

Mas transfer

It is the term that refers to the transport of a component in a mixture from a region in which its concentration is high to a region in which its concentration is lower. The process can take place in gas, vapor, liquid and solid.

Molecular Diffusion

It is the movement or transport of molecules of (A) in a medium (B) under the influence of concentration gradient (driving force). It is governed by Fick's first law:

$$N_A = -D_{AB} \frac{dC_A}{dy}$$

Where:

N_A = molar flux of A (kmol / m².s)

D_{AB} = diffusion coefficient (diffusivity) of A in B (m² / s)

C_A = concentration of A (kmol / m³)

y = distance by which A molecules have been moved (m)

Note:

Movement of A can be achieved as a result of concentration difference (molecular diffusion) and as a result of overall stream movement (convection). So, the basic equation will be:

$$N_A = -D_{AB} \frac{dC_A}{dy} + x_A(N_A + N_B)$$

Where:

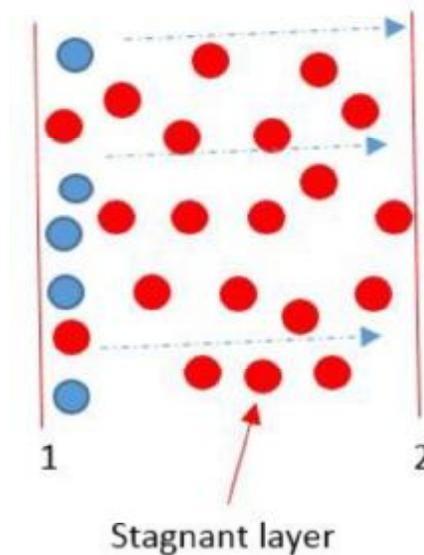
N_B = molar flux of B (kmol / m².s)

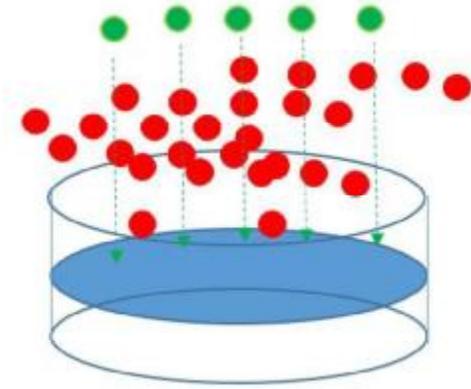
x_A = mole fraction of A in the mixture

Modes of diffusion

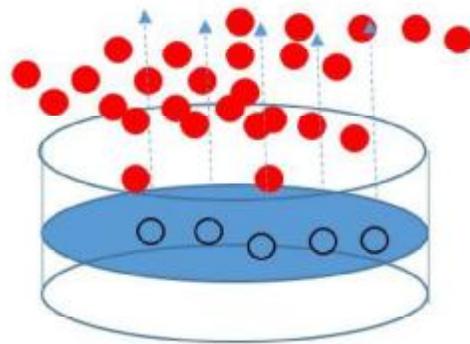
1- Diffusion through stagnant layer (stagnant film)

In this mode of diffusion, the molecules of A will move through a stagnant layer of the molecules of B, i.e., the molecules of A undergo a relative movement, while the molecules of B will undergo no net movement. For example, suppose that we have two gases A & B over a surface of a stagnant lake, gas A is soluble in the water, while gas B is insoluble in the water, molecules of A will dissolve in the water and move far away, while the molecules of B will stay stable (stagnant) since they are insoluble in the water. Thus, the molecules of A will move through a stagnant layer of the molecules of B (this operation is called absorption). Similarly, in evaporation from free surface, the molecules of vapor A will move away from the free surface, but the air have no net motion (i.e. stagnant film)





Absorption



Evaporation

To derive the mathematical relation that describes this mode of diffusion, we start from the overall equation:

$$N_A = -D_{AB} \frac{dC_A}{dy} + x_A(N_A + N_B)$$

$N_B = 0$ stagnant layer of B

$$C_A = x_A \cdot C_T$$

Where

C_T = total concentration

$$dC_A = C_T dx_A$$

$$N_A = -D_{AB} C_T \frac{dx_A}{dy} + x_A N_A$$

$$N_A - x_A N_A = -D_{AB} C_T \frac{dx_A}{dy}$$

$$N_A(1 - x_A) = -D_{AB} C_T \frac{dx_A}{dy}$$

$$N_A dy = -D_{AB} C_T \frac{dx_A}{1 - x_A}$$

$$N_A \int_0^y dy = -D_{AB} C_T \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{1 - x_A}$$

$$N_A \cdot y = D_{AB} C_T \ln \frac{1 - x_{A2}}{1 - x_{A1}}$$

$$N_A = \frac{D_{AB} C_T}{y} \ln \frac{1 - x_{A2}}{1 - x_{A1}} \dots\dots\dots \text{For liquids}$$

Note:

$$C = \frac{P}{RT} \quad \text{from ideal gas law}$$

Where:

C = concentration

P = pressure

R = universal gas constant

T = temperature

$$p_A = x_A \cdot P$$

So,

$$NA = \frac{D_{AB}P}{RTy} \ln \frac{P-p_{A2}}{P-p_{A1}} \dots\dots\dots \text{For gases}$$

2- Counter Diffusion

i. Equimolar counter diffusion

In this mode of diffusion:

$$N_A = -N_B$$

It means that the number of molecules of A moving in a particular direction is equal to the number of molecules of B moving in the opposite direction. This occurs in ideal distillation.

Starting from the overall equation:

$$N_A = -D_{AB} \frac{dC_A}{dy} + x_A(N_A + N_B)$$

But $N_A = -N_B$

$$N_A = -D_{AB} \frac{dC_A}{dy} + x_A(N_A - N_A)$$

$$N_A = -D_{AB} \frac{dC_A}{dy}$$

$$C_A = x_A \cdot C_T$$

Where

C_T = total concentration

x_A = mole fraction of A

$$dC_A = C_T dx_A$$

$$N_A = -CD_{AB} \frac{dx_A}{dy}$$

$$N_A \int_0^y dy = -CD_{AB} \int_{x_{A1}}^{x_{A2}} dx_A$$

$$NA \cdot y = CD_{AB}(x_{A1} - x_{A2})$$

$$NA = \frac{CD_{AB}}{y}(x_{A1} - x_{A2}) \dots\dots\dots \text{for liquids}$$

$$C = \frac{P}{RT} \quad \text{from ideal gas law}$$

Where:

C = concentration

P = pressure

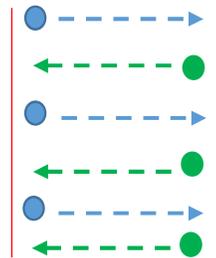
R = universal gas constant

T = temperature

$$p_A = x_A \cdot P$$

$$NA = \frac{PD_{AB}}{RTy}(x_{A1} - x_{A2})$$

$$NA = \frac{D_{AB}}{RTy}(p_{A1} - p_{A2}) \dots\dots\dots \text{for gases}$$



Equimolar counter diffusion

ii. Unequimolar counter diffusion

this mode occurs when a chemical reaction exists. In this mode of diffusion, the number of molecules of A diffusing in a particular direction will not equal the number of molecules of B diffusing in the opposite direction.

Consider the below reactions:

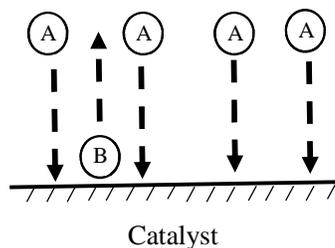


For this reaction:

$$N_A = -4 N_B$$

Or

$$N_B = -\frac{1}{4} N_A$$



For this reaction:

$$2 N_A = -3 N_B$$

Or,

$$N_B = -\frac{3}{2} N_A$$

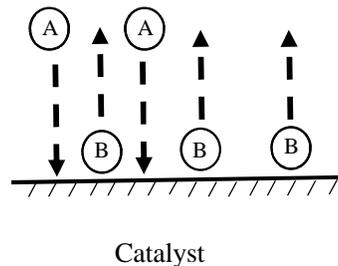
Consider the general reaction:



For this reaction:

$$N_B = -n N_A$$

Starting from the overall equation:



$$NA = -D_{AB} \frac{dC_A}{dy} + x_A(NA + NB)$$

But $NB = -nNA$

$$NA = -D_{AB} \frac{dC_A}{dy} + x_A(NA - nNA)$$

$$NA = -D_{AB} \frac{dC_A}{dy} + x_A NA(1 - n)$$

$$NA - x_A NA(1 - n) = -D_{AB} \frac{dC_A}{dy}$$

$$NA[1 - x_A(1 - n)] = -D_{AB} \frac{dC_A}{dy}$$

$$C_A = x_A \cdot C$$

Where

C = total concentration

x_A = mole fraction of A

$$dC_A = C dx_A$$

$$NA[1 - x_A(1 - n)] = -CD_{AB} \frac{dx_A}{dy}$$

$$NA \cdot dy = -CD_{AB} \frac{dx_A}{[1 - x_A(1 - n)]}$$

$$NA \cdot \int_0^y dy = -CD_{AB} \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{[1 - x_A(1 - n)]} \cdot \frac{(1 - n)}{(1 - n)}$$

$$NA = \frac{CD_{AB}}{(1 - n)y} \ln \frac{1 - x_{A2}(1 - n)}{1 - x_{A1}(1 - n)}$$

This equation is used for liquids. In order to use it for gases, it should be converted in terms of pressure.

$$C = \frac{P}{RT} \quad \text{from ideal gas law}$$

Where:

C = concentration

P = pressure

R = universal gas constant

T = temperature

$p_A = x_A \cdot P$

$$NA = \frac{PD_{AB}}{(1-n)RTy} \ln \frac{1-x_{A2}(1-n)}{1-x_{A1}(1-n)} * \frac{P}{P}$$

$$NA = \frac{PD_{AB}}{(1-n)RTy} \ln \frac{P-p_{A2}(1-n)}{P-p_{A1}(1-n)}$$

Which can be used for gases

Example:

A mixture consists of ammonia and air over a water container where the ammonia is soluble in water and the air is insoluble in water. Operating conditions are 1 bar pressure and 295 K temperature. At a particular point, the partial pressure of ammonia is 7 kN/m², and ammonia partial pressure over the water surface is negligible and resistance to transfer can be regarded as lying in a stationary gas film 1 mm thick. The diffusivity of ammonia in air is 2.36 X 10⁻⁵ m²/s. Calculate the molar flux of ammonia at this point.

Solution

The case diffusion through stagnant layer

$$p_{A1} = 7 \text{ kN/m}^2$$

$$p_{A2} = 0$$

$$y = 1 \text{ mm}$$

$$D_{AB} = 2.36 \times 10^{-5} \text{ m}^2/\text{s}$$

The equation that can be used for this case is:

$$N_A = \frac{D_{AB}P}{RTy} \ln \frac{P - p_{A2}}{P - p_{A1}}$$

$$p = 1 \text{ bar} \frac{101.3 \text{ kPa}}{1 \text{ bar}} = 101.3 \text{ kN/m}^2$$

$$N_A = \frac{101.3 * 2.36 * 10^{-5}}{8.314 * 295 * 10^{-3}} \ln \frac{101.3 - 0}{101.3 - 7} = 6.979 \times 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$$

Example:

Species A in a gaseous mixture diffuses through a 3 mm thick film to reach a catalyst surface where the reaction $[A \longrightarrow 2B]$ takes place. If the partial pressure of A in the bulk of the gas is 8.5 kN/m^2 , and the diffusivity of A can be taken as $2 \times 10^{-5} \text{ m}^2/\text{s}$, find the molar flux of A. The pressure and temperature of the system are 101.3 kN/m^2 and 297 K . Assume that the concentration of A on the catalyst surface is negligible.

Solution:

The case is unequimolar counter diffusion.

$$Y = 3 \text{ mm}$$

$$N = 2$$

$$P_{A1} = 8.5 \text{ kN/m}^2$$

$$D_{AB} = 2 \times 10^{-5} \text{ m}^2/\text{s}$$

$$P = 101.3 \text{ kN/m}^2$$

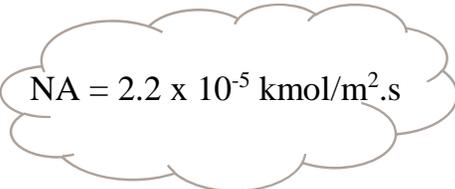
$$T = 297 \text{ K}$$

$$p_{A2} = 0 \text{ kN/m}^2$$

the equation for this case is:

$$N_A = \frac{PD_{AB}}{(1-n)RTy} \ln \frac{P - p_{A2}(1-n)}{P - p_{A1}(1-n)}$$

$$N_A = \frac{2 \times 10^{-5} \times 101.3}{(1-2) \times 8.314 \times 297 \times 3 \times 10^{-3}} \ln \frac{101.3 - 0 \times (1-n)}{101.3 - 8.5 \times (1-n)}$$



$$N_A = 2.2 \times 10^{-5} \text{ kmol/m}^2 \cdot \text{s}$$

Diffusivity (Diffusion coefficient)

Diffusivity can be calculated either theoretically or experimentally

Theoretical calculation of diffusivity (for binary mixture)

1- For liquids

$$D_{AB} = \frac{1.173 \times 10^{-16} \phi_B^2 M_B^2 T}{\mu V_A^{0.6}}$$

Where:

- D_{AB} = diffusivity of solute A in solvent B (m^2/s)
- ϕ = association factor for solvent (2.2 for water, 1.95 for methanol, 1.5 for ethanol and 1 for unassociated solvents such as hydrocarbons and ethers).
- M_B = molecular weight of solvent.
- μ = viscosity of the solution ($\text{N}\cdot\text{s}/\text{m}^2$)
- T = temperature (K)

V_A = molar volume of the solute (m^3/kmol)

2- For gases

Several equations exist to calculate the diffusivity of gases. One of these equations is called “Fuller equation” which can be mathematically expressed as:

$$D_{AB} = \frac{1.0133 \times 10^{-7} \cdot T^{1.75} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P \left[(V_A)^{\frac{1}{3}} + (V_B)^{\frac{1}{3}} \right]^2}$$

Where:

- D_{AB} = diffusivity of solute A in solvent B (m^2/s).
- T = temperature (K).
- M_A = molecular weight of A.
- M_B = molecular weight of B.
- P = total pressure (bar).
- V_A = molar volume of the A (m^3/kmol)
- V_B = molar volume of the B (m^3/kmol)

Note:

- Molar volume of a molecule = Σ (atomic volume of atoms)
- For liquids

$$D_{AB} \propto T$$

$$\left(\frac{D_{AB1}}{D_{AB2}}\right) = \left(\frac{T_1}{T_2}\right)$$

- For gases

$$D_{AB} \propto T^{1.5}$$

$$D_{AB} \propto \frac{1}{P}$$

$$\left(\frac{D_{AB1}}{D_{AB2}}\right) = \left(\frac{T_1}{T_2}\right)^{1.5} \left(\frac{P_2}{P_1}\right)$$

Example:

Estimate the diffusivity of methanol in air at atmospheric pressure and 25 °C. Given that the molar volume of methanol is 29.9 m³/kmol, molar volume of water is 20.1, and molecular weight of methanol is 32.

Solution:

The case is through diffusion in gas phase, so, Fuller equation may be used to estimate the diffusivity:

$$D_{AB} = \frac{1.0133 \times 10^{-7} \cdot T^{1.75} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P[(V_A)^{\frac{1}{3}} + (V_B)^{\frac{1}{3}}]^2}$$

$$D_{AB} = \frac{1.0133 \times 10^{-7} \cdot (298)^{1.75} \sqrt{\frac{1}{32} + \frac{1}{29}}}{(1.013)[29.9]^{\frac{1}{3}} + (20.1)^{\frac{1}{3}}]^2}$$

Example:

Estimate the diffusivity of phenol in ethanol at 20 °C. Given that the viscosity of ethanol at 20 °C is $1.2 \times 10^{-3} \text{ N.s/m}^2$, molecular weights for ethanol and phenol are 46 and 94 respectively and the molar volume of phenol is $0.1034 \text{ m}^3/\text{kmol}$.

Solution:

For liquids:

$$D_{AB} = \frac{1.173 \times 10^{-16} \phi_B^{\frac{1}{2}} M_B^{\frac{1}{2}} T}{\mu V_A^{0.6}}$$

$$D_{AB} = \frac{1.173 \times 10^{-16} (1.5)^{\frac{1}{2}} (46)^{\frac{1}{2}} (293)}{1.2 \times 10^{-3} (0.1034)^{0.6}}$$

Multicomponent mixtures

When a species A diffuse through a mixture of B, C, D, etc. the general equation of molar flux becomes:

$$N_A = -D_{Am} \frac{dC_A}{dy} + x_A(N_A + N_B + N_C + N_D + \dots .etc.)$$

Where

N_A = molar flux of species A in the mixture ($\text{kmol/m}^2.\text{s}$).

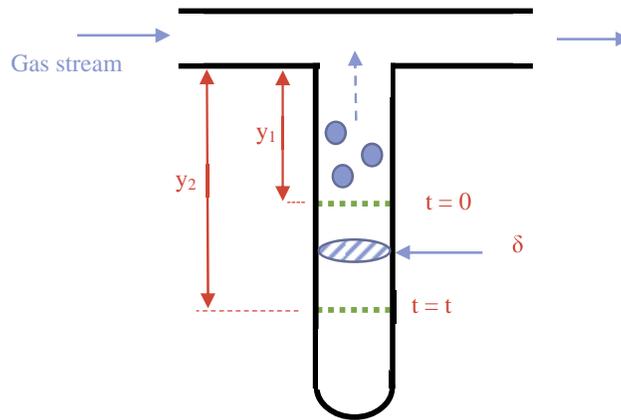
D_{Am} = diffusivity of component A in the mixture (m^2/s)

x_A = mole fraction of A in the mixture.

N_B, N_C, N_D = molar flux of B, C and D ($\text{kmol/m}^2.\text{s}$).

