MASS TRANSFER

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TOPICS:

- INTRODUCTION TO MASS TRANSFER
- SEPARATION PROCESS
  - MOLECULAR DIFFUSION
  - INTERPHASE MASS TRANSFER
  - MASS TRANSFER COEEFICEIENTS
  - GAS ABSORPTION
  - GAS LIQUID CONTACTING EQUIPMENTS
  - DISTILLATION
  - DRYING
  - CRYSTALLISATION

INTRODUCTION OF MASS TRANSFER

- Mass transfer may occur in a gas mixture, a liquid solution or solid.

- Mass transfer occurs whenever there is a gradient in the concentration of a species ⟶ Driving Force
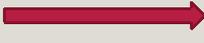
- The basic mechanisms are the same whether the phase is a gas, liquid, or solid.

- The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial process.

MASS TRANSFER IN NATURE

- Aquatic life uses dissolved oxygen for survival and supply of oxygen comes from air

- Absorption of O_2 into the blood stream occurs in the lungs of animals and removal of CO_2 from the animal cells into the blood stream

- Hydrolyzed food materials get absorbed in the intestines

- Process of doping the junctions of a semi-conductor

- Dispersion of a pollutant discharged at a point in flowing water

SEPARATION PROCESS

INTRODUCTION TO SEPARATION PROCESS

- Separation of mixtures constitutes major class of operations in CPI and allied industries

- The separation process involved are based on the principles of mass transfer and are called mass transfer operations

- Typical Examples Of Separation process:
  - Separation of ammonia from mixture of ammonia and air by water
  - Separation of organic vapor from mixture of gases by adsorption
  - Separation of CO_2 from flue gas ⟶ CO_2 capture
  - Separation of mixture on the basis of volatility by Heat input

CLASSIFICATION OF MASS TRANSFER OPERATIONS

- Direct Contact of two Immiscible phases

    ❑ Gas-Gas ⟶ All gases are soluble in each other. Not practically realizable

    ❑ Gas-Liquid ⟹⟶ Includes Distillation, Gas absorption, Stripping

    ❑ Liquid-Soild ⟹⟶

- **Miscible phases separated by Membranes:**
  - ❑ **Gas-gas**

  - ❑ **Gas-Liquid**

  - ❑ **Liquid-liquid**
  General Examples:

    - **Electrodialysis**

    - **Osmosis**

    - **Reverse Osmosis**

Separation Process	Separation agent	Typical Applications
Gas Absorption & Stripping	Solvent	Removal of CO_2 from synthesis gas and CO_2 and H_2S from natural gas.
Distillation	Heat	Fractionation of crude oil.
Liquid-Liquid Extraction	Solvent	Removal of aromatics from gasoline.
Solid- Liquid Extraction	Solvent	Extraction of caffein from coffee.
Drying	Heat/Drying gas	Drying of fruits and polymer beads.
Adsorption	Adsorbent Solid	Separation of organics from gas.
Ion Exchange	Ion Exchange Resin	Separation of salts.
Crystallization	Heat (Removal)	Production of salts and sugar.
Membrane separation	Membrane	Desalination of water.

DIFFUSION
UNDERSTANDING BY EXAMPLES

- A drop of ink released in water gradually spreads to make the water uniformly colored

- Fragrance of bunch of roses and perfume reaches out to a person

- Dissolution of sugar in water

MOLECULAR DIFFUSION

- **Def**: Molecular diffusion or molecular transport can be defined as the transfer or movement of individual molecules through a fluid by mean of the random, individual movements of the molecules.

- The phenomenon leads ultimately to uniform concentration

- The two modes of mass transfer:
  - Molecular diffusion
  - Convective mass transfer

FICK'S LAW OF DIFFUSION

- Fick's Law

$$J^*_{AZ} = -cD_{AB}\frac{dx_A}{dz}$$

J^*_{AZ} is the molar flux of component A in the z direction in kg mol A/s.m^2.

D_{AB} is the molecular diffusivity of the molecule A in B in m^2/s c is the concentration of A in kg mol/m^3.
z is the distance of diffusion in m

EXAMPLE:

Q. A mixture of He and N_2 gas is contained in a pipe at 298 K and 1 atm total pressure which is constant throughout. At one end of the pipe at point 1 the partial pressure p_{A1} of He is 0.6 atm and at the other end 0.2 m p_{A2} = 0.2 atm. Calculate the flux of He at steady state if D_{AB} of the He-N_2 mixture is 0.687 x 10^{-4} m^2/s.

A. Since a total pressure P is constant, the c is constant, where c is as follows for a gas according to the perfect gas law:

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT} = c$$

- Where n is kg mole A plus B, V is volume in m^3, T is temperature in K, R is 8314.3 m^3.Pa/kg mol.K or R is 82.057 x 10^{-3} cm^3. atm/g. mol. K, and c is kg mole A plus B/m^3.

- For steady state the flux J^*_{Az} in Eq.(6.1-3) is constant. Also D_{AB} for gas is constant. Rearranging Eq. (6.1-3) and integrating.

$$J^*_{Az} \int_{z_1}^{z_2} dz = -D_{AB} \int_{c_{A1}}^{c_{A2}} dc_A$$

$$J^*_{AZ} = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1}$$

- Also, from the perfect gas law, $p_A V = n_A RT$, and

$$c_{A1} = \frac{p_{A1}}{RT} = \frac{n_A}{V}$$

This is the final equation to use, which is in a form easily used for gases.

Partial pressures are $p_{A1} = 0.6$ atm $= 0.6 \times 1.01325 \times 10^5 = 6.04 \times 10^4$ Pa and $p_{A2} = 0.2$ atm $= 0.2 \times 1.01325 \times 10^5 = 2.027 \times 10^4$ Pa.

Then, using SI units,

$$J_{Az}^* = \frac{(0.687 \times 10^{-4})(6.08 \times 10^4 - 2.027 \times 10^4)}{8314(298)(0.20 - 0)}$$

$$= 5.63 \times 10^{-6} \text{ kg mol } A/\text{s} \cdot \text{m}^2$$

- In a non-uniform solution containing more than two constituents, leads to the use of two fluxes to describe the motion of one constituent:

- N, the flux relative to a fixed location in space

- J, the flux of a constituent relative to average molar velocity of all constituents

- For Binary mixture:

$$N_A = Nx_A + J_A$$

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

STEADY STATE MOLECULAR DIFFUSION IN FLUIDS AT REST AND IN LAMINAR FLOW

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} c}{z} \ln \frac{N_A/(N_A + N_B) - c_{A2}/c}{N_A/(N_A + N_B) - c_{A1}/c}$$

For gases,

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} p_t}{RTz} \ln \frac{[N_A/(N_A + N_B)] p_t - \bar{p}_{A2}}{[N_A/(N_A + N_B)] p_t - \bar{p}_{A1}}$$

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} p_t}{RTz} \ln \frac{N_A/(N_A + N_B) - y_{A2}}{N_A/(N_A + N_B) - y_{A1}}$$

- For diffusion of A in non-diffusing B;

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

- For equimolal counter-diffusion:

$$N_A = \frac{D_{AB}P}{RT(Z_2 - Z_1)}(y_{A_1} - y_{A_2})$$

$$= \frac{D_{AB}}{RT(Z_2 - Z_1)}(P_{A_1} - P_{A_2})$$

MASS TRANSFER COEFFICIENTS

- **The Rate of Mass transfer increases dramatically if there is motion in the medium**

- **Mass transfer occurring under the influence of motion in a fluid medium is called Convective mass transfer**

