition to a countercurrent-flow configuration, the flow in spray towers can be either a cocurrent or crosscurrent in configuration.



countercurrent-flow spray tower.

In cocurrent-flow spray towers, the inlet gas and liquid flow in the same direction. Because the gas stream does not "push" against the liquid sprays, the gas velocities through the vessels are higher than in countercurrent-flow spray towers. Consequently, cocurrent-flow spray towers are smaller than countercurrent-flow spray towers treating the same amount of exhaust flow. In crosscurrent-flow spray towers, also called horizontal-spray scrubbers, the gas and liquid flow in directions perpendicular to each other.

Mass Transfer-I

In this vessel, the gas flows horizontally through a number of spray sections. The amount and quality of liquid sprayed in each section can be varied, usually with the cleanest liquid (if recycled liquid is used) sprayed in the last set of sprays.

.....THE END.....

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