Experimental determination of diffusivity

Diffusivity will be determined experimentally according to the method developed by Winkelmann. In this method, a T-shaped tube will be used as illustrated in the figure below. The liquid is allowed to evaporate in the vertical tube over which a gas stream moves in the horizontal tube in sufficient velocity in order to keep the vapor pressure of the liquid zero at the top of the vertical tube.



Mass transfer in the vertical tube will take place by molecular diffusion alone. Rate of evaporation can be determined by noting the change in the liquid level in the vertical tube for a particular period of time. Equation used for this method can be derived as follows:

let the molecules of liquid = A

let the molecules of air (or gas) = B

starting from the overall equation:

$$N_A = -D_{AB} \frac{dC_A}{dy} + x_A(N_A + N_B)$$

$N_B = 0$ (diffusion through stagnant film)

so, the produced equation will be:

$$N_A = \frac{D_{AB}P}{RTy} \ln \frac{P - p_{A2}}{P - p_{A1}}$$

The units of N_A are $(\text{kmol}/\text{m}^2 \cdot \text{s})$

number of moles of evaporated A = $N_A \cdot \delta = (\text{kmol}/\text{m}^2 \cdot \text{s})(\text{m}^2) = \text{kmol}/\text{s}$

$$\text{number of moles of evaporated A} = \delta \frac{D_{AB}P}{RTy} \ln \frac{P - p_{A2}}{P - p_{A1}} \dots \dots \dots (1)$$

$$\text{number of moles of evaporated A} = \frac{dn_{\text{liquid}}}{dt}$$

when n_{liquid} = number of moles of liquid A

$$n = \frac{wt}{M.wt} = \frac{\rho_L V}{M.wt}$$

Where n = number of moles

wt = weight

M.wt = molecular weight

ρ_L = density of the liquid

V = volume

but $V = \delta \cdot y$

$$n = \left(\frac{\rho_L \cdot \delta \cdot y}{M.wt} \right)$$

$$\text{number of evaporated moles of A} = \frac{d}{dt} \left(\frac{\rho_L \cdot \delta \cdot y}{M.wt} \right)$$

$$\text{number of evaporated moles of A} = \frac{\rho_L \cdot \delta}{M.wt} \frac{dy}{dt} \dots\dots\dots (2)$$

equation 1 = equation 2

$$= \delta \frac{D_{AB} P}{RT y} \ln \frac{P - p_{A2}}{P - p_{A1}} = \frac{\rho_L \cdot \delta}{M.wt} \frac{dy}{dt}$$

$$\frac{D_{AB} \cdot P}{RT} \ln \frac{P - p_{A2}}{P - p_{A1}} \cdot \int_0^t dt = \frac{\rho_L}{M.wt} \cdot \int_{y_1}^{y_2} y \cdot dy$$

which will be after integration and rearrangement as:

$$D_{AB} = \frac{\rho_L \cdot R \cdot T}{P \cdot M.wt} * \frac{y_2^2 - y_1^2}{2t} * \frac{1}{\ln \frac{P - p_{A2}}{P - p_{A1}}}$$

Example:

Winkelmann method has been used in diffusivity determination with the following information for chloroform in air at 25 °C and 1 atm. Liquid density of chloroform at 25 °C is 1.485 g/cm³ and its vapor pressure at this temperature is 200 mmHg. At time = 0, the liquid chloroform surface was 7.4 cm from the top of the tube, and after 10 hours, the liquid surface height dropped by 0.44 cm. if the concentration of the chloroform is zero at the top of the tube and the molecular weight of chloroform is 119.5 kg/kmol, what will be the gas diffusivity of the chloroform in air?

Solution:

$$y_1 = 7.4 \text{ cm} = 0.074 \text{ m}$$

$$y_2 = 7.4 + 0.44 = 7.84 = 0.0784 \text{ m}$$

$$t = 10 \text{ hrs.} = 36000 \text{ s}$$

$$\rho_L = 1.485 \text{ g/cm}^3 = 1485 \text{ kg/m}^3$$

$$\text{M.wt} = 119.5 \text{ kg/kmol}$$

$$p_{A1} = 200 \text{ mmHg} = 26.657 \text{ kPa}$$

$$p_{A2} = 0$$

$$D_{AB} = \frac{\rho_L \cdot R \cdot T}{P \cdot \text{M.wt}} * \frac{y_2^2 - y_1^2}{2t} * \frac{1}{\ln \frac{P - p_{A2}}{P - p_{A1}}}$$

$$D_{AB} = \frac{1485 * 8.314 * 298}{101.3 * 119.5} * \frac{(0.078)^2 - (0.074)^2}{2 * 36000} * \frac{1}{\ln \frac{101.3 - 0}{101.3 - 26.657}}$$

Mass Transfer Theories

Basically, four theories had been suggested to describe the mechanism of conditions followed in mass transfer process in the region of the phase boundary. These theories are:

1. Two films theory.
2. Penetration theory.
3. Surface renewal theory.
4. Film-Penetration theory.

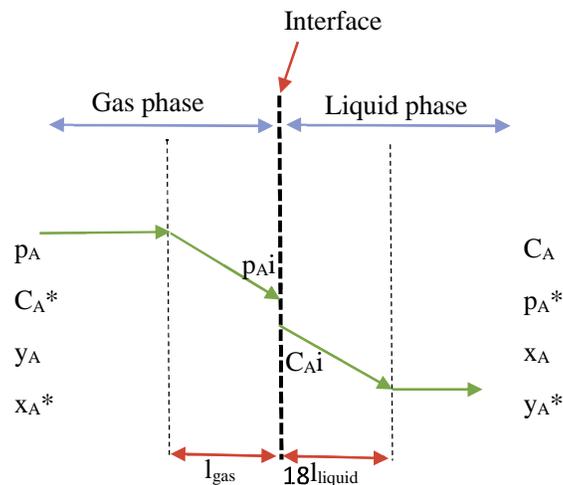
1- Two Films Theory

This theory assumes:

1. Resistance to transfer in each phase could be regarded as lying in a thin film close to the interface.
2. The transfer across these films is steady state molecular diffusion.
3. Fick's 1st law applies:

$$N_A = -D_{AB} \frac{dC_A}{dy}$$

4. Turbulence dies out at the interface and that a laminar layer exists in each of the two fluids.



2- Penetration Theory

This theory assumes:

1. Unsteady state molecular diffusion.
2. Molecules moves in groups to the interface, some of them penetrate to other phase moving far away from the interface, while the rest mix back with the bulk where they came from.
3. Fick's second law applies:

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial y^2}$$

4. Boundary conditions for this theory are:

$$t = 0 \quad 0 < y < \infty \quad C_A = C_{AO}$$

$$t > 0 \quad y = 0 \quad C_A = C_{Ai}$$

$$t > 0 \quad y = \infty \quad C_A = C_{AO}$$

5. $NA = 2(C_{Ai} - C_{AO})\sqrt{\frac{D_{AB}}{\pi t_e}}$

Where t_e = time of exposure

3- Surface Renewal Theory

This theory assumes:

1. Unsteady state diffusion.
2. $NA = (C_{Ai} - C_{AO})\sqrt{D_{AB} \cdot s}$

Where s is the rate of formation of fresh surface which must be found experimentally.

4- Film-Penetration Theory

This theory assumes:

1. The whole of the resistance to transfer is regarded as lying within a laminar film at the interface.
2. Mass transfer at the interface is unsteady state.
3. Fick's 2nd law applies:

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial y^2}$$

4. Fresh surface is formed at intervals from the fluid which is brought from the bulk of the fluid to the interface.
5. The boundary conditions for this theory are:

$$t = 0 \quad C_A = C_{AO}$$

$$y = 0 \quad C_A = C_{Ai}$$

$$y = l \quad C_A = C_{AO}$$

Mass Transfer Coefficient

It is the coefficient that relates the flux with the driving force. Consider the two film theory:

$$N_A = -D_{AB} \frac{dC_A}{dy}$$

$$N_A = -D_{AB} \frac{\Delta C_A}{\Delta y}$$

❖ **For gas phase:**

$$N_A = -D_{AB} \frac{\Delta C_A}{l_{gas}}$$

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

$$N_A = \frac{-D_{AB}}{RT l_{gas}} * \Delta p_A$$

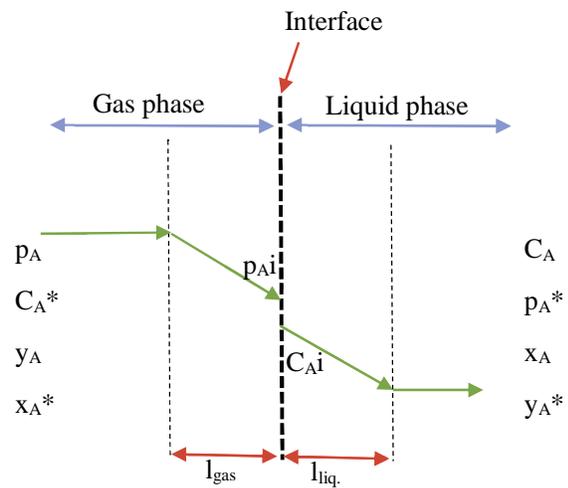
$$N_A = \frac{D_{AB}}{RT l_{gas}} * (p_A - p_{Ai}) \dots\dots\dots (1)$$

❖ **For liquids:**

$$N_A = -D_{AB} \frac{dC_A}{dy}$$

$$N_A = -D_{AB} \frac{\Delta C_A}{l_{liq.}}$$

$$N_A = \frac{-D_{AB}}{l_{liq.}} * \Delta C_A$$



$$NA = \frac{D_{AB}}{l_{liq.}} * (C_{Ai} - C_A) \dots\dots\dots (2)$$

Considering the overall system gives:

Based on the gas phase:

$$NA = \frac{D_{AB}}{RT(l_{gas}+l_{liq.})} * (p_A - p_A^*) \dots\dots\dots (3)$$

Based on the liquid phase:

$$NA = \frac{D_{AB}}{(l_{gas}+l_{liq.})} * (C_A^* - C_A) \dots\dots\dots(4)$$

Since the thicknesses of gas and liquid film are difficult to estimate, equations 1 to 4 could be written in the following forms:

$$NA = k_g * (p_A - p_{Ai})$$

$$NA = k_l * (C_{Ai} - C_A)$$

$$NA = KOG * (p_A - p_A^*)$$

$$NA = KOL * (C_A^* - C_A)$$

Where:

$$k_g = \frac{D_{AB}}{RTl_{gas}} = \text{individual gas phase mass transfer coefficient.}$$

$$k_l = \frac{D_{AB}}{l_{liq.}} = \text{individual liquid phase mass transfer coefficient.}$$

$$KOG = \frac{D_{AB}}{RT(l_{gas}+l_{liq.})} = \text{overall mass transfer coefficient based on gas phase.}$$

$$KOL = \frac{D_{AB}}{(l_{gas}+l_{liq.})} = \text{overall mass transfer coefficient based on liquid phase.}$$

Relation among Mass Transfer Coefficients

Based on the overall gas phase mass transfer coefficient:

$$NA = KOG * (p_A - p_A^*)$$

$$\frac{1}{KOG} = \frac{(p_A - p_A^*)}{NA}$$

$$\frac{1}{KOG} = \frac{(p_A - p_{Ai} - p_A^* + p_{Ai})}{NA}$$

$$\frac{1}{KOG} = \frac{(p_A - p_{Ai})}{NA} + \frac{(p_{Ai} - p_A^*)}{NA}$$

According to Henry's law:

$$p_{Ai} = H * C_{Ai}$$

$$y_{Ai} = H * x_{Ai}$$

$$p_A = H * C_A^*$$

$$p_A^* = H * C_A$$

Where H = Henry's law constant.

$$\frac{1}{KOG} = \frac{(p_A - p_{Ai})}{NA} + \frac{(HC_{Ai} - HC_A)}{NA}$$

$$\frac{1}{KOG} = \frac{(p_A - p_{Ai})}{NA} + \frac{H(C_{Ai} - C_A)}{NA}$$

$$NA = k_g * (p_A - p_{Ai})$$

$$NA = k_l * (C_{Ai} - C_A)$$

$$\frac{1}{KOG} = \frac{1}{k_g} + \frac{H}{k_l}$$

In terms of overall liquid phase mass transfer coefficient:

$$NA = KOL * (C_A^* - C_A)$$

$$\frac{1}{KOL} = \frac{C_A^* - C_A}{NA}$$

$$\frac{1}{KOL} = \frac{C_A^* - C_{Ai} + C_{Ai} - C_A}{NA}$$

$$\frac{1}{KOL} = \frac{C_A^* - C_{Ai}}{NA} + \frac{C_{Ai} - C_A}{NA}$$

$$p_A = H * C_A^*$$

$$p_{Ai} = H * C_{Ai}$$

$$\frac{1}{KOL} = \frac{p_A - p_{Ai}}{H * NA} + \frac{C_{Ai} - C_A}{NA}$$

$$NA = k_g * (p_A - p_{Ai})$$

$$NA = k_l * (C_{Ai} - C_A)$$

$$\frac{1}{KOL} = \frac{1}{H * k_g} + \frac{1}{k_l}$$

Note:

1. The reciprocal of mass transfer coefficient is termed as “Resistance of mass transfer”
2. The term “gas film control” refers to resistance in the gas film, i.e.

$$\frac{1}{KOG} = \frac{1}{k_g} + \frac{H}{k_l}$$

3. The term “liquid film control” refers to resistance in the liquid film:

$$\frac{1}{KOL} = \frac{1}{H * k_g} + \frac{1}{k_l}$$

Gas Absorption

It is a mass transfer operation in which a gas mixture is contacted with a liquid with the objective of preferentially dissolving one or more component(s) of the gas in the liquid and producing a solution of the dissolved gas (es) in the liquid.

The removed species are called “solute” and the liquid in which these species are dissolved is called “solvent”. The insoluble component(s) present in the gas which is not absorbed is called “carrier gas”. An intimate contact between the gas and the liquid is achieved in a suitable equipment or device like a packed column, tray tower, spray tower, venture scrubber, etc.

Acetone may be recovered from acetone-air mixture by bringing the gas into intimate contact with water in which acetone gets dissolved but air does not. In this case, the acetone is the (solute), air is the (carrier gas), and water is the (solvent). Similarly, ammonia may be recovered from ammonia-air stream by washing the mixture with water. Benzene and toluene vapors are removed from coke oven gas by washing the gas with oil. In all above examples, transfer is from gas phase to liquid phase. If the transfer is in the opposite direction, that is from liquid phase to gas phase, the operation is called desorption or stripping. Thus when benzene and toluene are removed from the absorption oil by passing steam through the solution, both benzene and toluene vapors pass on to the gas phase and are removed while the oil is reused. The basic principles of absorption and desorption or stripping are the same, the only difference being in the direction of mass transfer.

All the three examples of absorption of acetone, ammonia and benzene-toluene are physical processes since no chemical reaction is involved. However, during absorption of oxides of nitrogen in water to produce nitric acid or during absorption of carbon dioxide in a solution of sodium hydroxide, chemical reactions occur. So, absorption can be classified into two main types: physical absorption, and absorption with chemical reaction.

Equilibrium relations:

Equilibrium relationship play an important role in gas absorption as in other mass transfer operations. Equilibrium relations decide whether mass transfer will at all take place, and if so, in which direction.

During absorption, gas molecules will diffuse into the liquid as long as the concentration of the gas in the liquid is less than the equilibrium value. If the concentration of the gas in the liquid is higher than the equilibrium value, the gas

will diffuse out of the liquid into the gas, and this is what we call “desorption or stripping”. At any given temperature and concentration, each dissolved gas exerts a definite partial pressure. The degree to which each gas is absorbed from a mixture of gases depends upon the partial pressure of the concerned gas.

Note:

- When a certain amount of a gas and a relatively non-volatile liquid are allowed to remain in a mutual contact for a sufficiently long time so that no more net transfer of component A occurs between them, the system is said to be in equilibrium in respect of A, and the resulting concentration of the dissolved gas A in the liquid is known as “gas solubility” at the prevailing temperature and pressure.
- The solubility of a gas in liquid decreases with temperature almost as a rule. Absorption of a gas is done at rather lower temperature so that there is a larger driving force for transfer of the solute from the gas phase to the solvent. Desorption or stripping on the other hand, is carried out at an elevated temperature so that the direction of the driving force is reversed.
- For an ideal gas-liquid or vapor-liquid system, the solubility is given by Raoult’s law. Henry’s law is often applicable at low solute concentrations for real gas-liquid system.