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          ┌─────────────┐
          │ Convective  │
          └─────────────┘
            │         │
    ┌──────────┐   ┌──────────┐
    │  Forced  │   │   Free   │
    └──────────┘   └──────────┘
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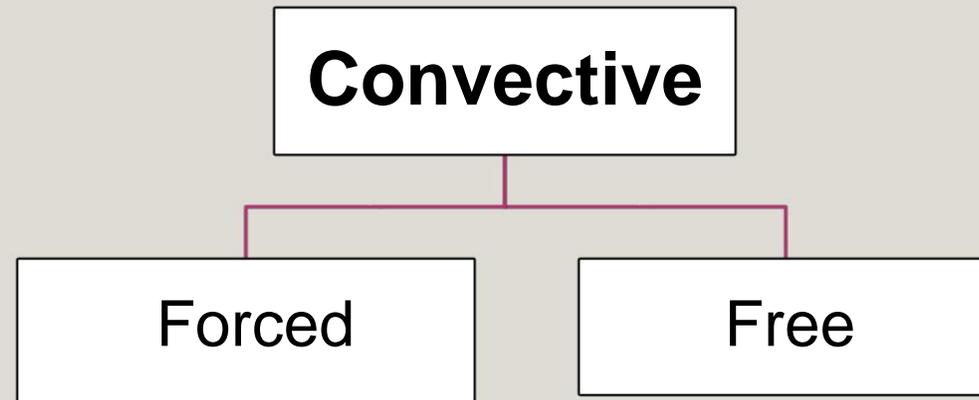
DIFFERENT MASS TRANSFER COEFFICIENTS

$$\text{Mass transfer coefficient, } k_c = \frac{N_A}{\Delta C_A} = \frac{\text{molar flux}}{\text{concentration driving force}}$$

Diffusion of A through non-diffusing B		Equimolar counterdiffusion of A and B		Unit of the mass transfer coefficient
Flux, N_A	Mass transfer coefficient	Flux, N_A	Mass transfer coefficient	
Gas-phase mass transfer				
$k_G(p_{A1} - p_{A2})$	$k_G = \dfrac{D_{AB}P}{RT\delta p_{BM}}$	$k'_G(p_{A1} - p_{A2})$	$k'_G = \dfrac{D_{AB}}{\delta RT}$	$\dfrac{\text{mol}}{(\text{time})(\text{area})(\Delta p_A)}$
$k_y(y_{A1} - y_{A2})$	$k_y = \dfrac{D_{AB}P^2}{RT\delta p_{BM}}$	$k'_y(y_{A1} - y_{A2})$	$k'_y = \dfrac{D_{AB}P}{\delta RT}$	$\dfrac{\text{mol}}{(\text{time})(\text{area})(\Delta y_A)}$
$k_c(C_{A1} - C_{A2})$	$k_c = \dfrac{D_{AB}P}{\delta p_{BM}}$	$k'_c(C_{A1} - C_{A2})$	$k'_c = \dfrac{D_{AB}}{\delta}$	$\dfrac{\text{mol}}{(\text{time})(\text{area})(\Delta C_A)}$
Liquid-phase mass transfer.				
$k_L(C_{A1} - C_{A2})$	$k_L = \dfrac{D_{AB}}{\delta x_{BM}}$	$k'_L(C_{A1} - C_{A2})$	$k'_L = \dfrac{D_{AB}}{\delta}$	$\dfrac{\text{mol}}{(\text{time})(\text{area})(\Delta C_A)}$
$k_x(x_{A1} - x_{A2})$	$k_x = \dfrac{CD_{AB}}{\delta x_{BM}}$	$k'_x(x_{A1} - x_{A2})$	$k'_x = \dfrac{CD_{AB}}{\delta}$	$\dfrac{\text{mol}}{(\text{time})(\text{area})(\Delta x_A)}$
Conversion				
	$k_G RT = \dfrac{RT}{P} k_y = k_c \; ; \; k_L = \dfrac{k_x}{C_{av}}$		$k'_c = k'_G RT = \dfrac{RT}{P} k'_y \; ; \; k'_L = \dfrac{k'_x}{C_{av}}$	

DIMENSIONLESS GROUPS IN MASS TRANSFER
ANALOGY WITH HEAT TRANSFER

Dimensionless groups and their physical significance	Analogous groups in heat transfer
Reynolds number, $Re = \dfrac{lv\rho}{\mu} = \dfrac{lv}{\nu} = \dfrac{\text{inertial forces}}{\text{viscous forces}}$	The same
Schmidt number, $Sc = \dfrac{\mu}{\rho D} = \dfrac{\nu}{D} = \dfrac{\text{momemntum diffusivity}}{\text{molecular diffusivity}}$	$Pr = \dfrac{c_p \mu}{k} = \dfrac{\mu/\rho}{k/\rho c_p} = \dfrac{\nu}{\alpha} = \dfrac{\text{momentum diffusivity}}{\text{thermal diffusivity}}$
Sherwood number*, $Sh = \dfrac{k_L l}{D} = \dfrac{k_L \Delta C}{(D/l)\Delta C} = \dfrac{\text{convective mass flux}}{\text{diffusive flux across a layer of thickness } l}$	$Nu = \dfrac{hl}{k} = \dfrac{\text{convective heat flux}}{\text{conduction heat flux across a layer of thickness } l}$
Stanton number, $St_M = \dfrac{Sh}{(Re)(Sc)} = \dfrac{k_L}{v} = \dfrac{k_L \Delta C}{v\Delta C} = \dfrac{\text{convective mass flux}}{\text{flux due to bulk flow of the medium}}$	$St_H = \dfrac{Nu}{(Re)(Pr)} = \dfrac{h\Delta T}{v\Delta T} = \dfrac{\text{convective heat flux}}{\text{heat flux due to bulk flow}}$
Peclet number, $Pe_M = (Re)(Sc) = \dfrac{lv}{D} = \dfrac{v\Delta C}{(l/D)\Delta C} = \dfrac{\text{flux due to bulk flow of the medium}}{\text{diffusive flux across a layer of thickness } l}$	$Pe_H = (Re)(Pr) = \dfrac{(v\rho c_p)\Delta T}{(k/l)\Delta T} = \dfrac{\text{heat flux due to bulk flow}}{\text{conduction flux across a thickness } l}$
Colburn factor, $j_D = St_M (Sc)^{2/3} = \dfrac{Sh}{(Re)(Sc)^{1/3}}$	$j_H = St_H (Pr)^{2/3} = \dfrac{Nu}{(Re)(Pr)^{1/3}}$
Grashof number, $Gr = \dfrac{l^3 \Delta\rho g}{\mu\nu}$	The same

INTERPHASE MASS TRANSFER
UNDERSTANDING BY EXAMPLES

- Absorption of ammonia from Ammonia-Air Mixture by liquid water

- Absorption of CO_2 from flue gas by amine solvents

- Removal of H_2S from natural gas

  - **In above examples gas is absorbed at the interface of two phases and gets transported to the bulk of liquid**

EQUILIBRIUM BETWEEN PHASES

- Equilibrium between two phases in contact means a state in which there is no net transfer of solute from one phase to other.

- At equilibrium the concentrations in two phases aren't equal but chemical potential of solute in both phases is same

- Diffusion of components between phases continues till Equilibrium is attained
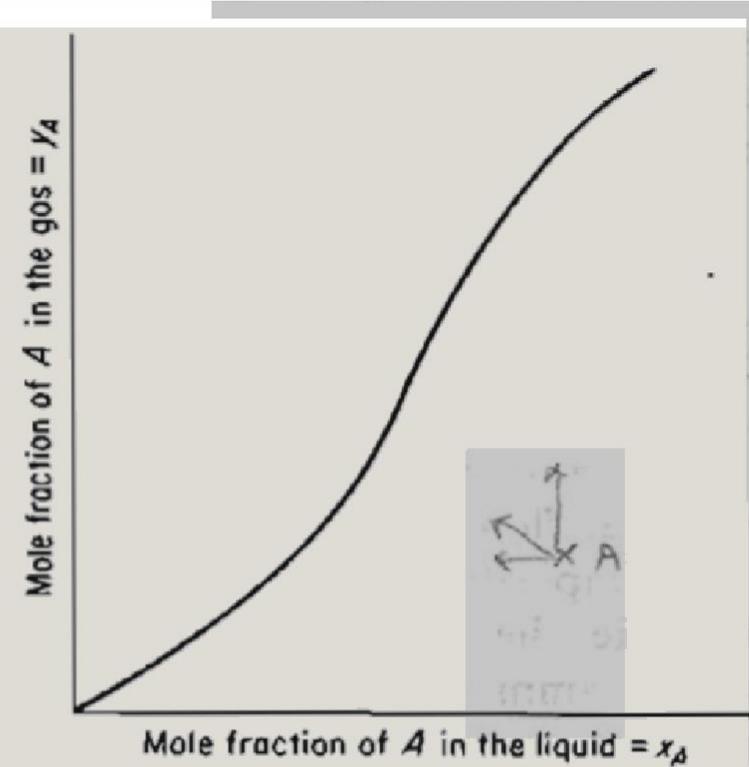
TWO FILM THEORY