Raoult’s law:

If a gas mixture in equilibrium with an ideal liquid solution, follows the ideal gas law, then it obeys Raoult’s law:

$$p_A = p_A^0 x_A$$

In a binary system:

$$P = p_A + p_B = p_A^0 x_A + p_B^0 x_B$$

Where:

P = total pressure

p_A, p_B = partial pressures of A and B respectively.

p_A^0 and p_B^0 = vapor pressures of A and B respectively

x_A and x_B = mole fractions of A and B respectively in the solution

Also,

$$y_A = \frac{p_A}{P} = \frac{p_A^0 x_A}{P}$$

$$y_B = \frac{p_B}{P} = \frac{p_B^0 x_{AB}}{P}$$

Where:

y_A and y_B = mole fractions of A and B respectively in the gas

Henry's law:

For moderately soluble gases with relatively little interaction between the gas and the liquid molecules, Henry's law is applicable:

$$p_A = H * x_A$$

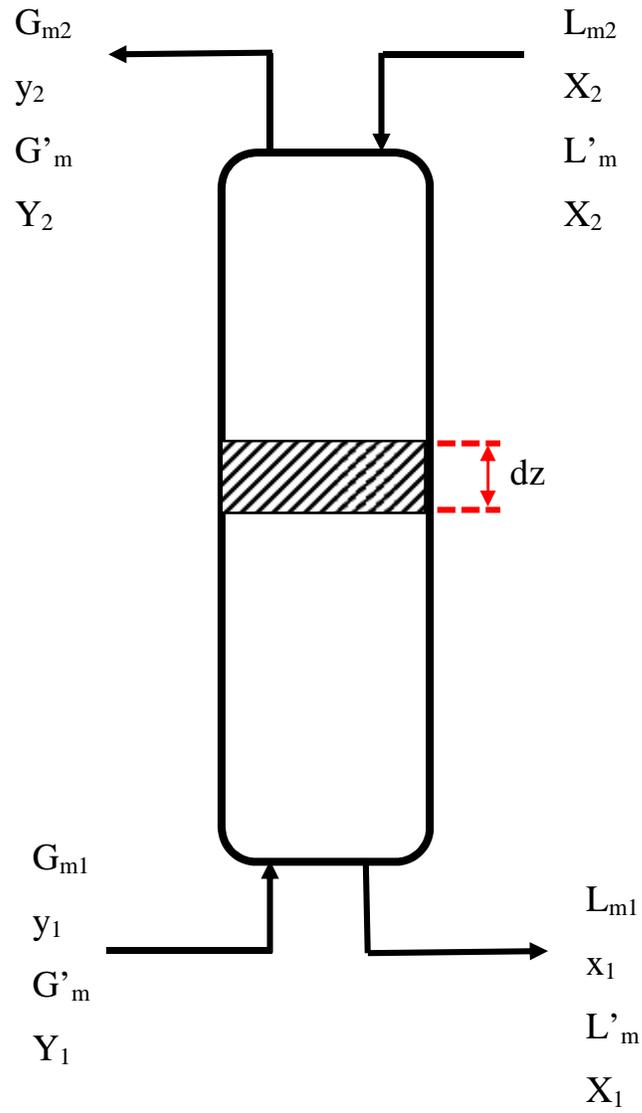
$$y_A = \frac{p_A}{P} = \frac{H * x_A}{P}$$

Where:

H = Henry's law constant.

Nomenclature and material balance:

Consider the counter-current flow of a gas and a liquid through an absorption column shown below:



Where:

G_m = total flow rate of the gas (moles / unit time. Unit x-area)

L_m = total flow rate of the liquid (moles / unit time. Unit x-area)

G'_m = flow rate of inert carrier gas (moles / unit time. Unit x-area)

L'_m = flow rate of the pure solvent (moles / unit time. Unit x-area)

y = mole fraction of the solute in the gas.

x = mole fraction of the solute in the liquid.

Y = moles of solute per moles of solute-free carrier gas.

X = moles of solute per moles of pure solvent.

Note:

- Y and X are called “mole ratios”.

$$Y = \frac{y}{1 - y}$$

$$X = \frac{x}{1 - x}$$

- Since the gas entering at the bottom gradually loses its solute content as it moves up and the liquid picks up the solute as it falls down, both G_m and L_m change through the tower having their highest values at the bottom, called (rich end), and lowest value at the top, called (lean end).
- Since the total quantities of gas and liquid flowing through the tower are changing continuously, values of x and y cannot such be used directly for stoichiometric computations.
- Since the values of flow rates of inert gas G'_m and pure solvent L'_m do not change during the process, values of Y and X can be directly used for computation of material balance.

Overall material balance:

$$G_{m1} + L_{m2} = G_{m2} + L_{m1}$$

Solute balance:

$$L'_m(X_1 - X_2) = G'_m(Y_1 - Y_2) = G'_m \left[\frac{p_1}{P - p_1} - \frac{p_2}{P - p_2} \right]$$

Where:

$$Y_1 = \left[\frac{p_1}{P - p_1} \right]$$

$$Y_2 = \left[\frac{p_2}{P - p_2} \right]$$

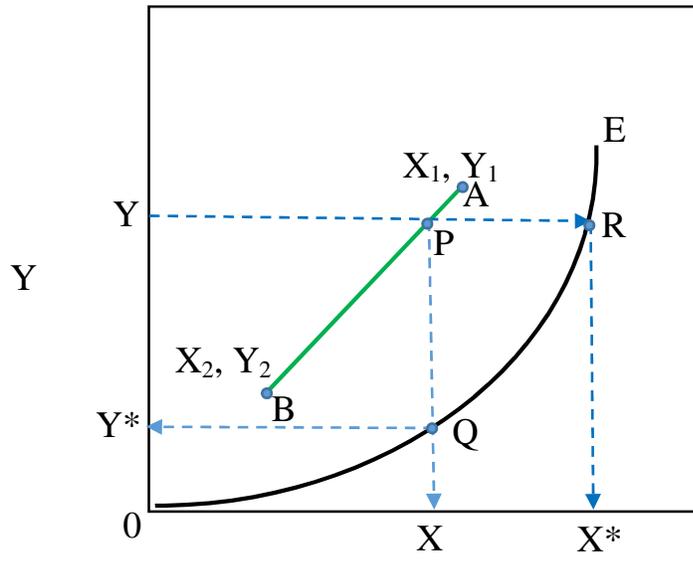
Considering any intermediate point within the tower where the compositions are Y and X for gas and liquid respectively:

$$L'_m(X_1 - X) = G'_m(Y_1 - Y)$$

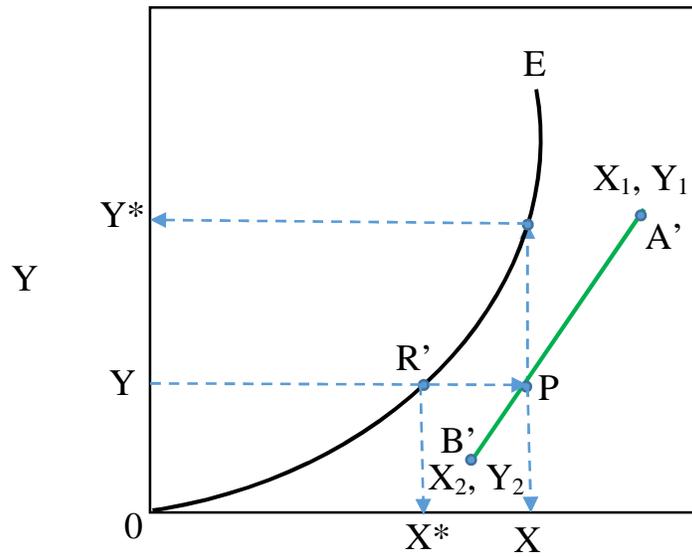
Or

$$Y = \frac{L'_m}{G'_m}(X - X_1) + Y_1$$

This is the equation of the operating line. It is a straight line with slope equals to (L'_m / G'_m) and passes through the points (X_1, Y_1) and (X_2, Y_2) which are called terminal points, and this operating line represents the real conditions in the column.



X
Absorption ($Y > Y^*$ & $X < X^*$)



X
Stripping ($Y < Y^*$ & $X > X^*$)

Considering the above figures:

For absorption to take place, the concentration of the solute in the gas should be higher than the equilibrium value, and the operating line must therefore lie above the equilibrium curve.

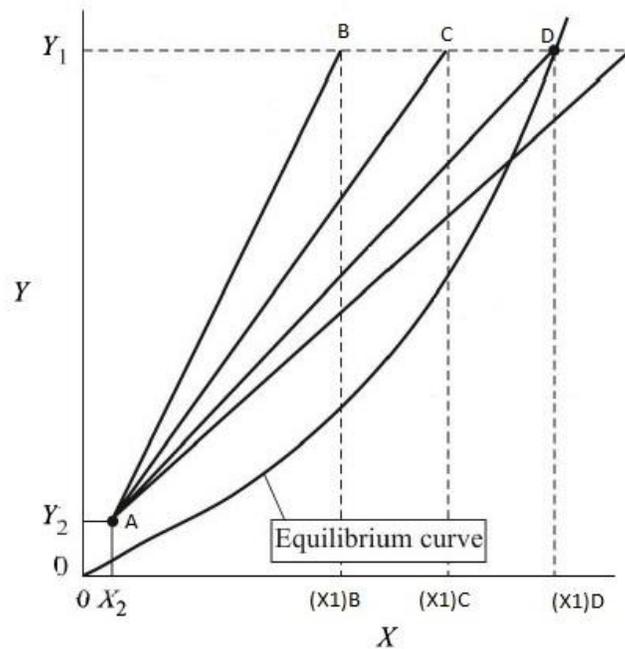
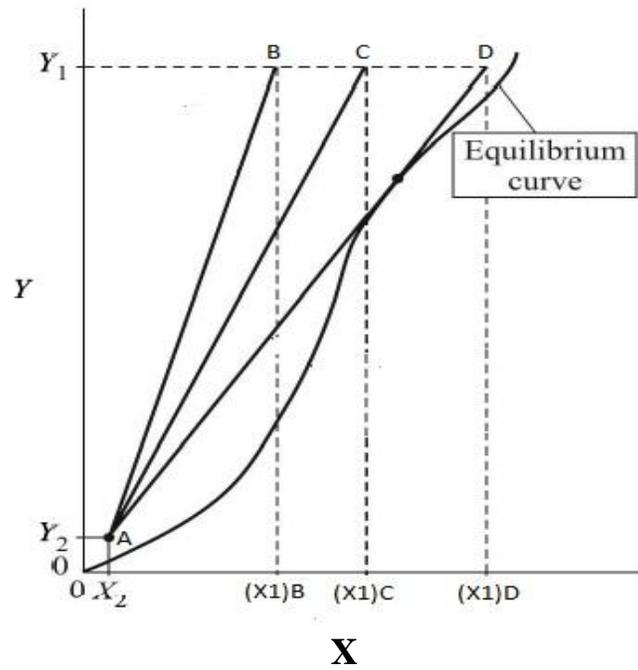
For stripping to take place, the concentration of the solute in the liquid phase should be higher than the equilibrium value, and the operating line therefore should lie under the equilibrium curve.

For absorption, the vertical distance PQ is the driving force in terms of the gas phase concentration and the horizontal distance PR is the driving force (X^*-X) in terms of liquid phase concentration.

For stripping, the vertical and horizontal distances between the equilibrium curve and the operating line still representing the driving force in terms of gas phase and liquid phase concentrations respectively.

Minimum liquid rate for absorption

In gas absorption, the amount of gas to be handled, the entering and exit gas compositions and the composition of the entering solvent are fixed by process requirements. The amount of the solvent to be used has to be fixed by the designer.



Refer to the operating line in the above figures, the slope equals to (L'_m / G'_m) and starts from the fixed point (X_2, Y_2) (point A). As the amount of solvent is gradually decreased, the slope of the operating line decreases and it comes closer to the equilibrium curve. The driving force will decrease as a result, and the larger height of packing, or a larger number of plates has to be used to achieve the desired degree of separation.

In the situation at which the operating line meets the equilibrium curve at a certain point, the driving force at this point is zero, and the corresponding liquid rate is the theoretical “minimum liquid rate”. The slope of the operating line in this situation could be mathematically expressed as:

$$\text{slope} = \frac{(L'_m)_{\min}}{G'_m}$$

And the concentration of the exit liquid is (X_{\max}) and the driving force is zero at the meeting point between the operating line and equilibrium curve, and this point is called “pinch point”.

Notes:

- For the stripping operation, at the pinch point, the determined term will be “minimum gas flow rate $(G'_m)_{\min}$ ”.
- If the equilibrium relation expressed in terms of mole ratio unit is linear $(Y=\alpha X)$, the minimum liquid flow rate can be determined by calculating $X_{\max} = \frac{Y_1}{\alpha}$, and substitute this value in the overall material balance equation to get:

$$(L'_m)_{\min} = G'_m \frac{Y_1 - Y_2}{\left(\frac{Y_1}{\alpha}\right) - X_2}$$

- The absorption column should be operated as a liquid rate higher than the minimum value. The frequently used value is:

$$L'_m = (1.2 - 2) (L'_m)_{\min}$$

Example: (Calculation of the minimum solvent rate)

In a petrochemical plant, a gas containing 4% cyclo-hexane and 96% inert has to be treated with a non-volatile absorption oil in a packed tower. It is required to remove 98% of the cyclo-hexane of the feed gas. The feed solvent is free from cyclo-hexane. If the feed gas rate is 80 kmol / hr, calculate the minimum solvent rate. The equilibrium relation is given as:

$$Y = \frac{0.2X}{1 + 0.8X}$$

Solution:

$$G_m = 80 \text{ kmol/hr}$$

$$y_1 = 0.04$$

$$y_2 = 0.02 * 0.04 = 0.0008$$

$$x_2 = 0$$

$$Y_1 = \frac{y_1}{1 - y_1} = \frac{0.04}{1 - 0.04} = 0.0417$$

$$Y_2 = \frac{y_2}{1 - y_2} = \frac{0.0008}{1 - 0.0008} = 0.0008$$

$$G'_m = G_m(1 - y_1) = 80 * (1 - 0.04) = 76.8 \text{ kmol/hr}$$

Now we construct the equilibrium data (X, Y) using the given equilibrium relationship:

X	0	0.01	0.03	0.05	0.07	0.09	0.12
Y	0	0.00198	0.00586	0.0097	0.0132	0.0168	0.0219

Now we plot this data on XY plot in combination with the operating line that starts at (X₂, Y₂) and change the slope until the operating line touches the equilibrium line to form pinch point as shown below.

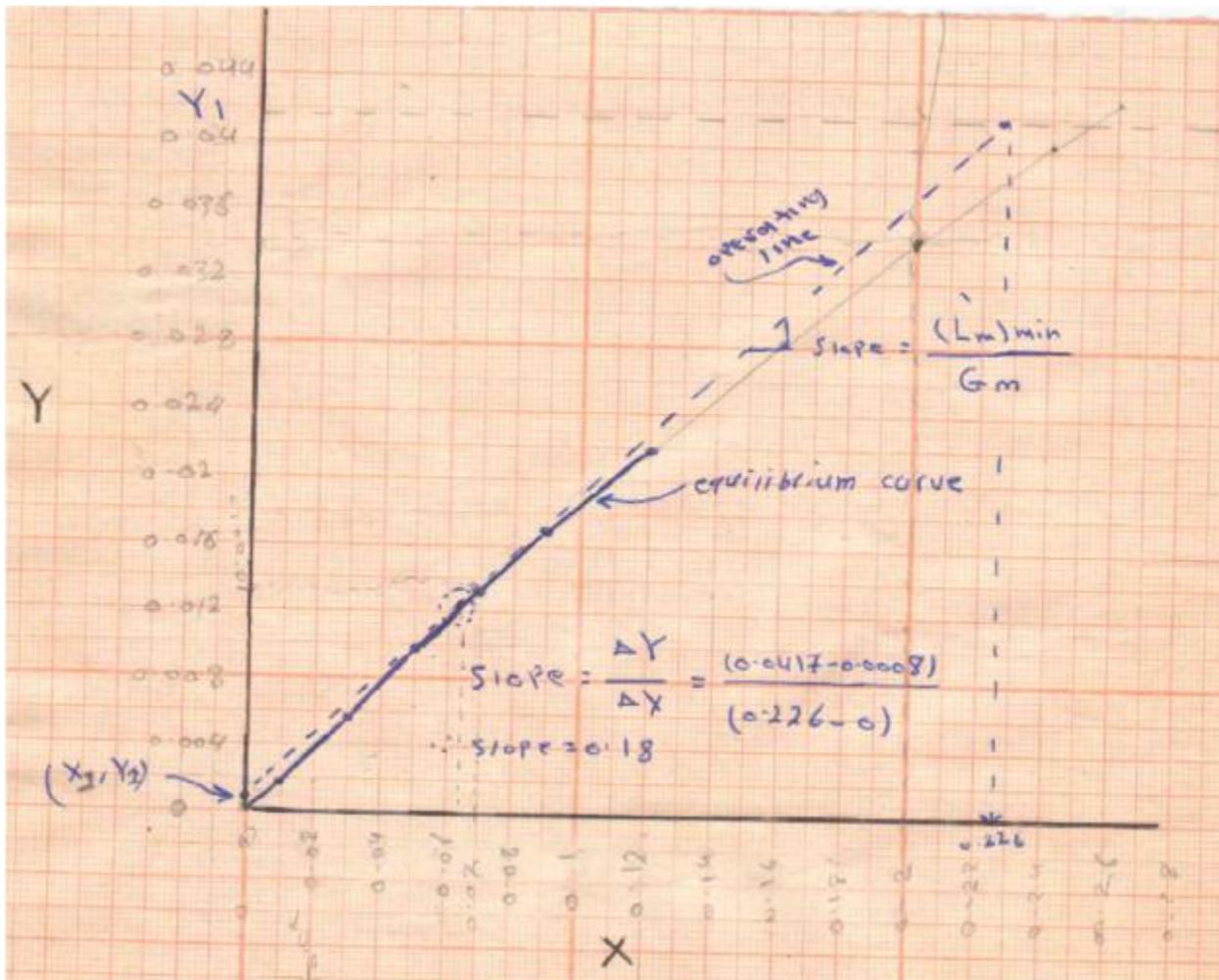
At this point, the slope = 0.18

$$\frac{(L'_m)_{min}}{G'_m} = 0.18$$

From which:

$$(L'_m)_{\min} = 0.18 * G_m = 0.18 * 76.8 = 13.824 \text{ kmol/hr}$$

$$(L'_m)_{\min} = 13.824 \text{ kmol/hr}$$



Design of a packed tower

The packed tower and the plate tower are the two common choices for carrying out a gas absorption operation (there are other options like the venture scrubber, the spray column, the agitated contactor, etc.). In a plate column, the gas and the liquid phases come into contact on discrete stages. So, it is called “stage-wise contact”, and the gas and liquid concentrations undergo step change from one plate to the next. In a packed tower, on the other hand, the liquid moving down through the packing remains in contact with the up-flowing gas at every point of the packed section, also, the concentration of both phases change continuously, so, a packed column is called a “continuous differential contact equipment”.