- ***Mass transfer from one phase to another involves three steps:***
    1. Solute is transported from bulk of one phase to interface
    2. Diffusion of solute occurs across the interface
    3. Transport of solute to bulk of second phase

- ***Two phase theory states:***　　　　➡　　 ***Lewis & Whitman***
    - Basic concept – the resistance to diffusion can be considered equivalent to that in stagnant film of a certain thickness
    - Two stagnant film exist on both side of interface
    - Mass transfer through these films occurs by Molecular diffusion
    - No resistance to solute transfer exists across the interface separating the phases
    - Resistances in fluid are the only resistances.

Concentration profile of A in the gas:
True profile
According to the film theory

y_{Ab}

y_A x_A Interface

Bulk liquid

Liquid film

Solute A diffuses through the liquid film

y_{Ai}

A A A

A

Solute A diffuses through the gas film

x_{Ai}

Concentration profile of A in the liquid:
True profile
According to the film theory

Gas film

Bulk gas

x_{Ab}

0 z
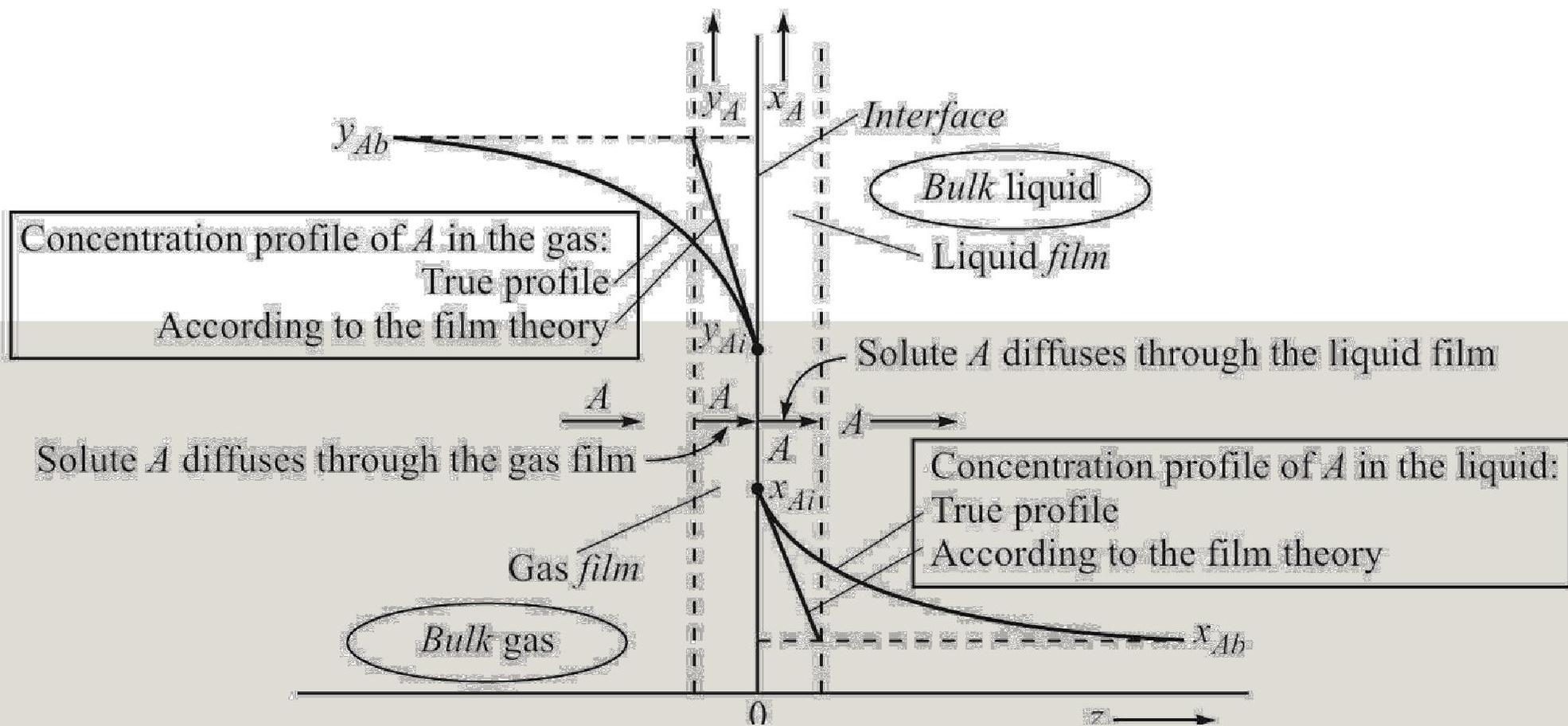
$$r = k_x(x_A - x_{Ai}) \qquad (17.56)$$

$$r = k_y(y_{Ai} - y_A) \qquad (17.57)$$

OVERALL MASS TRANSFER COEFFICIENTS

- We define two overall mass transfer coefficients, as shown below:

$$N_A = K_y (y_{Ab} - y_{Ab}^*)$$
$$= K_x (x_{Ab}^* - x_{Ab})$$

- Resistances to mass transfer are expressed in terms of Overall and local mass transfer coefficients as;

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

$$\frac{1}{K_x} = \frac{1}{m'' k_y} + \frac{1}{k_x}$$
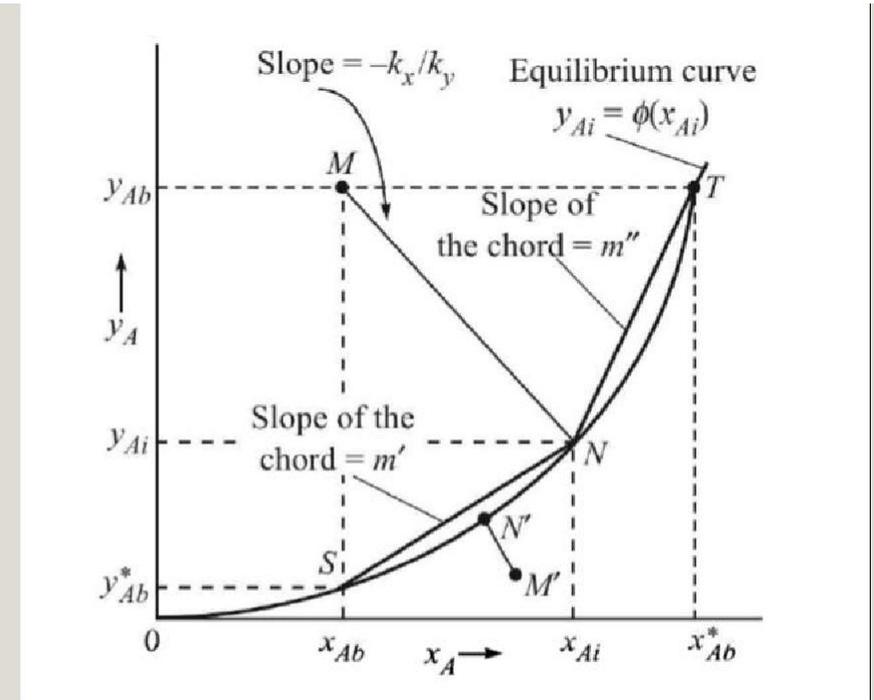
The fractional resistance offered by the gas-phase

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

The fractional mass transfer offered by the liquid-phase

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

$1/K_y$ = overall resistance to mass transfer

m/k_x = the resistance in liquid film

$1/k_y$ = the resistance in gas film

- When m` is small

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

$$y_{A,G} - y_A^* \approx y_{A,G} - y_{A,i}$$

When m`` is very large

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

$$x_A^* - x_{A,L} \approx x_{A,i} - x_{A,L}$$

GAS ABSORTION & STRIPPING

- Gas absorption is a mass transfer operation in which one or more species is removed from a gaseous stream by dissolution in a liquid [Solvent]

- The insoluble component(s) present in the gas which is not absorbed is called Carrier gas

- Examples:
  - ❑ Removal of H2S from natural gas

- The reverse of absorption is stripping or desorption

SELECTING A SOLVENT FOR ABSORPTION

- Solubility   Selective solubility for the solute

- Volatility   Less volatile solvent is preferred

- Viscocity ⟶ Low viscosity

- Corrosiveness ⟶ Less corrosive solvent

- Cost   Low cost solvent

- Hazard & Toxicity   Non hazardous and non-toxic

GAS-LIQUID CONTACTING EQUIPMENTS

TRAY TOWERS

- Vertical cylinders in which the liquid and gas are contacted in stepwise fashion on trays or plates.

- To provide good contact between the up flowing vapor and the down flowing liquid inside an industrial fractionating column.

- Liquid enters-top and gas-from downwards through the opening

- Each tray – act as a stage

- The tray fluid are brought into intimate contact

- Interphase diffusion occurs

- Fluids are separated.

CHARACTERISTICS OF TRAY TOWER

- Shell and trays

- Tray spacing

- Tower diameter

- Downspouts / downcomer

- Weirs

SHELL AND TRAY

- Can be made of any number of materials.

- Glass, Glass-lined metal, impervious carbon, plastic, even wood can be used.

- But most frequently metals are used.

- For metal towers the shells are usually cylindrical for reason of cost.

- For cleaning, small-diameter tower are fitted with hand holes.

- Large towers with manholes about every tenth tray.

TRAY SPACING

- It is usually chosen on the basis of :

  ➤ expediency in construction

  ➤ maintenance

  ➤ cost

  ➤ For special cases where tower height is an important consideration spacing of 15 cm has been used.

Conventional Tray: tall downcomer

tall
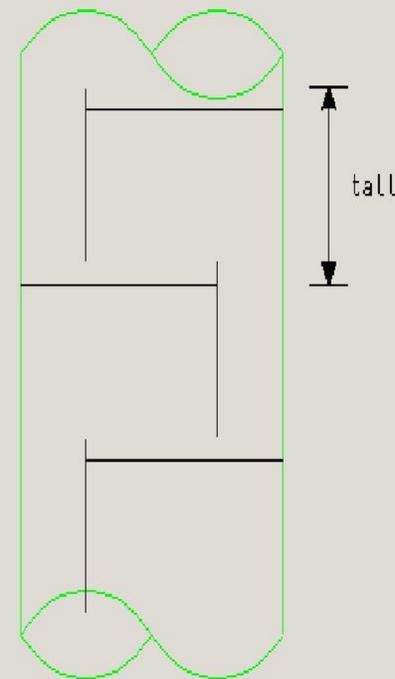
High-capacity Tray: short downcomer

short
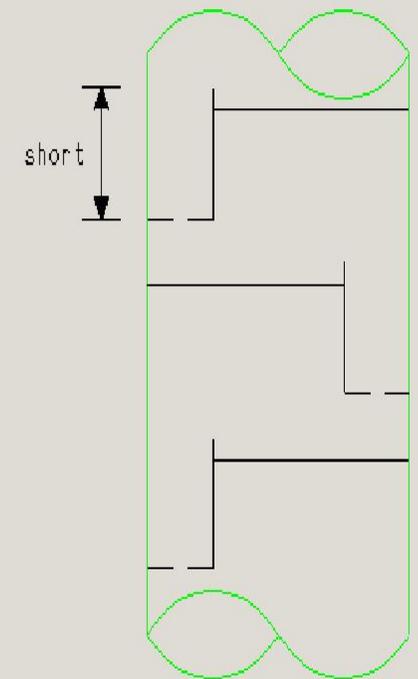
PROBLEMS ASSOCIATED WITH TRAY TOWERS

- Entrainment

- High pressure drops

- Priming

- Flooding

- Weeping/Dumping

- Foaming

- Coning

PACKED TOWERS
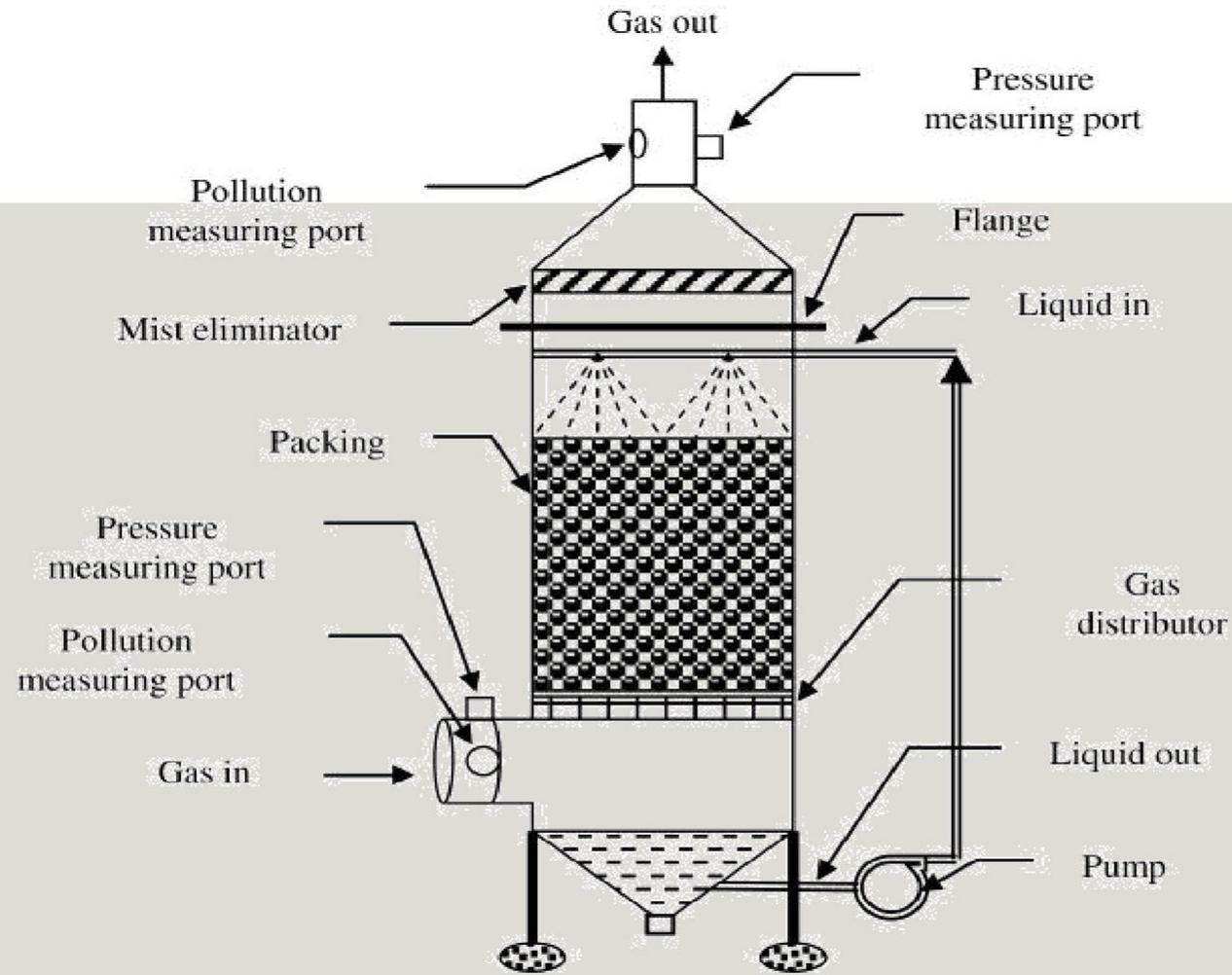
- A common apparatus used in gas absorption is the packed tower as shown in previous Figure