Design method based on the individual mass transfer coefficients:

Consider the packed column schematically shown below:

Take a basis of one unit area, and let (a) be the specific interfacial area (interfacial area / unit volume of packing m^2 / m^3)

Making a steady state material balance of the column thickness dh:

$$\text{Rate of flow of solute (with carrier gas)} = G_m * y \left(\frac{\text{mol}}{\text{time.area}} \right)$$

$$\text{The change in the solute flow rate over the section} = d(G_m * y)$$

$$\text{The volume of unit cross – sectional area} = 1(dh)$$

$$\text{Interfacial area of contact in the differential section} = a * 1 * dh$$

$$\text{Rate of mass transfer of solute} = a * dh * N_A$$

A mass balance over the elementary section of the bed:

$$a * dh * N_A = -d(G_m * y) = -G_m * dy - y * dG_m \dots\dots\dots (1)$$

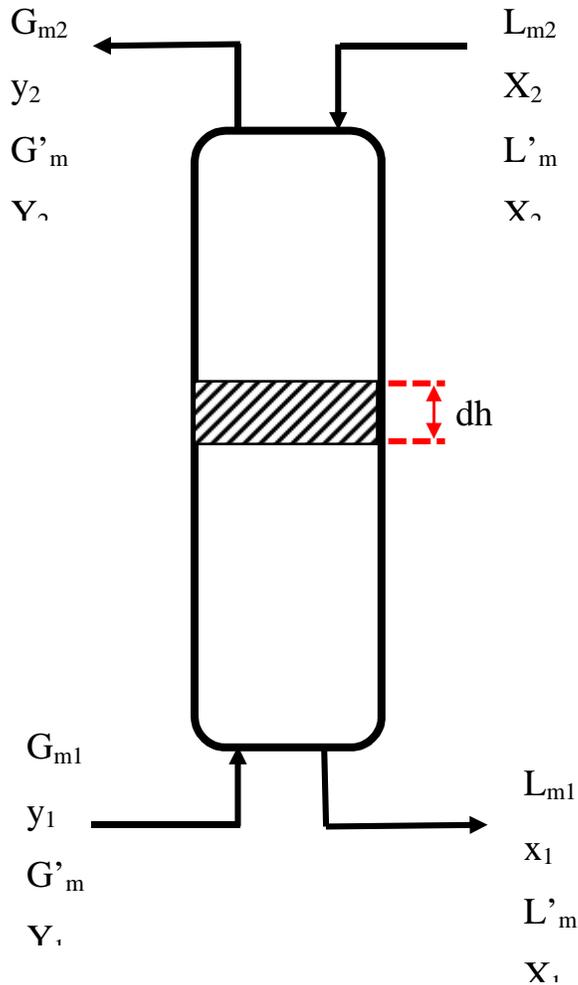
Since the carrier gas is not soluble, the change in the total gas flow rate equals to the rate of mass transfer of solute, i.e.

$$-dG_m = a * dh * N_A \dots\dots\dots (2)$$

Substitute equation (1) in equation (2)

$$a * dh * N_A = -G_m * dy + y(a * dh * N_A)$$

$$a * dh * N_A - y(a * dh * N_A) = -G_m * dy$$



$$a * dh * N_A(1 - y) = -G_m * dy$$

$$dh = \frac{-G_m * dy}{a * N_A(1 - y)} \dots\dots\dots (3)$$

$$N_A = k_y(y - y_i) \dots\dots\dots (4)$$

Substitute (3) in (4)

$$dh = \frac{-G_m * dy}{a * k_y(y - y_i)(1 - y)} \dots\dots\dots (5)$$

$$\int_0^{h_T} dh = - \int_{y_1}^{y_2} \frac{G_m * dy}{a * k_y(y - y_i)(1 - y)}$$

$$h_T = - \int_{y_1}^{y_2} \frac{G_m * dy}{a * k_y(y - y_i)(1 - y)} \dots\dots\dots (6)$$

The integration of equation (6) can be found numerically or graphically by finding the values of y_i corresponding to different values of y chosen between y_1 and y_2 , and finding the values of G_m for each value of y .

Use the following steps to solve equation (6):

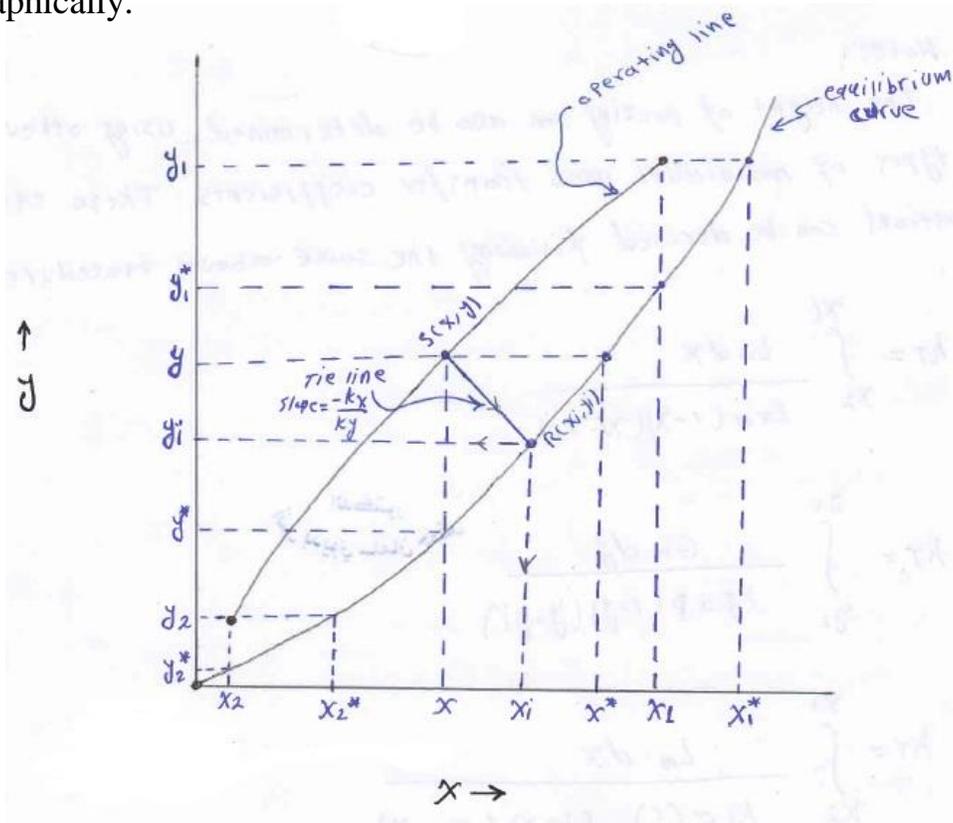
1. Draw the equilibrium curve on the x-y plane for the given gas-liquid system.
2. Draw the operating line from the material balance equation:

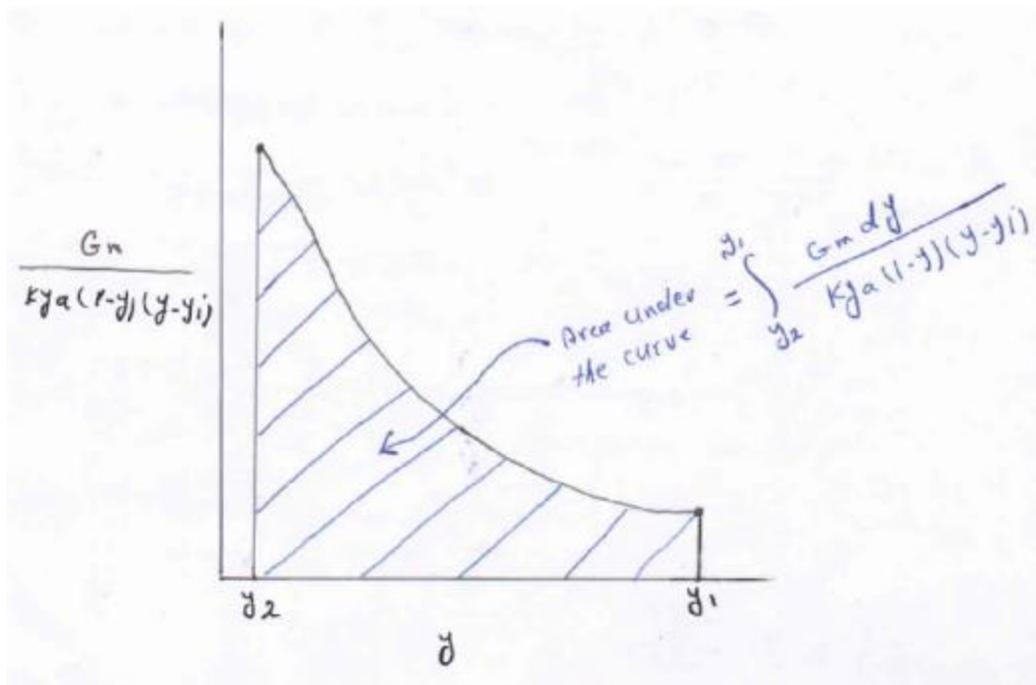
$$G'_m \left[\frac{y}{1-y} - \frac{y_2}{1-y_2} \right] = L'_m \left[\frac{x}{1-x} - \frac{x_2}{1-x_2} \right]$$

3. Take any point (x,y) on the operating line, using the known values of k_x and k_y (or $k_x a$ & $k_y a$) and draw a line of slope $-k_x / k_y$ from point S (x,y) to meet the equilibrium curve at R (x_i, y_i) . So, y_i is known for the particular value of y . The line SR is called "tie line".
4. Repeat step 3 for a number of other points on the operating line. If k_x & k_y or their ratio are constant, a set of lines parallel to that drawn in step (3) may be constructed. These chosen points should be lying between y_1 and y_2 .
5. Calculate G_m at each point where:

$$G_m = G'_m (1 + Y)$$

6. Use the constructed above data and solve the integral numerically or graphically.





Note:

The height of packing can also be determined using other types of individual mass transfer coefficients. These equations can be derived following the same above procedure:

$$h_T = \int_{x_2}^{x_1} \frac{L_m * dx}{a * k_x (x_i - x) (1 - x)}$$

$$h_T = \int_{y_2}^{y_1} \frac{G_m * dy}{a * k_g * P * (y - y_i) (1 - y)}$$

$$h_T = \int_{x_2}^{x_1} \frac{L_m * dx}{a * k_l * C_{av} (x_i - x) (1 - x)}$$

Where:

P = pressure

C_{av} = average concentration

Design method based on the overall mass transfer coefficient

Conducting the same material balance on the differential section of the packed column (for unit cross sectional area):

$$a * dh * N_A = -d(G_m * y)$$

$$a * dh * N_A = -G_m dy - ydG_m$$

But

$$-dG_m = adhN_A$$

$$a * dh * N_A = -G_m dy + (a * dh * N_A)y$$

$$a * dh * N_A(1 - y) = -G_m dy$$

$$dh = \frac{-G_m dy}{N_A a(1 - y)}$$

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

$$dh = \frac{-G_m dy}{koy \cdot a(y - y^*)(1 - y)}$$

$$\int_0^{h_T} dh = \int_{y_1}^{y_2} \frac{-G_m dy}{koy \cdot a(y - y^*)(1 - y)}$$

$$h_T = \int_{y_2}^{y_1} \frac{G_m dy}{koy \cdot a(y - y^*)(1 - y)}$$

By the same way, height of packing can be expressed as:

$$h_T = \int_{x_2}^{x_1} \frac{L_m dx}{kox \cdot a(x^* - x)(1 - x)}$$

$$h_T = \int_{y_2}^{y_1} \frac{G_m dy}{KOG \cdot a(y - y^*)(1 - y)}$$

$$h_T = \int_{x_2}^{x_1} \frac{L_m dx}{KOL. a. (C)_{av} (x^* - x) (1 - x)}$$

These integrals can be solved graphically or numerically by choosing different values of x and y (values of x and y should be chosen between x_1, x_2 and y_1, y_2 respectively) on the operating line, and finding the corresponding values y^* and x^* , and finding L_m, G_m at each point and solve the integration.

Design method base on height of a transfer unit

The following equation has been derived previously:

$$h_T = \int_{y_2}^{y_1} \frac{G_m * dy}{a * k_y (y - y_i) (1 - y)}$$

$$\frac{G_m}{k_y. a (1 - y)_{iM}} = \frac{G_m}{k_y. a y_{BiM}} \cong \text{constant}$$

Where:

$$(1 - y)_{iM} = \frac{(1 - y_i) - (1 - y)}{\ln \frac{(1 - y_i)}{(1 - y)}}$$

$$(1 - y) = y_B$$

$$h_T = \int_{y_2}^{y_1} \frac{G_m (1 - y)_{iM} * dy}{a * k_y. (1 - y)_{iM}. (y - y_i) (1 - y)}$$

$$h_T = \frac{G_m}{k_y. a (1 - y)_{iM}} \int_{y_2}^{y_1} \frac{(1 - y)_{iM} * dy}{(y - y_i) (1 - y)}$$

$$h_T = H_{tG} \int_{y_2}^{y_1} \frac{(1 - y)_{iM} * dy}{(y - y_i) (1 - y)}$$

Where:

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

Where:

$$k'_y = k_y(1 - y)_{iM}$$

And

$$\int_{y_2}^{y_1} \frac{(1 - y)_{iM} * dy}{(y - y_i)(1 - y)} = N_{tG} = NTUG = \text{number of individual gas transfer units}$$

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

By the same way, using any other kind of mass transfer coefficient, height of transfer units and the number of transfer units can be defined. If the rate of mass transfer is expressed in terms of individual liquid phase mass transfer coefficient, the height of packing can be written as:

$$h_T = N_{tL} \cdot H_{tL}$$

Where:

$$H_{tL} = \frac{L_m}{k_x \cdot a(1 - x)_{iM}} = \frac{L_m}{k_x \cdot a \cdot x_{iBM}}$$

$$N_{tL} = \int_{x_2}^{x_1} \frac{(1 - x)_{iM}}{(1 - x)(x_i - x)}$$

And

$$(1 - x)_{iM} = \frac{(1 - x) - (1 - x_i)}{\ln \frac{(1 - x)}{(1 - x_i)}}$$

H_{tL} = height of individual liquid phase transfer unit.

N_{tL} = number of individual liquid phase transfer units.

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

$$h_T = \int_{y_2}^{y_1} \frac{G_m(1 - y)_M^* \cdot dy}{k_{oy} \cdot a \cdot (1 - y)_M^* (1 - y)(y - y^*)}$$

$$h_T = \frac{G_m}{koy. a. (1 - y)_M^*} \int_{y_2}^{y_1} \frac{(1 - y)_M^* \cdot dy}{(1 - y)(y - y^*)}$$

$$h_T = H_{tOG} \cdot N_{tOG}$$

H_{tOG} = height of overall gas phase transfer units.

N_{tOG} = number of overall gas phase transfer units.

$$H_{tOG} = \frac{G_m}{koy. a. (1 - y)_M^*}$$

$$N_{tOG} = \int_{y_2}^{y_1} \frac{(1 - y)_M^* \cdot dy}{(1 - y)(y - y^*)}$$

$$(1 - y)_M^* = \frac{(1 - y^*) - (1 - y)}{\ln \frac{(1 - y^*)}{(1 - y)}}$$

Example:

A gas mixture containing 10% SO₂ and 90% air at 1 atm total pressure and 30 °C is to be scrubbed with water to remove 97% of the SO₂ in a tower packed with 25 mm ceramic Rasching rings. The feed gas rate is 1500 kg per hour. If the column cross-sectional area is 0.781 m², calculate (a) the minimum liquid rate (b) the packed height if the liquid rate is 1.25 times the minimum.

The Colburn-Drew volumetric mass transfer coefficients at the given conditions are: $kx'.a = 1.25$ (kmol/m³.s (Δx)) and $ky'.a = 0.075$ (kmol/m³.s (Δy))

Molecular weight of SO₂ = 64

Molecular weight of air = 28.8

Equilibrium data for SO₂-water system is given as:

10 ⁴ x	0	0.562	1.403	2.8	4.22	8.42	14.03	19.65	27.9
10 ³ y	0	0.79	2.23	6.19	10.65	25.9	47.3	68.5	104

Solution:

$$y_1 = 0.1$$

$$P = 1 \text{ atm}$$

$$T = 30 \text{ }^\circ\text{C}$$

$$x_2 = 0$$

$$\text{Removal percent} = 97\%$$

$$\text{Feed gas} = 1500 \text{ kg / hr}$$

$$\text{x-area} = 0.781 \text{ m}^2$$

$$kx'.a = 1.25 \text{ (kmol/m}^3\text{.s (}\Delta x\text{))}$$

$$ky'.a = 0.075 \text{ (kmol/m}^3\text{.s (}\Delta y\text{))}$$

$$\text{m.wt of SO}_2 = 64$$

$$\text{m.wt of air} = 28.8$$

$$\text{average molecular weight of entering gas mixture} = (0.1)(64) + (0.9)(28.8) = 32.2$$

$$Gm_1 = \frac{1500 \left(\frac{kg}{hr}\right)}{32.32 (kg/kmol)} = 46.41 \text{ kmol/hr}$$

$$Gm' = Gm(1 - y)$$

$$Gm' = 46.41(1 - 0.1) = 41.769 \text{ kmol/hr}$$

$$SO_2 \text{ entering} = Gm_1 \cdot y_1 = (46.41)(0.1) = 4.641 \text{ kmol / hr}$$