- The device consist of:

  a) cylindrical column or tower

  b) gas inlet and distributing space at the bottom

  c) liquid inlet and distributor at the top

  d) gas & liquid outlets at the top & bottom, respectively

  e) tower packing – supported mass of inert solid shapes

PACKINGS

- The packing

    - provides a large area of contact between the liquid and gas

    - encourage intimates contact between the phases

- Common dumped packings are shown in the figure:

FIGURE 18.2
Common tower packings: (a) Raschig rings; (b) metal Pall ring; (c) plastic Pall ring; (d) Berl saddle; (e) ceramic Intalox saddle; (f) plastic Super Intalox saddle; (g) metal Intalox saddle.
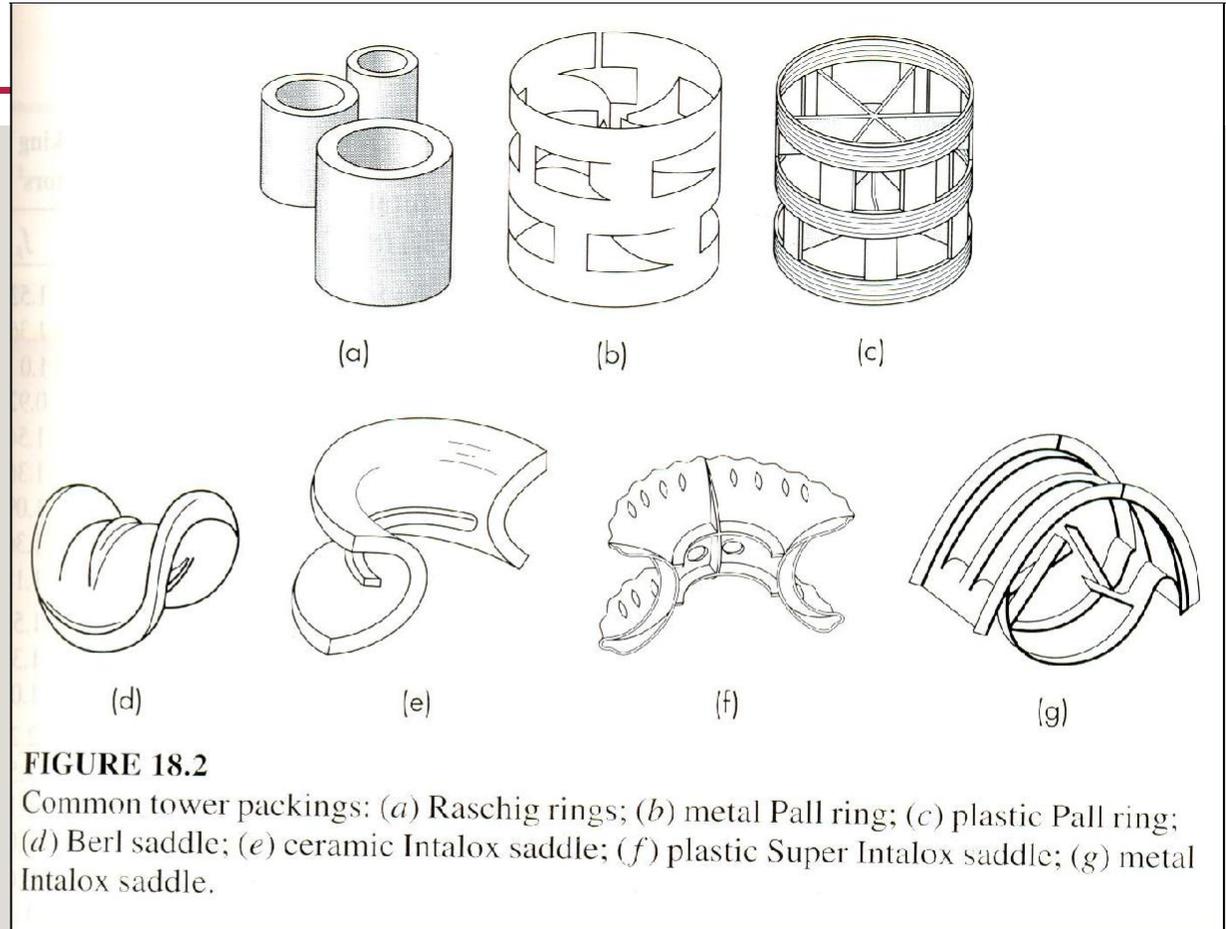
CALCULATION OF TOWER HEIGHT

- The equation for packed height (h_T) can be written as follows:

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

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

$$\int_{y_2}^{y_1} \frac{(1-y)_{iM} \, dy}{(1-y)(y-y_i)} \longrightarrow N_{TG}$$

If the overall gas-phase mass transfer coefficient is used to express the rate of mass the height of the packing can be obtained from the following equation:

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

where

$$H_{tOG} = \text{height of an overall gas-phase transfer unit} = \frac{G'}{K_y \, \bar{a} \, y^*_{BM}}$$

$$N_{tOG} = \text{number of overall gas-phase transfer units} = \int_{y_2}^{y_1} \frac{y^*_{BM} \, dy}{(1-y)(y-y^*)}$$

and

$$y^*_{BM} = (1-y)^*_M = \frac{(1-y^*)-(1-y)}{\ln[(1-y^*)/(1-y)]}$$

- The number of transfer units is somewhat like the number of ideal stages (theoretical plates).

- The NTU = ideal stage if the operating line and equilibrium line are straight and parallel as in figure
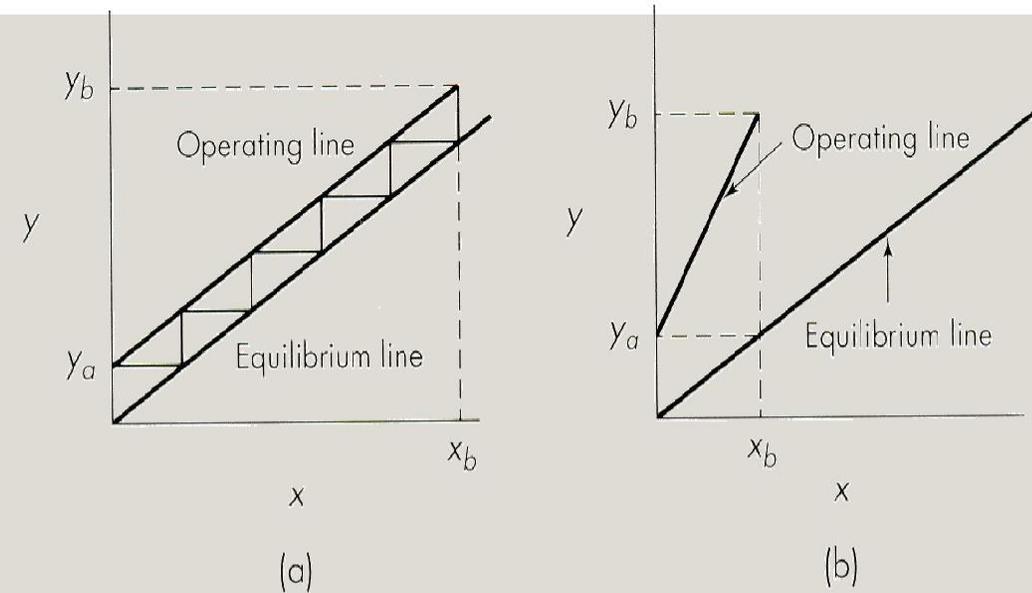
FIGURE 18.13
Relationship between number of transfer units (NTU) and number of theoretical plates (NTP): (*a*) NTU = NTP; (*b*) NTU > NTP.

FOUR BASIC TYPES OF MASS TRANSFER COEFFICIENT

Driving force	Height of a Transfer Unit (HTU)			Number of Transfer Units (NTU)	
	Symbol	DANB	ECD	Symbol	
$y - y_i$	H_{tG}	$\dfrac{G'}{k_y\,\bar{a}\,(1-y)_{iM}}$	$\dfrac{G'}{k'_y\,\bar{a}}$	N_{tG}	$\displaystyle\int_{y_2}^{y_1} \dfrac{(1-y)_{iM}\,dy}{(1-y)(y-y_i)}$
$y - y^*$	H_{tOG}	$\dfrac{G'}{K_y\,\bar{a}\,(1-y)^*_M}$	$\dfrac{G'}{K'_y\,\bar{a}}$	N_{tOG}	$\displaystyle\int_{y_2}^{y_1} \dfrac{(1-y)^*_M\,dy}{(1-y)(y-y^*)}$
$Y - Y^*$	H_{tOG}	$\dfrac{G'_s}{K_Y\,\bar{a}}$	$\dfrac{G'_s}{K_Y\,\bar{a}}$	N_{tOG}	$\displaystyle\int_{Y_2}^{Y_1} \dfrac{dY}{(Y-Y^*)}$
$x_i - x$	H_{tL}	$\dfrac{L'}{k_x\,\bar{a}\,(1-x)_{iM}}$	$\dfrac{L'}{k'_x\,\bar{a}}$	N_{tL}	$\displaystyle\int_{x_2}^{x_1} \dfrac{(1-x)_{iM}\,dx}{(1-x)(x_i-x)}$
$x^* - x$	H_{tOL}	$\dfrac{L'}{K_x\,\bar{a}\,(1-x)^*_M}$	$\dfrac{L'}{K'_x\,\bar{a}}$	N_{tOL}	$\displaystyle\int_{x_2}^{x_1} \dfrac{(1-x)^*_M\,dx}{(1-x)(x^*-x)}$
$X^* - X$	H_{tOL}	$\dfrac{L'_s}{K_X\,\bar{a}}$	$\dfrac{L'_s}{K_X\,\bar{a}}$	N_{tOL}	$\displaystyle\int_{X_2}^{X_1} \dfrac{dX}{(X^*-X)}$

$$(1-y)_{iM} = \frac{(1-y_i)-(1-y)}{\ln[(1-y_i)/(1-y)]}; \qquad (1-y)^*_M = \frac{(1-y^*)-(1-y)}{\ln[(1-y^*)/(1-y)]}$$

For Dilute Gases

Making the approximation $y_{BM}^* \approx (1 - y) \approx 1$ for a dilute gas,

$$N_{tOG} \approx \int_{y_2}^{y_1} \frac{dy}{y - y^*}$$

$$N_{tOG} = \frac{y_1 - y_2}{(y_1 - y_1^*) - (y_2 - y_2^*)} \ln \frac{y_1 - y_1^*}{y_2 - y_2^*} = \frac{y_1 - y_2}{\dfrac{(y_1 - y_1^*) - (y_2 - y_2^*)}{\ln \dfrac{y_1 - y_1^*}{y_2 - y_2^*}}} = \frac{y_1 - y_2}{(y - y^*)_M} \Bigg|$$

DRYING
UNDERSTANDING BY EXAMPLES

- Wood, cloth, paper etc. can be dried by evaporation of the moisture into a gas stream.

- A solution can be dried by spraying it's fine droplets into a hot, dry gas which results in the evaporation of the liquid.

- A liquid such as Benzene can be dried of any small water content by distillation but removal of small amount of acetone by same process would not usually be called drying.

PHYSICAL MECHANISM OF DRYING

- The removal of moisture from a substance is termed as drying

- Drying is governed by principle of transport of heat and mass

- First the surface moisture vaporizes, as soon as surface moisture is exhausted more moisture is transported from inside the solid to its surface

- Broadly three transport resistances play important roles in drying:

  - Resistance inside the solid to the liquid

  - Convective heat transfer resistance at surface

  - Convective mass transfer resistance at surface

DRYING EQUILIBRIUM

- Moisture contained in a wet solid or liquid solution exerts a vapor pressure to an extent depending upon the nature of moisture, nature of solid and temperature

- If a wet solid is exposed to a continuous supply of fresh gas containing a fixed partial pressure of vapor p, the solid will either lose moisture by evaporation or gain moisture from the gas until the vapor pressure of moisture of solid equals p

- The solid and the gas are then in equilibrium, and the moisture content of solid is termed its Equilibrium-Moisture content at prevailing condition

- The equilibrium moisture of a given species of solid may depend upon the particle size or specific surface, if the moisture is largely physically adsorbed

- Different solids have different moisture curves as shown in figure

- Generally inorganic solids which are insoluble in the liquid and show no special adsorptive properties such as Zinc oxide, show relatively low equilibrium

- A solid which is hygroscopic shows a relatively high equilibrium moisture
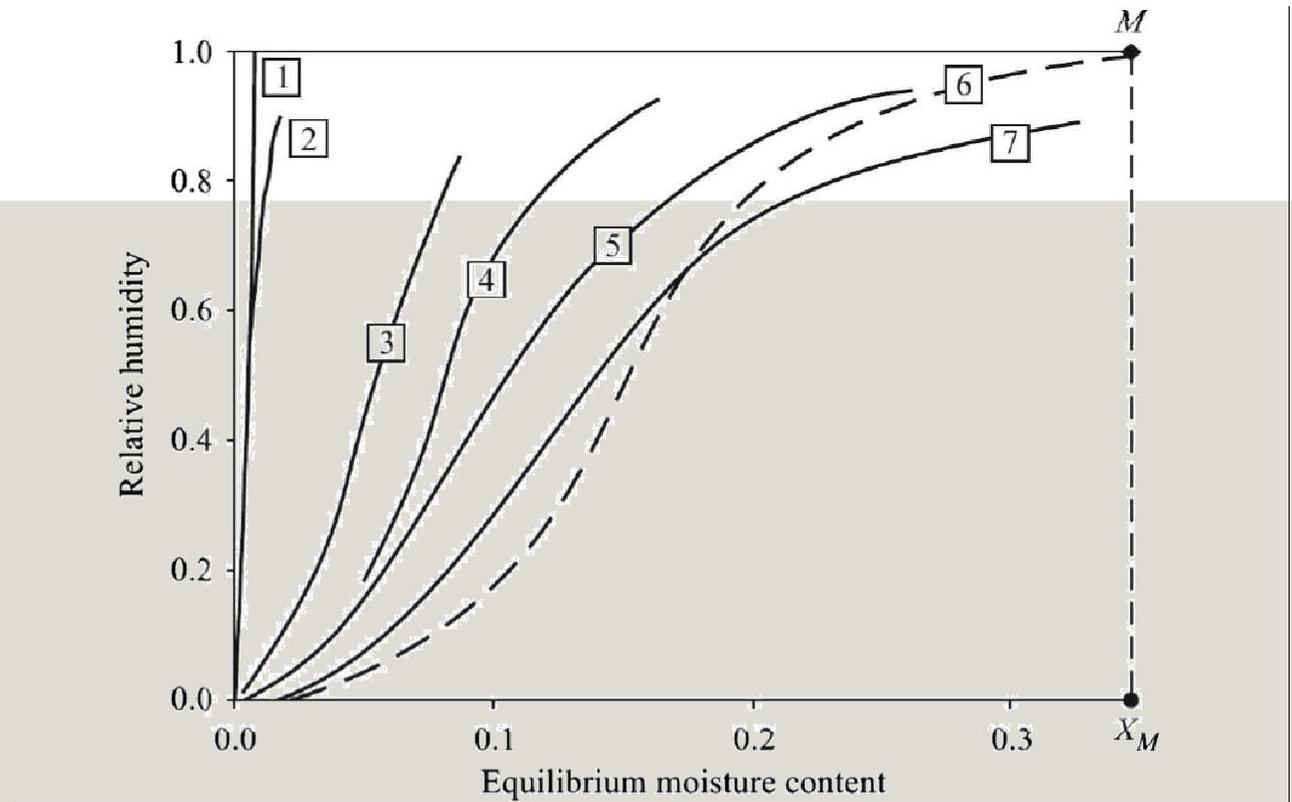
The following term are commonly used in designing of drying systems:

- Moisture content of a substance which exerts as equilibrium vapour pressure less than of the pure liquid at the same temperature is referred to as ***bound moisture.***

- Moisture content of the solid which exerts an equilibrium vapour pressure equal to that of pure liquid at the given temperature is the ***unbound moisture.***

- The moisture content of solid in excess of the equilibrium moisture content is referred as ***free moisture***. During drying, only free moisture can be evaporated. The free moisture content of a solid depends upon the vapor concentration in the gas.
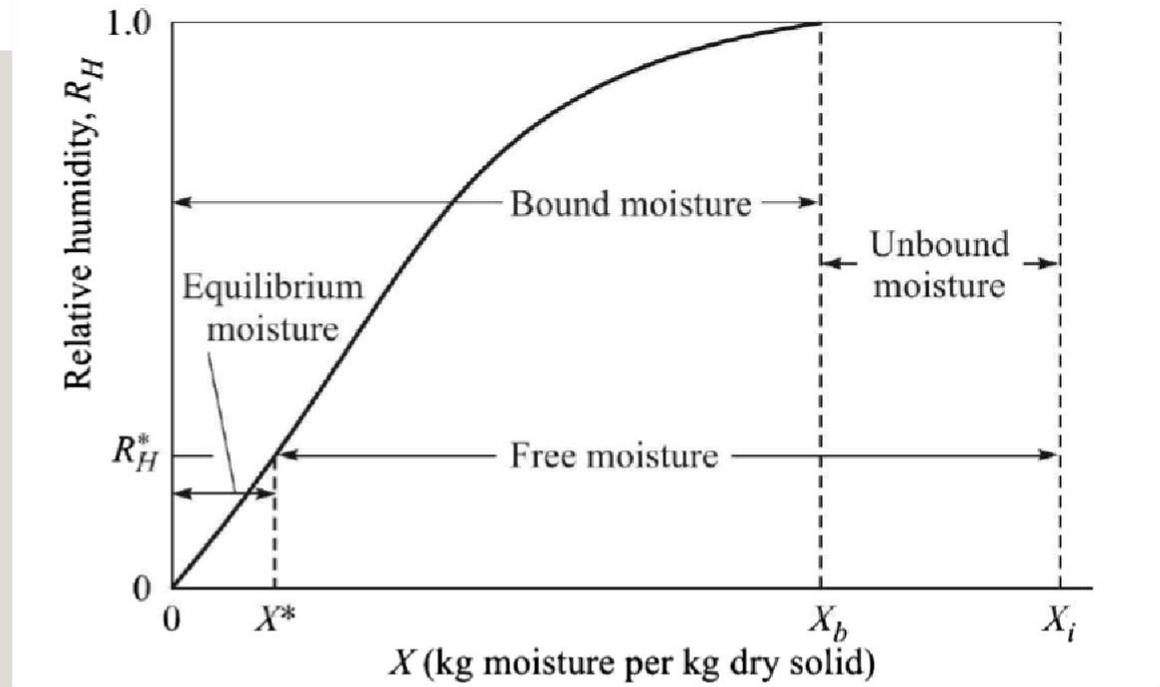
DRYING RATE

- The rate of drying can be determined by suspending it in a cabinet or duct in a steam of air, from a balance

- From the data a curve of moisture content as a function of time can be plotted
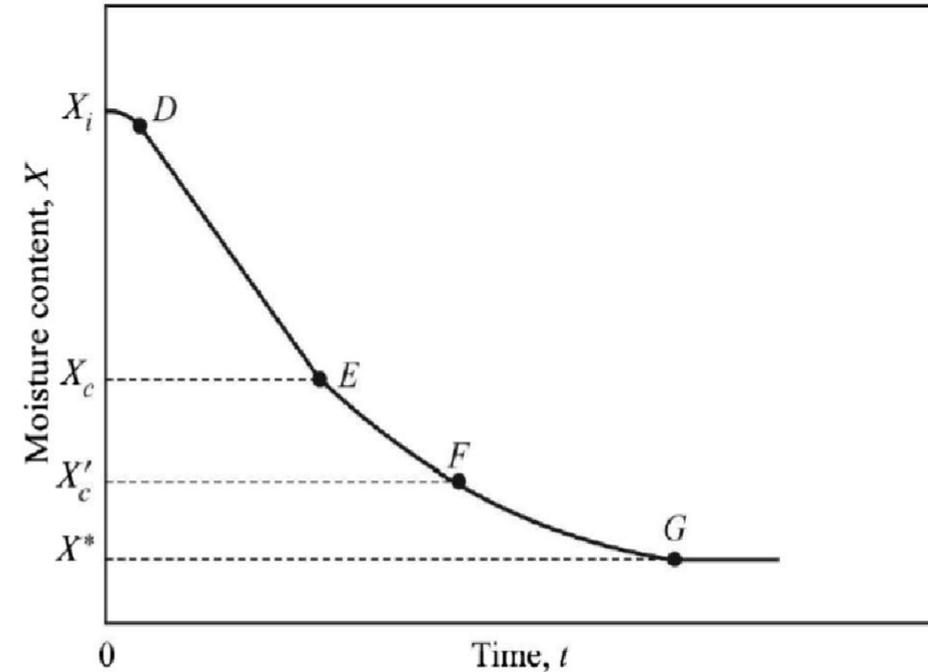
- If the data are converted into rates or fluxes of drying, expressed as *N,* much information can be obtained when plotted against moisture content.

$$N = -\frac{W_s}{a}\frac{dX}{dt} \approx -\frac{W_s}{a}\frac{\Delta X}{\Delta t} \quad \frac{\text{kg moisture}}{\text{m}^2 \cdot \text{s}}$$

- There are two major parts in the rate curve:

❑ A period of constant rate (region RQ)

❑ A period of falling rate (region RT)
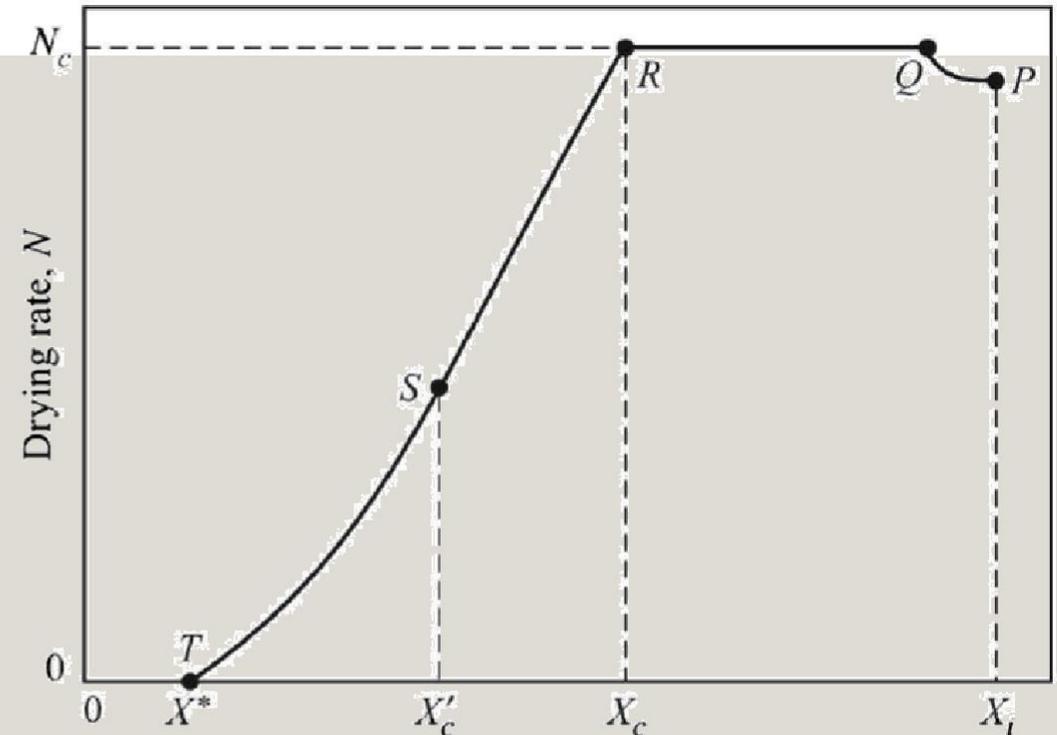
DRYING TIME