97% of this SO₂ should be absorbed

$$SO_2 \text{ removed} = (0.97)(4.641) = 4.502 \text{ kmol / hr}$$

$$SO_2 \text{ leaving the column} = 4.641 - 4.502 = 0.14 \text{ kmol/hr}$$

$$Y_2 = \frac{SO_2 \text{ leaving}}{Gm'} = \frac{0.14}{41.769} = 0.00335$$

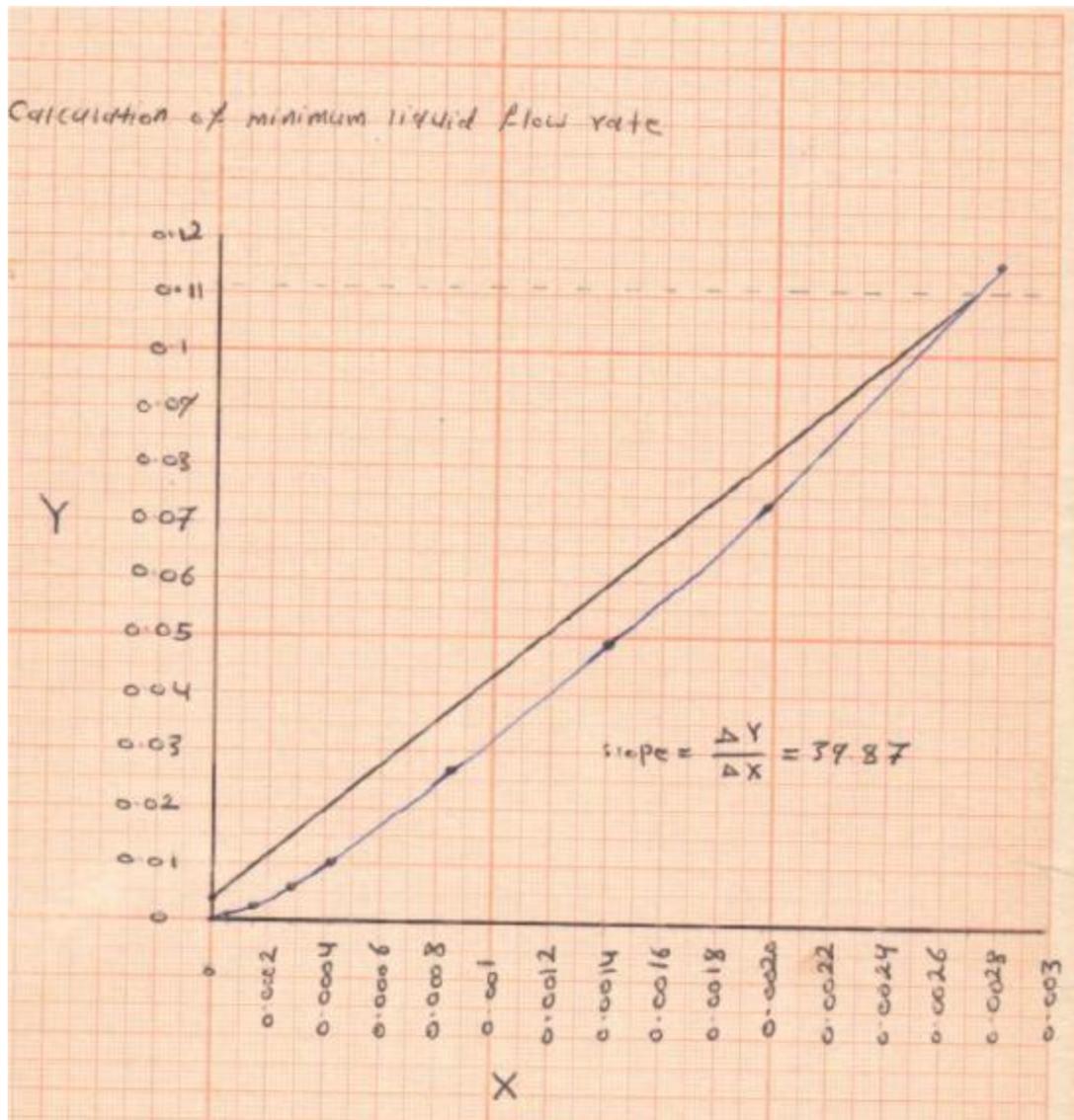
$$y_2 = \frac{Y_2}{1 + Y_2} = \frac{0.00335}{1 + 0.00335} = 0.00334$$

$$Y_1 = \frac{y_1}{1 - y_1} = \frac{0.1}{1 - 0.1} = 0.111$$

(a) Minimum liquid flow rate:

1. Convert the given equilibrium data from (x,y) to (X,Y).
2. Plot this data on X-Y plane.
3. Starting from (X₂, Y₂) and ending with Y₂, draw the operating line and get the pinch point.
4. Calculate the slope of this line to get the minimum liquid flow rate.

10⁴x	X	10³y	Y
0	0	0	0
0.562	5.62 x 10 ⁻⁵	0.79	7.9 x 10 ⁻⁴
1.403	1.403 x 10 ⁻⁵	2.23	2.234 x 10 ⁻⁴
2.8	2.8 x 10 ⁻⁴	6.19	6.23 x 10 ⁻³
4.22	4.22 x 10 ⁻⁴	10.65	0.0107
8.42	8.42 x 10 ⁻⁴	25.9	0.0265
14.03	1.405 x 10 ⁻³	47.3	0.0496
19.65	1.97 x 10 ⁻³	68.5	0.0735
27.9	2.8 x 10 ⁻³	104	0.116



From the plot we can find that the slope is 39.87

So,

$$(L'_m)_{min} = 1665.33 \text{ kmol/hr}$$

$$L'_m = (1.25)(1665.33) = 2081.662 \text{ kmol/hr}$$

b- Determination of the packing height

Using the given data, height of packing can be calculated from the equation:

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

$$H_{tG} = \frac{G_m}{k'_y \cdot a}$$

$$\int_{y_2}^{y_1} \frac{(1-y)_{iM} * dy}{(y-y_i)(1-y)} = N_{tG}$$

$$G_{m1} = 46.41 \text{ kmol/hr}$$

$$G_{m2} = G_{m1} - (\text{SO}_2)_{\text{removed}} = 46.41 - 4.502 = 41.908 \text{ kmol/hr}$$

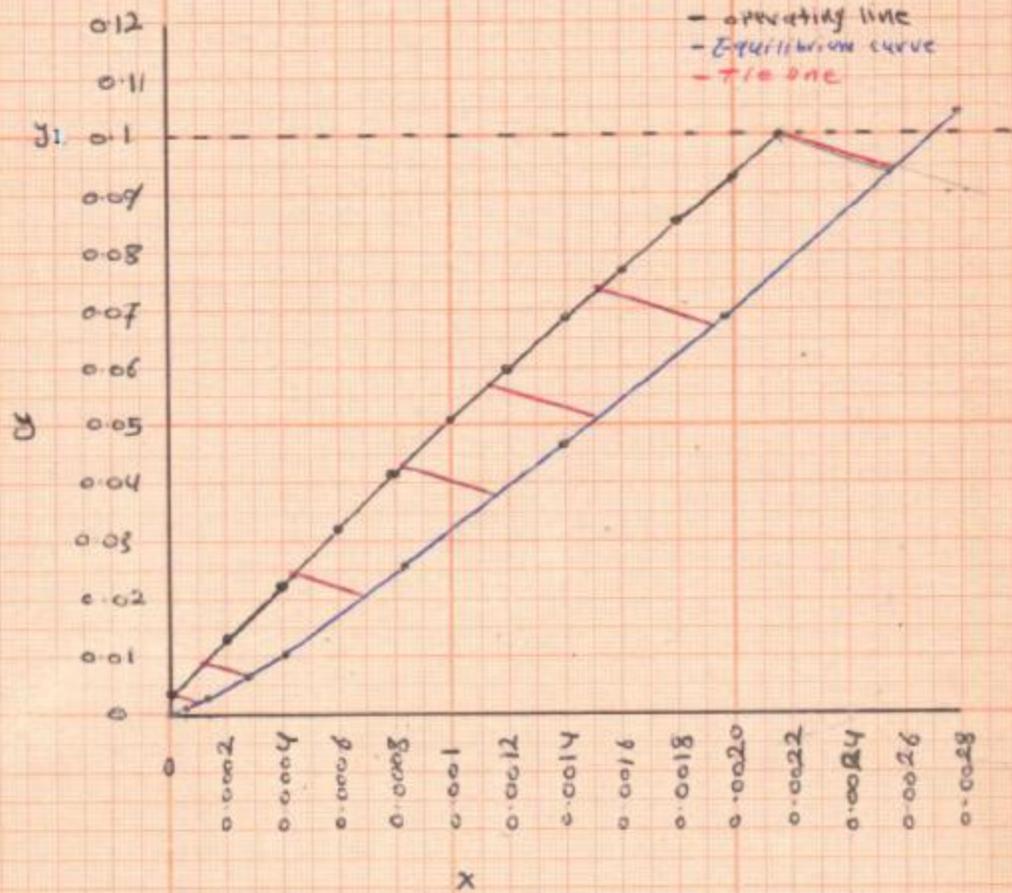
These values should be divided by x-area in order to be used in HtG equation:

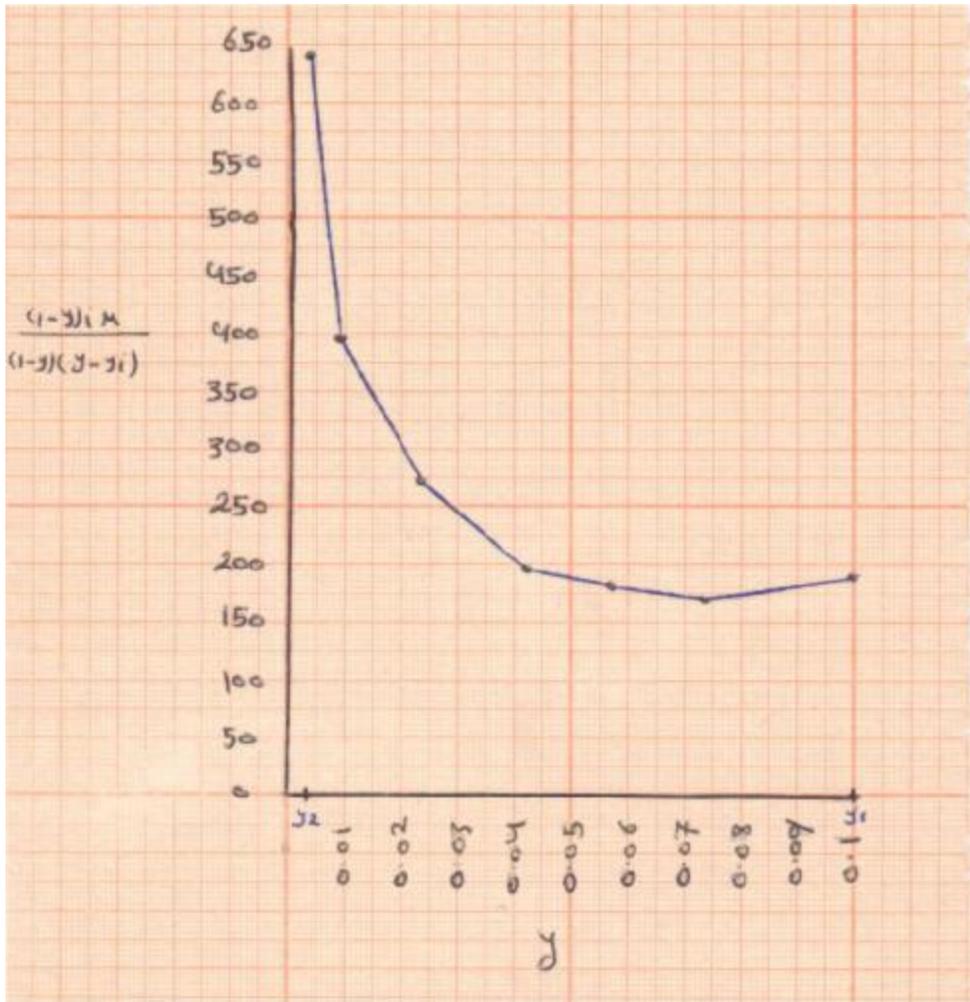
$$G_{m1} = 46.41 / 0.781 = 59.423 \text{ kmol / hr.m}^2$$

$$G_{m2} = 41.908 / 0.781 = 53.66 \text{ kmol / hr.m}^2$$

$$G_m = \frac{G_{m1} + G_{m2}}{2} = \frac{59.423 + 53.66}{2} = 56.54 \frac{\text{kmol}}{\text{hr.m}^2}$$

Prediction of β_1





Simplified design procedure for dilute gases

In case of that the concentration of the solute in the gas stream is (<25%), the following approximations are safe:

$$\frac{(1 - y)_{iM}}{1 - y} \approx 1$$

$$\frac{(1 - y)_M^*}{1 - y} \approx 1$$

$$(1 - y)_M^* \approx 1 - y$$

$$NtOG = \int_{y_2}^{y_1} \frac{(1 - y)_M^*}{(1 - y)(y - y^*)} \cdot dy \approx \int_{y_2}^{y_1} \frac{dy}{(y - y^*)}$$

$$NtOG = \int_{y_2}^{y_1} \frac{dy}{(y - y^*)}$$

If the equilibrium relationship is linear, the above integral can be evaluated analytically assuming that the gas and liquid rates remain reasonably constant over the height of the packing. If L_m and G_m remain nearly constant (which is true for dilute gases), the equation of the operating line will be:

$$G_m(y - y_2) = L_m(x - x_2)$$

$$x = \frac{G_m}{L_m}(y - y_2) + x_2$$

Since the equilibrium relationship is linear,

$$y^* = m \cdot x$$

$$NtOG = \int_{y_2}^{y_1} \frac{dy}{(y - y^*)} = \int_{y_2}^{y_1} \frac{dy}{(y - m \cdot x)}$$

But

$$x = \frac{G_m}{L_m}(y - y_2) + x_2$$

$$NtOG = \int_{y_2}^{y_1} \frac{dy}{y - m\left[\frac{Gm}{Lm}(y - y_2) + x_2\right]}$$

$$NtOG = \int_{y_2}^{y_1} \frac{dy}{y - \frac{mGm}{Lm}y + \frac{mGm}{Lm}y_2 - mx_2}$$

Let

$$\frac{mGm}{Lm} = \theta$$

$$NtOG = \int_{y_2}^{y_1} \frac{dy}{y(1 - \theta) + \theta y_2 - mx_2}$$

$$NtOG = \frac{1}{1 - \theta} \ln \frac{y_1(1 - \theta) + \theta y_2 - mx_2}{y_2(1 - \theta) + \theta y_2 - mx_2}$$

Overall material balance:

$$Gm(y_1 - y_2) = Lm(x_1 - x_2)$$

$$Gm(y_1 - y_2) = \frac{Lm}{m}(mx_1 - mx_2)$$

$$Gm(y_1 - y_2) = \frac{Lm}{m}(y_1^* - y_2^*)$$

$$\frac{Gm}{Lm} = \frac{y_1^* - y_2^*}{m(y_1 - y_2)}$$

$$\theta = \frac{mGm}{Lm} = m \frac{y_1^* - y_2^*}{m(y_1 - y_2)} = \frac{y_1^* - y_2^*}{(y_1 - y_2)}$$

$$1 - \theta = 1 - \frac{y_1^* - y_2^*}{(y_1 - y_2)} = \frac{(y_1 - y_1^*) - (y_2 - y_2^*)}{(y_1 - y_2)}$$

$$NtOG = \frac{y_1 - y_2}{(y_1 - y_1^*) - (y_2 - y_2^*)} \ln \frac{y_1 - m\left[\frac{Gm}{Lm}(y_1 - y_2) + x_2\right]}{y_2 - mx_2}$$

Previously, we found that:

$$x = \frac{Gm}{Lm} (y - y_2) + x_2$$

$$x_1 = \frac{Gm}{Lm} (y_1 - y_2) + x_2$$

$$NtOG = \frac{y_1 - y_2}{(y_1 - y_1^*) - (y_2 - y_2^*)} \ln \frac{y_1 - mx_1}{y_2 - mx_2}$$

But

$$y^* = mx$$

$$NtOG = \frac{y_1 - y_2}{(y_1 - y_1^*) - (y_2 - y_2^*)} \ln \frac{y_1 - y_1^*}{y_2 - y_2^*}$$

$$NtOG = \frac{y_1 - y_2}{(y_1 - y_1^*) - (y_2 - y_2^*)} = \frac{y_1 - y_2}{(y - y^*)_M} \ln \frac{y_1 - y_1^*}{y_2 - y_2^*}$$

where $(y - y^*)_M = \log \text{mean of the driving force at the top and bottom terminals}$

$$(y - y^*)_M = \frac{(y_1 - y_1^*) - (y_2 - y_2^*)}{\ln \frac{y_1 - y_1^*}{y_2 - y_2^*}}$$

Example:

A stream of waste gas containing 0.6% ammonia in air is to be cleaned by removing 99.5% of the ammonia before it can be discharged into the atmosphere. Because of the low concentration of the gas and very high degree of removal desired, a dilute mineral acid is a good solvent. Dilute sulphuric acid is selected as the absorbent because of its low cost and negligible vapor pressure of the acid.

Removal of ammonia is to be done in a packed tower 1 m² in cross-section, in which the feed gas rate is 2000 kg/hr.m² and the liquid is supplied at a rate of 2200 kg/hr.m². The absorption is gas film resistance controlled and the overall volumetric mass transfer coefficient of ammonia on the gas phase basis is $KOG.a = 1350$ (kg/hr.m³.bar). The total pressure of the column is 101.3 kpa and the temperature is 28 °C, molecular weight of ammonia is 17 and for air it is 28.8.

- (a) What total packed height is required to accomplish the separation?
- (b) Recalculate the packed height if only 95% of the ammonia in the feed gas is removed.
- (c) What would be the value of the individual gas phase mass transfer coefficient if the specific surface area of the packing is 60 m²/m³
- (d) Estimate the thickness of the gas film if the diffusivity of ammonia in the carrier gas is 0.0765 m²/hr.