- The drying rate is given as: $N = \dfrac{-S_S \, dX}{A \, d\theta}$

- Rearranging and integrating over a time interval while moisture content changes from X_1 to X_2 gives:

$$\theta = \int_0^\theta d\theta = \frac{S_S}{A} \int_{X_2}^{X_1} \frac{dX}{N}$$

- For constant-rate period:

$$\theta = \frac{S_S(X_1 - X_2)}{AN_c}$$

- For falling-rate period and N is linear in X:
$$\theta = \frac{S_S(X_1 - X_2)}{A(N_1 - N_2)} \ln \frac{N_1}{N_2} = \frac{S_S(X_1 - X_2)}{AN_m}$$

CRYSTALLIZATION

- Crystallization is the formation of solid particles within a homogenous phase.

- It may occur as the formation of solid particles in a vapor, as solidification from a liquid melt, or as crystallization from liquid solution.

- Crystallization from solution is important industrially because of the variety of materials that are marketed in the crystalline form.

CRYSTALLIZATION KINETICS

- Crystallization is a complex phenomenon involving three steps:

    (1) nucleation,

    (2) mass transfer of solute to the crystal surface, and

    (3) incorporation of solute into the crystal lattice

- **Supersaturation** is the driving force for crystallization kinetics

- As crystal size decreases, solubility noticeably increases, making it possible to supersaturate a solution if it is cooled slowly without agitation

- The solubility of very small crystals can fall in the metastable region
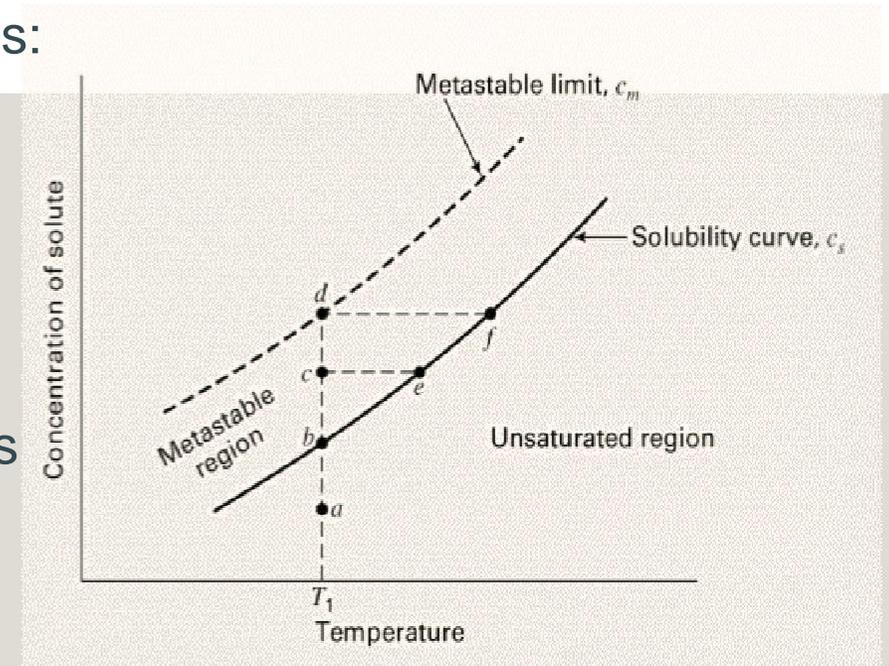
SUPERSATURATION

- **Supersaturation** is the concentration difference between that of the supersaturated solution (C) in which the crystal is growing and that of a solution in equilibrium with the crystal (C_S).

$$\Delta C = C - C_S$$

- **Fractional Supersaturation:**

$$s = \frac{c - c_s}{c_s} = \frac{c}{c_s} - 1 = S - 1$$

where **S** is concentration ratio and **s** is fractional

supersaturation • In practice, **s** is usually less than 2%

NUCLEATION

- Nucleation means formation of tiny new crystals in a supersaturated solution.

- The rate of nucleation is the number of new crystals formed per unit time per unit volume of magma or solid-free mother liquor'.

- Relative rates of nucleation and growth are important because they determine crystal size and size distribution.
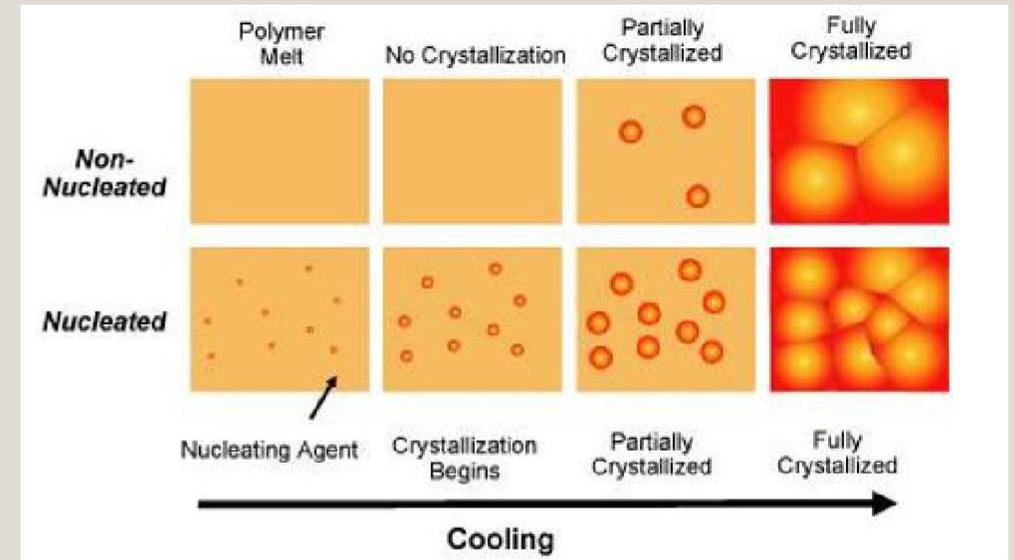
NUCLEATION TYPES

PRIMARY NUCLEATION

- Supersaturated solution is free of crystalline surface

- Requires high supersaturation and is the principal mechanism in precipitation

- It can be homogenous or heterogenous

SECONDARY NUCLEATION

- Supersaturated solution contains crystals

- Key in commercial crystallizers, where crystalline surfaces are present and large crystals are desired

- Initiated by fluid shear past crystal surfaces that sweeps away nuclei, collisions of crystals with each other, and collisions of crystals with metal surfaces (crystallizer vessel wall or agitator blades)

- most common since they happen at the low values of relative supersaturation,

TYPES OF PRIMARY NUCLEATION

HOMOGENOUS NUCLEATION

- Occurs with supersaturated solutions in the absence of foreign matter, such as dust

- molecules in the solution first associate to form a cluster, which may dissociate or grow

- if a cluster gets large enough to take on the appearance of a lattice structure, it becomes an embryo → stable crystalline nucleus

HETEROGENOUS NUCLEATION

- The formation of crystals on tiny suspended foreign particles or on the surface of the crystallizer

- The rate of nucleation depends not only on the supersaturation but also on the availability of active sites for nucleation

THE END

THANKS!