Solution:

Average molecular weight of the entering gas = (0.994)(28.8) + (0.006)(17) = 28.73

$$Gm = \frac{G}{M.Wt} = \frac{2000}{28.73} = 69.61 \frac{kmol}{m^2.hr}$$

$$NH_3 \text{ entering with feed} = (0.006)(69.61) = 0.417 \frac{kmol}{m^2.hr}$$

$$NH_3 \text{ absorbed} = (0.995)(0.4171) = 0.415 \frac{kmol}{m^2.hr}$$

$$NH_3 \text{ leaving} = NH_3 \text{ entering} - NH_3 \text{ absorbed} = 0.417 - 0.415 = 0.002 \frac{kmol}{m^2.hr}$$

$$\text{Total gas leaving} = 69.61 - 0.415 = 69.195 \text{ kmol} / m^2.hr$$

$$\text{Mole fraction of } NH_3 \text{ in the leaving gas} = 0.002 / 69.195 = 3 \times 10^{-5}$$

- (a) The feed concentration is very low

$$(1 - y)_M^* \approx 1$$

$$y^* = 0$$

$Gm \approx \text{constant}$

$$h_t = \text{HtOG} \cdot \text{NtOG}$$

$$\text{HtOG} = \frac{Gm}{KOG \cdot a \cdot P} = \frac{69.402}{\left(\frac{1350}{17}\right)(1.013)} = 0.862 \text{ m}$$

$$\text{NtOG} = \int_{y_2}^{y_1} \frac{dy}{(y - y^*)} = \int_{y_2}^{y_1} \frac{dy}{y} = \ln \frac{y_1}{y_2} = \ln \frac{0.006}{3 \times 10^{-5}} = 5.298$$

$$h_t = (0.865)(5.298) = 4.573 \text{ m}$$

(b)

$$\text{HtOG} = 0.863 \text{ m}$$

$$\text{NH}_3 \text{ leaving} = (1 - 0.95)(0.417) = 0.0208$$

$$y_2 = (1 - 0.95)(0.006) = 3 \times 10^{-4}$$

$$\text{NH}_3 \text{ absorbed} = 0.3961$$

$$Gm_2 = 89.61 - 0.3961 = 69.2139$$

Similarly

$$\text{NtOG} = \int_{y_2}^{y_1} \frac{dy}{y} = \ln \frac{y_1}{y_2} = \ln \frac{0.006}{3 \times 10^{-4}} = 2.995$$

$$h_t = \text{HtOG} \cdot \text{NtOG} = (0.865)(2.995) = 2.591 \text{ m}$$

(c)

The process is gas film control

$$\frac{1}{KOG} = \frac{1}{kg} \text{ or } \frac{1}{KOG \cdot a} = \frac{1}{kg \cdot a}$$

So

$$KOG \cdot a = kg \cdot a$$

$$K_g a = 1350 \text{ kg/hr.m}^3 \cdot \text{bar}$$

$$a = 20 \text{ m}^2/\text{m}^3$$

$$k_g = \frac{1350}{(60)(17)} = 1.323 \frac{\text{kmol}}{\text{hr.m}^3 \cdot \text{bar}}$$

(d)

The individual gas phase mass transfer coefficient can be mathematically expressed as:

$$k_g = \frac{D_{AB}}{R \cdot T \cdot l_{gas}}$$

Where l_{gas} is the thickness of the gas film

So

$$1.323 = \frac{0.0756 \text{ (m}^2/\text{s)}}{(0.08137)(28 + 273)l_{gas}} = 2.315 \times 10^{-3}$$

An approximate design method for concentrated gases

For concentrated gases, the following assumption can be adopted:

$$(1 - y)_M^* \approx \frac{(1 - y^*) + (1 - y)}{2}$$

$$NtOG = \int_{y_2}^{y_1} \frac{(1 - y)_M^*}{(1 - y)(y - y^*)} dy$$

$$NtOG = \int_{y_2}^{y_1} \frac{[(1 - y^*) + (1 - y)]}{2(1 - y)(y - y^*)} dy = \int_{y_2}^{y_1} \frac{2 - y^* - y}{2(1 - y)(y - y^*)} dy$$

$$NtOG = \int_{y_2}^{y_1} \frac{2 - y^* - y + y - y}{2(1 - y)(y - y^*)} dy$$

$$NtOG = \int_{y_2}^{y_1} \frac{(2 - 2y) + (y - y^*)}{2(1 - y)(y - y^*)} dy$$

$$NtOG = \int_{y_2}^{y_1} \frac{[2(1 - y) + (y - y^*)]}{2(1 - y)(y - y^*)} dy$$

$$NtOG = \int_{y_2}^{y_1} \frac{dy}{(y - y^*)} + \frac{1}{2} \int_{y_2}^{y_1} \frac{dy}{(1 - y)}$$

$$NtOG = \int_{y_2}^{y_1} \frac{dy}{(y - y^*)} + \frac{1}{2} \ln \frac{1 - y_2}{1 - y_1}$$

The integral on the right hand side can be evaluated graphically or numerically. At the top of the column, both y and y^* are very small and the integral will be very large. This may make the integral cumbersome. Numerical integration becomes more convenient if the integral is expressed in the form:

$$\int_{y_2}^{y_1} \frac{dy}{(y - y^*)} = \int_{y_2}^{y_1} \left[\frac{y}{(y - y^*)} \cdot \frac{dy}{y} \right] = \int_{y_2}^{y_1} \left[\frac{y}{(y - y^*)} \cdot d(\ln y) \right]$$

$$NtOG = \int_{y_2}^{y_1} \frac{y}{(y - y^*)} d(\ln y) + \frac{1}{2} \ln \frac{1 - y_2}{1 - y_1}$$

The first part of this integration can be determined graphically.

Example:

Ammonia is to be scrubbed from a stream of air containing 16% of solute by water at 25 °C and 1 atm total pressure. The feed gas rate is 60 kmol/m².h and the water rate is 70 kmol/m².h. It is required to remove 99% of the ammonia in the feed. If the overall gas phase volumetric mass transfer coefficient is $k_{o,y} = 100 \text{ kmol/m}^3\cdot\text{h}$, determine the HTU, NTU and the height of packing required using the approximate method for concentrated gas.

Equilibrium relationship may be expressed as:

$$\log \frac{p(1-x)y^*}{55.5x} = 4.699 - \frac{1922}{T}$$

Where:

Vapor pressure of water at 25 °C = 0.4574 psi

p = total pressure (atm) – vapor pressure of water at the given temperature

T = temperature K

x = mole fraction of the solute in the liquid

y^* = equilibrium mole fraction of NH₃ in air.

Solution:

$$Gm' = Gm_1(1 - y_1) = (60)(1 - 0.16) = 50.4 \frac{\text{kmol}}{\text{m}^2\cdot\text{h}}$$

$$\text{NH}_3 \text{ input} = 60(0.16) = 9.6 \text{ kmol/m}^2\cdot\text{h}$$

$$\text{NH}_3 \text{ absorbed} = (0.99)(9.6) = 9.504 \text{ kmol/m}^2\cdot\text{h}$$

$$\text{NH}_3 \text{ leaving with the gas} = 9.6 - 9.504 = 0.096 \text{ kmol/m}^2\cdot\text{h}$$

$$Gm_2 = Gm_1 - \text{NH}_3 \text{ absorbed} = 60 - 9.504 = 50.496 \text{ kmol/m}^2\cdot\text{h}$$

$$y_2 = \frac{0.096}{50.496} = 0.002$$

$$Lm_1 = Lm_2 + \text{NH}_3 \text{ absorbed} = 70 + 9.504 = 79.504 \text{ kmol/m}^2\cdot\text{h}$$

$$x_1 = \frac{\text{NH}_3 \text{ absorbed}}{Lm_1} = \frac{9.504}{79.504} = 0.1195$$

$$Lm' = 70 \frac{kmol}{m^2 \cdot h}$$

Equilibrium relationship

p = total pressure – water vapor pressure

$$p = 1 - (0.4574/14.7) = 0.969 \text{ atm}$$

The equilibrium relationship will be:

$$\log \frac{0.969(1-x)y^*}{55.5x} = 4.699 - \frac{1395.011}{298}$$

$$y^* = 1.017 \frac{x}{1-x} \dots\dots\dots(1)$$

Equation of the operating line:

$$Gm'(Y_1 - Y) = Lm'(X_1 - X)$$

$$Y = \frac{Lm'}{Gm'}(X - X_1) + Y_1$$

Or

$$\frac{y}{1-y} = \frac{Lm'}{Gm'} \left(\frac{x}{1-x} - \frac{x_1}{1-x_1} \right) + \frac{y_1}{1-y_1}$$

$$\frac{y}{1-y} = \frac{70}{50.4} \left(\frac{x}{1-x} - \frac{0.1195}{1-0.1195} \right) + \frac{0.16}{1-0.16}$$

$$\frac{y}{1-y} = 1.3889 \left(\frac{x}{1-x} \right) + 0.002 \dots\dots\dots (2)$$

For concentrated gas:

$$NtOG = \int_{y_2}^{y_1} \frac{y}{(y-y^*)} d(\ln y) + \frac{1}{2} \ln \frac{1-y_2}{1-y_1} \dots\dots\dots (3)$$

We need to obtain a set of values of y and y* along the packed bed, and this can be done either by graphical method (plotting the equilibrium line and the equilibrium data on the same graph paper, choosing different values of y (between y1 and y2) and finding out the corresponding values of y* for each y value, or by using the operating line equation in combination with the equilibrium relation according to the following steps:

1. Assume the value of y , use the operating line equation to find the corresponding actual value of x .
2. Substitute the value of actual x in the equilibrium relationship to find the corresponding value of y^* .
3. Alternative solution, you can find an expression for x in term of y from the operating line equation, substitute this expression in the equilibrium relation to get:

$$y^* = f(y)$$

So, you can find the corresponding value of y^* for each value of y directly.

From the operating line equation:

$$\frac{x}{1-x} = 0.72 \left[\left(\frac{y}{1-y} \right) - 0.002 \right] \dots\dots\dots (4)$$

Substitute (4) in (1)

$$y^* = (1.017)(0.72) \left[\left(\frac{y}{1-y} \right) - 0.002 \right]$$

$$y^* = 0.7322 \left[\left(\frac{y}{1-y} \right) - 0.002 \right] \dots\dots\dots (5)$$

Now assume different values of y and find the corresponding value of y^* (between y_1 and y_2):

y	y*	y/(y-y*)	lny
0.002	0	1	-6.215
0.01578	0.0103	3.522	-4.15
0.02945	0.02075	3.385	-3.525
0.04302	0.03145	3.72	-3.146
0.06985	0.0535	4.272	-2.66
0.1093	0.08843	5.24	-2.214
0.1352	0.113	6.09	-2
0.16	0.1381	7.3	-1.83

The area under the plot of $y/(y-y^*)$ vs $\ln y$ is 17.887

$$NtOG = 17.887 + \frac{1}{2} \ln \frac{1 - 0.002}{1 - 0.16} = 17.973$$

$$Gm = \frac{Gm_1 + Gm_2}{2} = \frac{60 + 50.496}{2} = 55.248$$

$$HtOG = \frac{Gm}{koy \cdot a(1 - y)_M^*} = \frac{Gm}{koy' \cdot a} = \frac{55.248}{100} = 0.552 \text{ m}$$

$$h_T = HtOG \cdot NtOG = (0.552)(17.973) = 9.93 \text{ m}$$

Counter-current multi-stage absorption (Tray absorber)

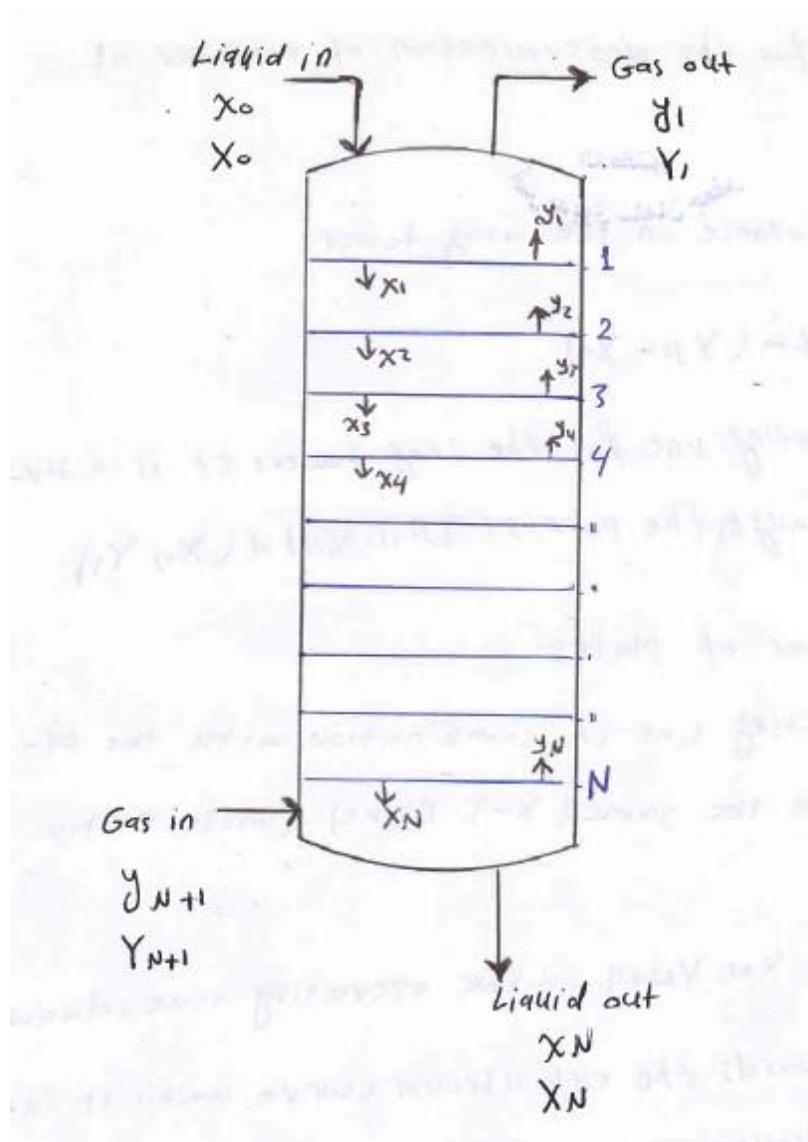
In plate column, gas and liquid come into contact on discrete stages, so, it is called (stage-wise), and the concentration of gas and liquid streams show step changes in concentration from one plate to the next. Determination of the number of the ideal stages is a major step in the design of a tray tower.

In each tray, the liquid is brought into intimate contact with the gas and equilibrium is reached thus making ideal stage. In ideal stage, average composition of the liquid leaving the tray is in equilibrium with average composition of the gas leaving the same tray.

The efficiency of the stages can be calculated as:

$$\text{stage efficiency} = \frac{\text{number of ideal stages}}{\text{number of real stages}}$$

Schematic diagram with standard notation is shown in the following figure:



The following parameters should be known for the determination of “number of stages”:

1. Gas feed rate
2. Concentration of the streams at the inlet and outlet of the tower
3. Actual liquid rate (or minimum liquid rate by which actual liquid rate is determined)
4. Equilibrium data for construction of equilibrium curve.

By these information, number of plates (theoretical stages) can be obtained graphically or algebraically.

Graphical method for the determination of ideal stages

Overall material balance on the tray tower:

$$Gm'(Y_{N+1} - Y_1) = Lm'(X_N - X_0)$$

This is the operating line for the tray tower. It is a straight line passes through the point (X_N, Y_{N+1}) , (X_0, Y_1) .

To find the number of plates:

1. Draw the operating line in combination with the equilibrium curve on the same (X-Y plane) (mole ratio plane).
2. From the point (X_N, Y_{N+1}) on the operating line, draw a vertical line towards the equilibrium curve until it intersect with the equilibrium curve.
3. From this intersection point, draw a horizontal line towards left to intercept with the operating line.
4. From this intersection point, draw a vertical line to intersect with the equilibrium curve.
5. Repeat steps 3 and 4 until you reach the point (X_0, Y_1) .
6. Calculate the number of triangles formed, and this represents the number of plates.

Algebraic determination of number of ideal stages

If both operating line and equilibrium data are straight, number of ideal stages can be calculated algebraically. For absorption:

If the equilibrium relation is $Y = \alpha X$, then

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

Where

$$A = \frac{\text{slope of operating line}}{\text{slope of equilibrium line}} = \frac{Lm'}{Gm'\alpha} = \text{absorption factor}$$

Or

$$N = \frac{(Y_{N+1} - Y_1)}{Y_1 - \alpha X_O} \quad \text{when } A = 1$$

For stripping:

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

$$N = \frac{(X_O - X_N)}{X_N - Y_{N+1}/\alpha} \quad \text{when } A = 1$$

These equations are called “Kremser equations”.

Example:

It is desired to absorb 95% of acetone by water from a mixture of acetone and nitrogen containing 1.5% of acetone in a counter current tray tower. Total gas input is 30 kmol/h and water enters the tower at a rate of 90 kmol/h. the tower operates at 27 °C and 1 atm. The equilibrium relation is $Y = 2.53X$. Determine the number of ideal stages necessary for the separation using (a) graphical method (b) algebraic method.

Solution

$$\text{Removal\%} = 95\%$$

$$y_{N+1} = 0.015$$

$$x_0 = 0$$

$$(Gm)_{N+1} = 30 \text{ kmol/h}$$

$$(Lm)_0 = 90 \text{ kmol/h}$$

$$T = 27 \text{ }^\circ\text{C}$$

$$P = 1 \text{ atm}$$

$$Y = 2.53X$$

(a) Using graphical method

$$\text{Moles of acetone in} = (0.015)(30) = 0.45 \text{ kmol/h}$$

$$\text{Absorbed acetone} = (0.95)(0.45) = 0.4275 \text{ kmol/h}$$

$$\text{Acetone leaving} = 0.45 - 0.4275 = 0.0225 \text{ kmol/h}$$

$$Gm_1 = (Gm)_{N+1} - \text{Absorbed acetone} = 30 - 0.4275 = 29.572 \text{ kmol/h}$$

$$y_1 = \frac{\text{acetone leaving}}{Gm_1} = \frac{0.0225}{29.572} = 7.6 \times 10^{-4}$$

$$Y_1 = \frac{y_1}{1 - y_1} = \frac{7.6 \times 10^{-4}}{1 - 7.6 \times 10^{-4}} = 7.6 \times 10^{-4}$$

$$Y_{N+1} = \frac{y_{N+1}}{1 - y_{N+1}} = \frac{0.015}{1 - 0.015} = 0.015$$

$$Gm' = (1 - y_{N+1})(Gm)_{N+1} = (1 - 0.015)(30) = 29.55 \text{ kmol/h}$$

$$Lm' = 90 \text{ kmol/h}$$

Overall material balance

$$Gm'(Y_{N+1} - Y_1) = Lm'(X_N - X_0)$$

$$29.55(0.015 - 7.6 \times 10^{-4}) = 90(X_N - 0)$$

$$X_N = 4.67 \times 10^{-3}$$

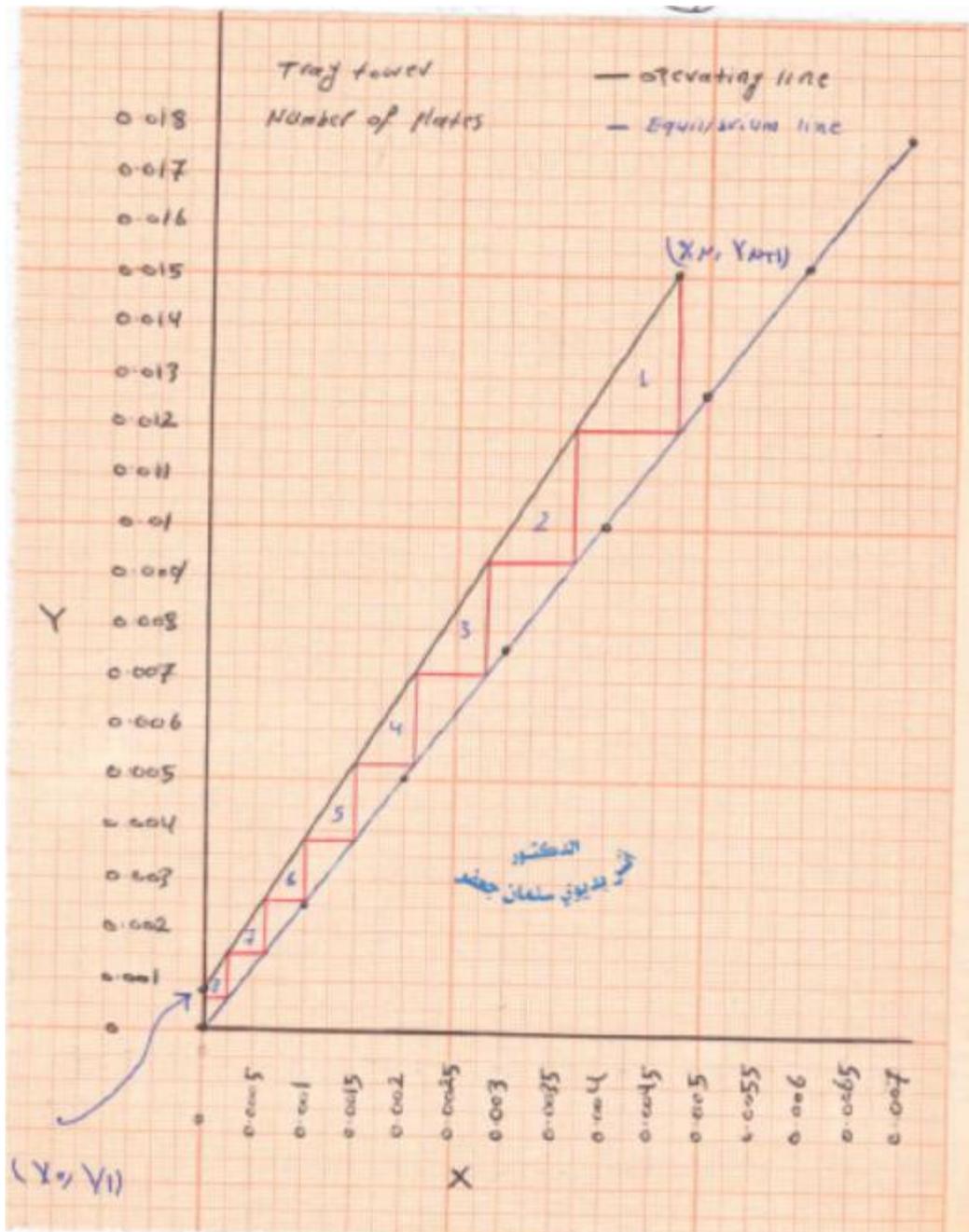
Operating line passes through the points (X_N, Y_{N+1}) and (X_0, Y_1) .

Now use the given equilibrium relation to construct the equilibrium line:
 $(Y = 2.53X)$

X	0	0.001	0.002	0.003	0.004	0.005
Y	0	0.00253	0.00506	0.00759	0.01012	0.01265

From the graph of operating line and equilibrium line on the X-Y plane, we find that

$N = 8$ plates.



(b) Using algebraic method

$$A = \frac{\text{slope of operating line}}{\text{slope of equilibrium line}} = \frac{Lm'}{Gm'\alpha} = \frac{90}{(29.55)(2.53)} = 1.204$$

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

$$N = \frac{\ln\left[\left(\frac{0.015-(2.53)(0)}{7.6 \times 10^{-4}-(2.53)(0)}\right)\left(1-\frac{1}{1.204}\right)+\frac{1}{1.204}\right]}{\ln 1.204} = 8 \text{ plates}$$

$$N = 8 \text{ plates}$$

Liquid-liquid extraction

Liquid extraction is the separation of constituents of a liquid by contact with another insoluble liquid called (solvent). The constituents get distributed between the two phases.

The solvent rich phase is called (extract) and the residual liquid from which the solute has been removed is called (Raffinate). Some of the components which are difficult to separate by other separation processes like distillation can effectively be separated by extraction or extraction followed by distillation.

Liquid-liquid equilibrium (LLE)

A liquid-liquid extraction system contains at least three components; the solute (C), the carrier liquid in the feed (A), and the extraction solvent (B).

Quite often, the total number of components in the liquid-liquid extraction mixture contains more than three components when the carrier liquid in the feed contains more than one liquid, or there may be more than one solute, or when the extraction solvent is a mixed solvent.

Classification of ternary systems

Consider that we have a ternary mixture that consists of three components, solute (C), carrier in the feed (A), and extraction solvent (B). Three binary mixtures may be formed in this case; A-B, B-C, and A-C. The mutual miscibility behavior of components in each mixture determines the nature of the equilibrium diagram for the ternary system.

Three kinds of ternary systems exist:

1. The carrier (A) and the solvent (B) are immiscible. In this kind, the equilibrium data may be represented on x-y plane.
2. The solute is miscible with the carrier and the solvent in all proportions, but the carrier (A) and the solvent (B) are partially miscible. This system is called type I system.
3. The solute (C) is completely miscible with the carrier (A), but both (C) and (A) are partially miscible with (B). This system is called type II system.

Graphical representation of liquid-liquid equilibrium data

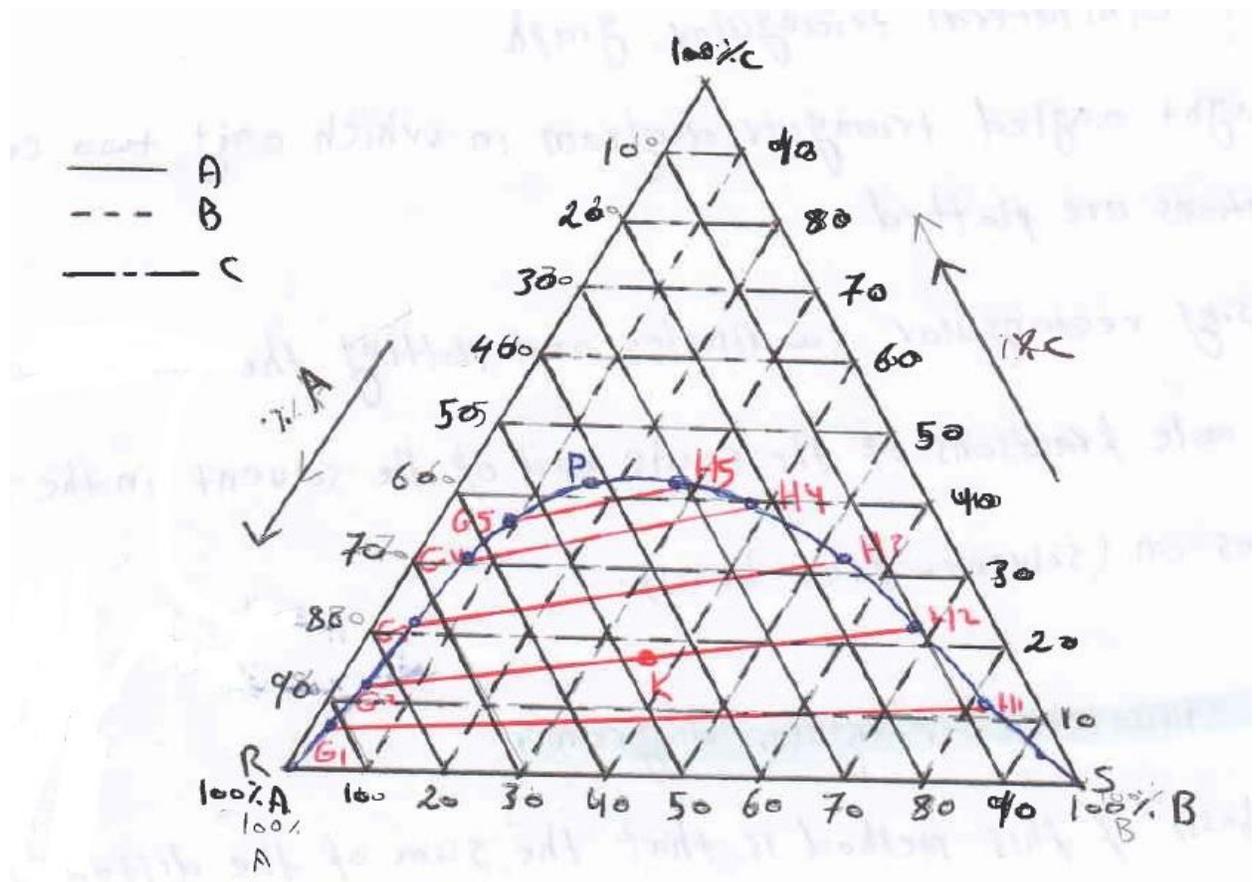
Equilibrium data for a ternary system (in which there are three concentration terms) can be expressed by one of the following methods:

1. On equilateral triangular graph.
2. Right angled triangular diagram in which only two concentrations are plotted.
3. Using rectangular coordinates and plotting the mass fractions or mole fractions of the solute and of the solvent in the two phases on (solvent free basis).

The equilateral triangular diagram

The basis of this method is that the sum of the distances of a point within an equilateral triangle from the three sides is equal to the height of the triangle.

The vertices A, B, and C represent the pure components A, B, and C respectively; the sides AB, BC, and CA represent mixtures of A-B, B-C, and C-A respectively. A point within the triangle ABC represents a mixture of the components A, B, and C.



This plot represents equilibrium data for a type I ternary system (C is miscible with both A and B, but A and B are partially miscible). The curve RPS is the equilibrium diagram on the equilateral triangular coordinate system. It can be constructed by plotting the data points representing the two liquid phases in equilibrium.

Point R on the line AB represents the solubility of B in A and the point S represents that of A in B if there is no solute.

The pair of points G1 and H1 on the equilibrium curve represents two liquid phases in equilibrium, G1 is the raffinate phase and H1 is the extract phase. The line G1H1 is called a tie line. In each plot, there are an infinite number of tie lines those connecting between the two phases in equilibrium, and these tie lines are usually not parallel and the length of the tie lines decreases as we move away from the side AB, and the last tie line reduces to point P. The point P that separates the raffinate side from the extract side of the equilibrium curve is called "plait point". This type of equilibrium curve RPS is called binodal because it has two arms RP and PS representing the raffinate and extract sides.

Any point below the equilibrium curve RPS represents a two-phase mixture. Such a mixture when left undisturbed will separate into two phases at equilibrium and the compositions of these two phases are given by the terminals of the tie line that passes through this point.

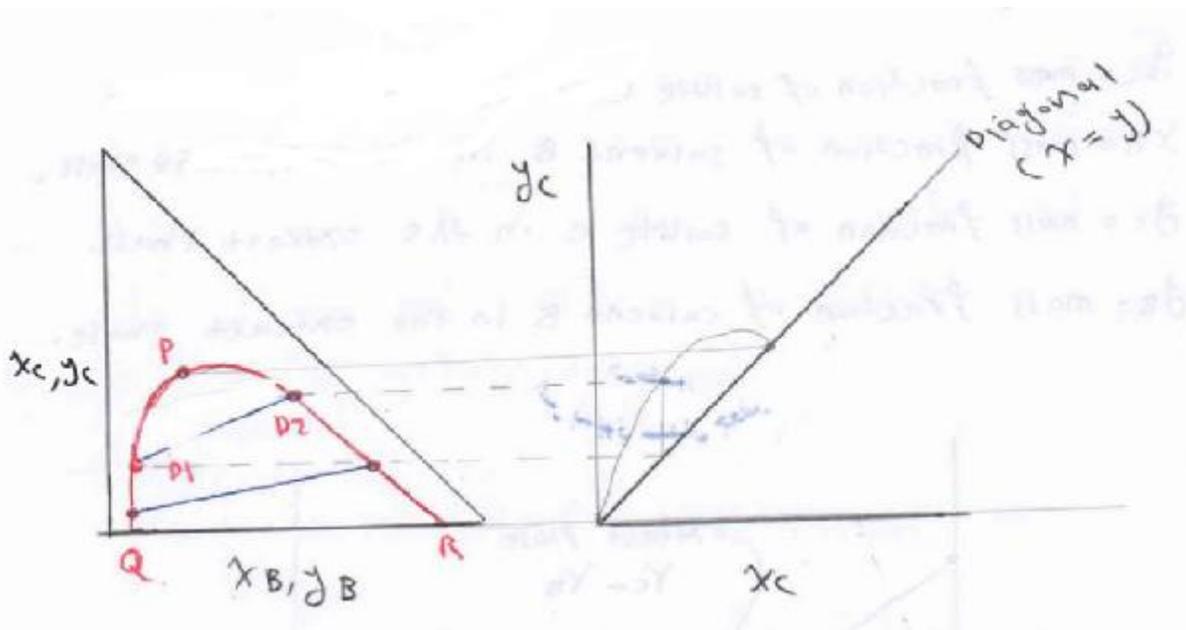
For example, point K under the equilibrium curve represents a two-phase mixture, and when this mixture is separated into two phases at equilibrium, the concentrations of these two phases are G1 for the raffinate phase and H1 for the extract phase.

For a type II ternary system, the equilibrium curve will be different. In this kind of system, the raffinate arm will not meet with the extract arm, and there will not be a plait point.

The right angled triangular diagram

The concentration (mole fraction or mass fraction) of any component (A, B or C) will be denoted by x for the raffinate side, and it will be denoted by y for the extract side.

In this kind of the equilibrium data representation, mass fraction of the solute in the two phases (x_C and y_C) at equilibrium are plotted against the corresponding mass fractions of solvent B in raffinate and extract phases (x_B, y_B). The raffinate arm is constructed by plotting the points (x_C versus x_B), while the extract arm is constructed by plotting (y_C versus y_B). The equilibrium diagram can also be constructed on the x_C - y_C plane.



Equilibrium plot on solvent free basis

In this kind of plot, the mass ratio of solute in raffinate phase is plotted versus the mass ratio of the solvent in the raffinate phase, the mass ratio of the solute in the extract phase is plotted versus the mass ratio of the solvent in the extract phase.

Plot (X_C versus X_B) and (Y_C versus Y_B) where:

$$X_C = \frac{x_C}{x_A + x_C} = \text{mass ratio of solute in raffinate phase}$$

$$X_B = \frac{x_B}{x_A + x_C} = \text{mass ratio of solvent in raffinate phase}$$

$$Y_C = \frac{y_C}{y_A + y_C} = \text{mass ratio of solute in extract phase}$$

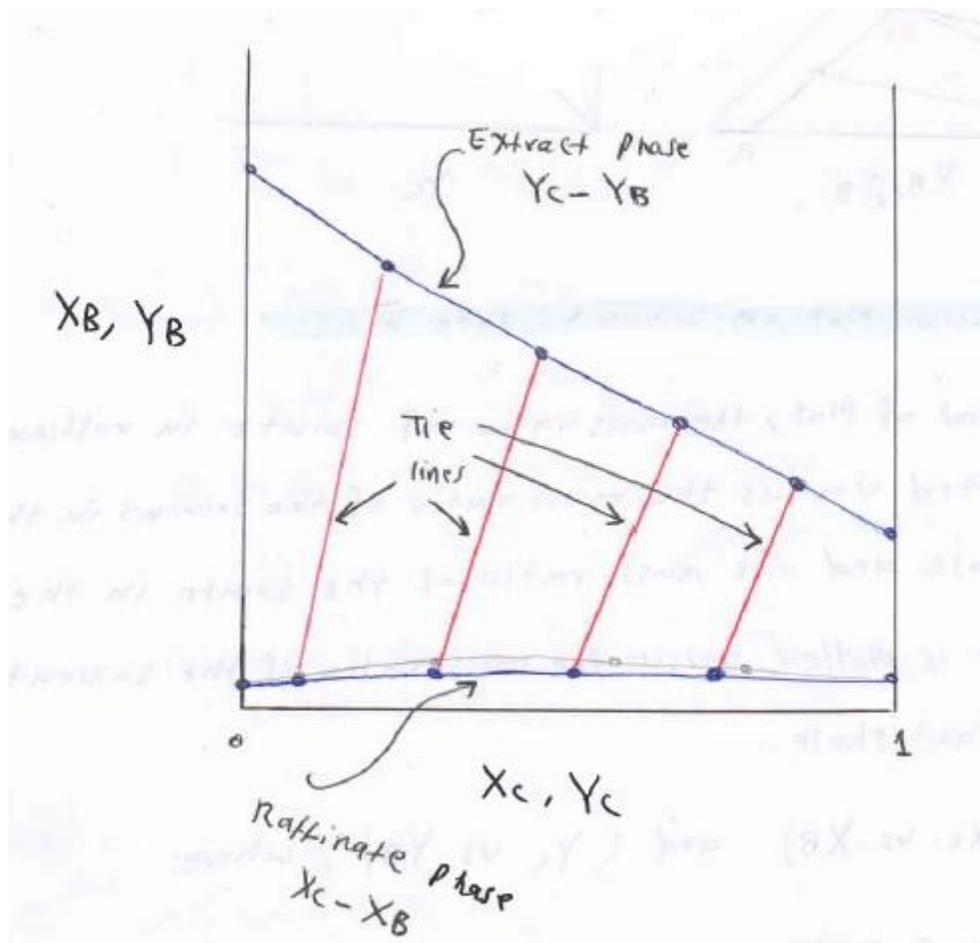
$$Y_B = \frac{y_B}{y_A + y_C} = \text{mass ratio of solvent in extract phase}$$

x_C = mass fraction of solute C in the raffinate phase

x_B = mass fraction of solvent B in the raffinate phase

y_C = mass fraction of solute C in the extract phase

y_B = mass fraction of solvent B in the extract phase

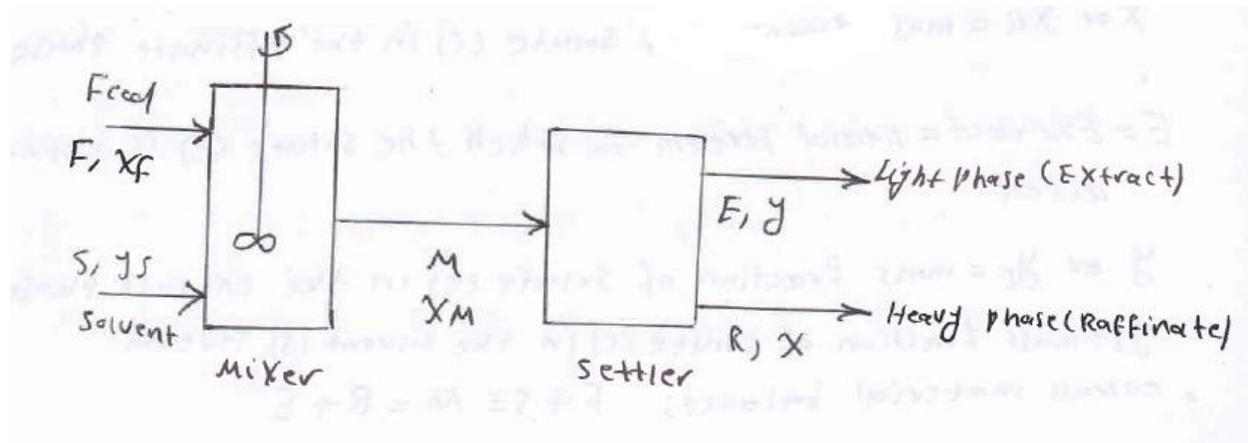


Calculation of stage-wise extraction (Partially miscible)

Liquid-liquid extraction may be conducted either in staged or in a continuous contact equipments. Stage wise extraction can be achieved in a single stage operation or in a multistage operation.

Single stage operation

In this mode of operation, extraction occurs in a mixer-settler assembly as shown below:



The feed that contains the solute that desired to be separated and the solvent used for separation enter the mixer in which intensive mixing occurs to attain liquid-liquid dispersion to produce a rate of M with concentration of x_M leaving the mixer towards the settler in which the produced mixture is allowed to separate into two phases. These two phases will be withdrawn separately from the settler.

Let:

A = carrier liquid in the feed stream.

C = solute that to be separated.

B = solvent used for extraction.

F = feed stream = $A + C$.

M = mixture produced from mixing of F & solvent stream.

x_M = mass fraction of solute in the produced mixture (leaving the mixer).

R = Raffinate.

x or x_R = mass fraction of solute in the raffinate phase.

E = extract

y or y_E = mass fraction of solute C in the extract phase.

y_S = mass fraction of solute C in the solvent S stream.

Overall material balance:

$$F + S = R + E$$

Solute material balance:

$$Fx_{C,F} + Sy_{C,S} = Mx_{C,M} = Rx_{C,R} + Ey_{C,E}$$

$$x_M = \frac{Fx_{C,F} + Sy_{C,S}}{F + S}$$

$$Fx_{C,F} + Sy_{C,S} = (F + S)x_{C,M}$$

$$Fx_{C,F} + Sy_{C,S} = Fx_{C,M} + Sx_{C,M}$$

$$F(x_{C,F} - x_M) = S(x_M - y_S)$$

$$\frac{F}{S} = \frac{(x_M - y_S)}{(x_{C,F} - x_M)}$$

$$Rx_R + Ey_E = (R + E)x_M$$

$$\frac{E}{R} = \frac{x_R - x_M}{x_M - y_E}$$

Or

$$\frac{E}{R} = \frac{x_M - x_R}{y_E - x_M}$$

The ternary equilibrium data are plotted on a suitable diagram.

Use the following steps to estimate the values of the raffinate, extract and their concentrations:

1. Draw the ternary equilibrium data on a suitable plot.
2. Locate the feed point and the solvent point (F & S) on the ternary data plot.
3. Join the points F & S.
4. Calculate the value of x_M and use this value to locate the point M on the FS corresponding to x_M .
5. Draw the tie line through the point M with the help of the equilibrium curve.
6. The terminals of this tie line at which the tie line intersects with the equilibrium curve give the values of raffinate and extract concentrations (x_R & y_E).
7. Use the following two equations to calculate the values of raffinate and extract (R & E):

$$F + S = R + E \dots\dots\dots (1)$$

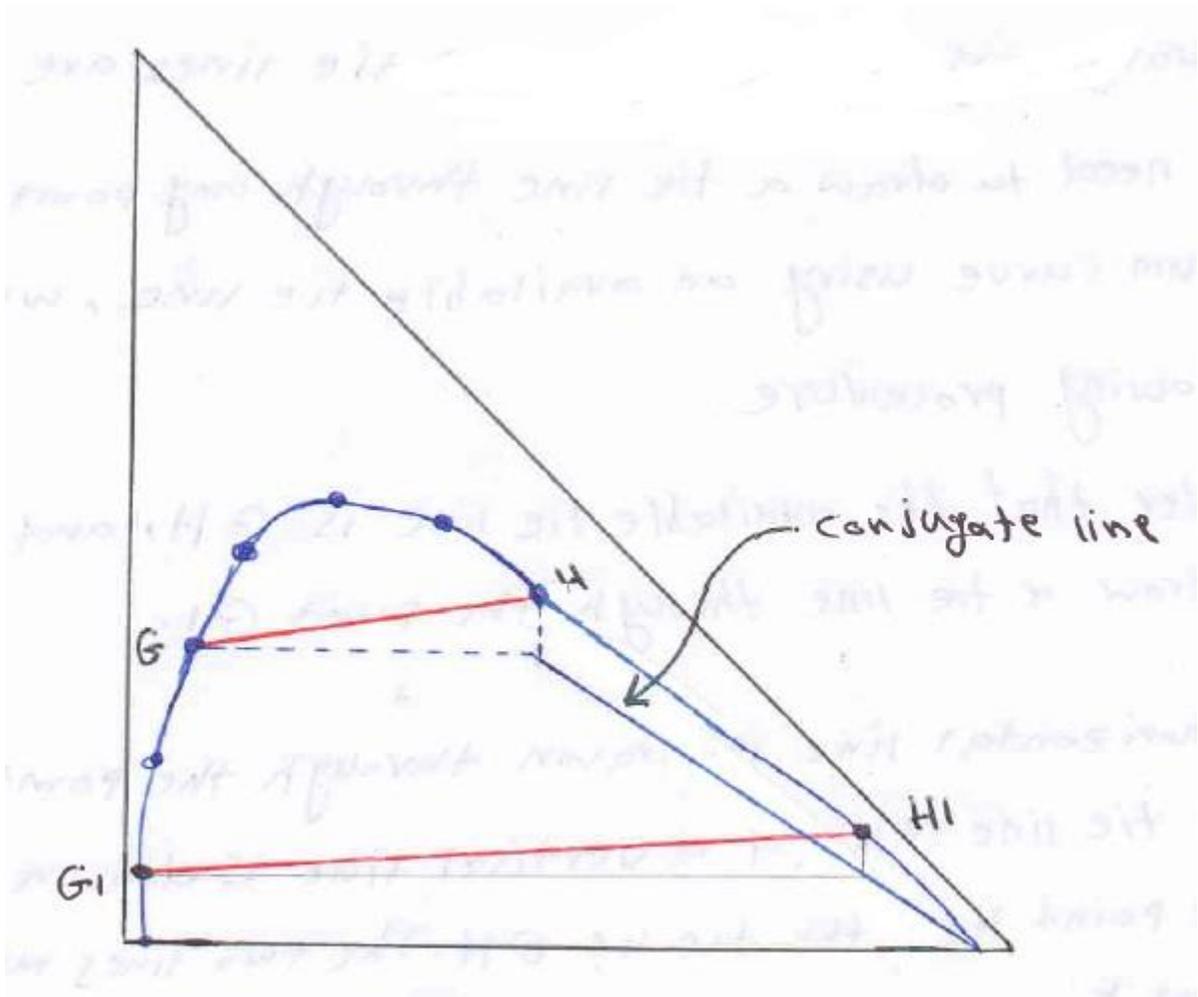
$$Fx_F + Sy_S = Rx_R + Ey_E \dots\dots\dots (2)$$

How to draw a tie line through a point on the equilibrium graph

Generally, only few experimental tie lines are available. If we need to draw a tie line through any point on the equilibrium curve using available tie line, we can use the following procedure.

Consider that the available tie line is GH, and you need to draw a tie line through the point G_1 .

1. A horizontal line is drawn through the point G of the tie line GH and a vertical line is drawn through the point H of the tie line GH. The two lines meet at point K.
2. Draw a straight line between the point K and the end point of the extract arm. This line is called “the conjugate line”.
3. Draw a horizontal line from the point G_1 to meet the conjugate line at the point K_1 .
4. Draw a vertical line through the point K_1 to meet the equilibrium curve at H_1 .
5. Connect G_1 with H_1 to draw the line that passes through the point G_1 .



Example:

1000 kg of an aqueous solution containing 50% mass acetone is contacted with 800 kg of chlorobenzene containing 0.5% mass acetone in a mixer-settler unit followed by separation of the extract and the raffinate phases.

- a- Determine the composition of the extract and the raffinate phases and the fraction of acetone extracted.
- b- Calculate the amount of solvent required if 90% of the acetone is to be removed. Equilibrium and tie line data are given below:

Raffinate			Extract		
Water x_A	Chlorobenzene x_B	Acetone x_C	Water y_A	Chlorobenzene y_B	Acetone y_C
0.9989	0.0011	0	0.0018	0.9982	0
0.8979	0.0021	0.1	0.0049	0.8872	0.1079
0.7969	0.0031	0.2	0.0079	0.7698	0.2223
0.6942	0.0058	0.3	0.0172	0.608	0.3748
0.5864	0.0136	0.4	0.0305	0.4751	0.4944
0.4628	0.0372	0.5	0.0724	0.3357	0.5919
0.2714	0.1259	0.6	0.2285	0.1508	0.6107
0.2566	0.1376	0.6058	0.2566	0.1376	0.6058

Solution:

$$F = 1000 \text{ kg}$$

$$x_F = 0.5$$

$$x_{B,F} = 0$$

$$S = 800 \text{ kg}$$

(a)

$$M = F + S = 1000 + 800 = 1800 \text{ kg}$$

$$x_M = \frac{F x_{C,F} + S y_{C,S}}{F + S} = \frac{(1000)(0.5) + (800)(0.005)}{1800} = 0.28$$

From the graph. We find that

$$x_{C,R} = 0.236$$

$$y_{C,E} = 0.302$$

it is known that

$$F + S = M = E + R = 1800$$

$$E + R = 1800 \dots\dots\dots (1)$$

$$\frac{E}{R} = \frac{x_M - x_R}{y_E - x_M} = \frac{0.28 - 0.236}{0.302 - 0.28} \dots\dots\dots (2)$$

From equation 2,

$$E = 2R$$

Substitute in equation (1) and solve for R & E:

$$R = 600 \text{ kg}$$

$$E = 1200 \text{ kg}$$

$$\text{Mass of acetone leaving with raffinate} = R \cdot x_{C,R} = (600)(0.236) = 141.6 \text{ kg}$$

$$\text{Mass of acetone in the feed} = (1000)(0.5) = 500 \text{ kg}$$

$$\text{Acetone entering with the solvent} = (800)(0.005) = 4 \text{ kg}$$

$$\text{Acetone leaving with the extract} = (1200)(0.302) = 362.4 \text{ kg}$$

$$\text{Net amount of acetone transferred to extract stream} = 362.4 - 4 = 358.4 \text{ kg}$$

$$\text{fraction of extracted acetone} = \frac{358.4}{500} = 0.7168$$

$$\text{acetone removal \%} = 71.68\%$$

(b)

When 90% of acetone is removed

$$\text{Input acetone} = 500 \text{ kg}$$

$$\text{Acetone remained with the raffinate} = (1 - 0.9)(500) = 50 \text{ kg}$$

$$\text{Total mass of remained raffinate} = 500 + 50 = 550 \text{ kg}$$

$$x_{C,R} = \frac{50}{550} = 0.0909$$

From the graph:

$$y_C = 0.105$$

$$R = 500 + 50 = 550 \text{ kg}$$

Overall material balance:

Solute in = solute out

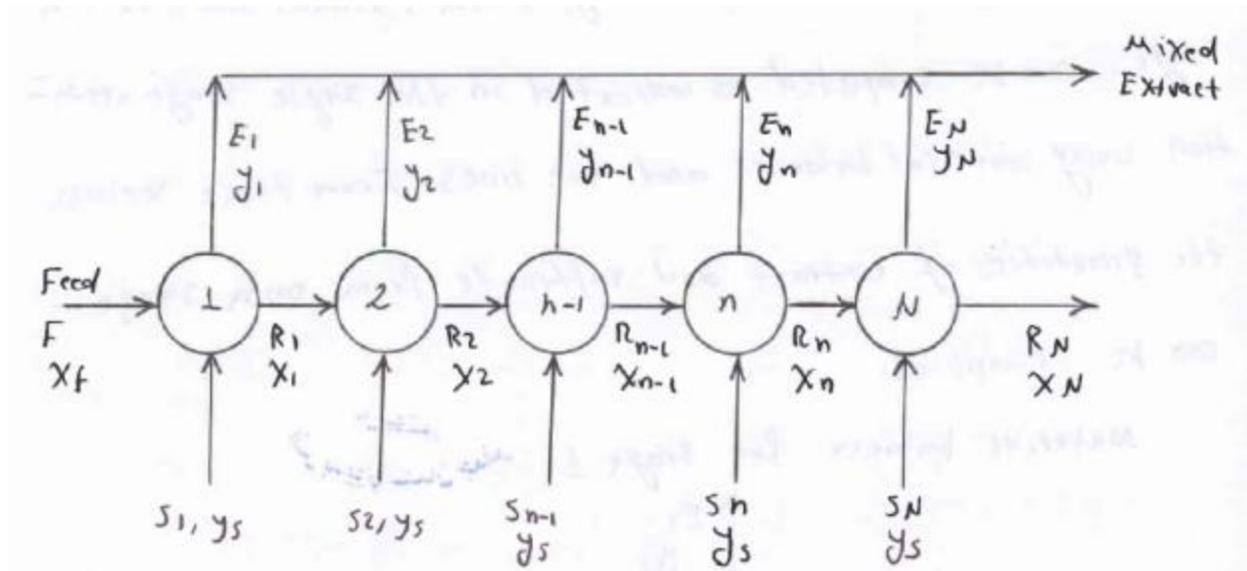
$$F x_{C,F} + S y_{C,S} = M x_{C,M} = R x_{C,R} + E y_{C,E}$$

$$(1000)(0.5) + S(0.005) = (550)(0.0909) + (S + 450)(0.105)$$

from which $S = 4027.72 \text{ kg}$

Multistage cross-current operation

A typical flow diagram of a multistage cross-current operation is shown below:



Where:

F = feed

E = extract phase

R = raffinate phase

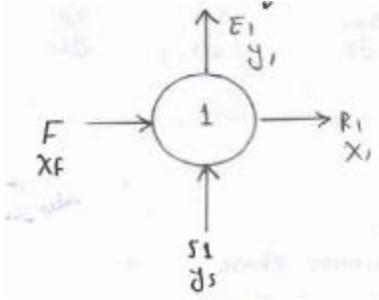
x = mass fraction in raffinate phase

y = mass fraction in extract phase

The feed enters the process at stage (1), and the raffinate successively passes from stage 1 to stage 2 to 3 and so on, until it leaves stage N. the solute concentration decreases gradually as long as the raffinate passes from stage to stage. Fresh or recovered solvent enters each stage. The solvent used could be of different concentration for each stage, but generally, it will have the same values as it enters either fresh or after recovery from extract.

The values of M_i , x_{Mi} , x_i and y_i where I stands for the i th stage can be computed as indicated in the single stage operation using material balances and tie lines. From these values, the quantities of extract and raffinate from each stage can be computed.

Material balance for stage 1

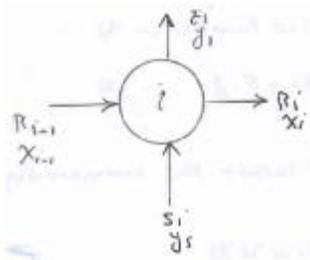


$$F + S_1 = R_1 + E_1 = M_1$$

$$Fx_F + S_1 y_S = R_1 x_1 + E_1 y_1 = M_1 x_{M1}$$

$$x_{M1} = \frac{Fx_F + y_S S_1}{F + S_1}$$

Similarly for any stage i



$$x_{Mi} = \frac{R_{i-1} x_i + y_S S_i}{R_{i-1} + S_i}$$

Or

$$x_{Mi} = \frac{R_{i-1} x_i + y_S S_i}{R_i + E_i}$$

Use the following steps to conduct the calculations of the multistage cross-current partially miscible extraction:

1. Plot the ternary data on a suitable plot.
2. Locate the feed point F and solvent S_1 on ternary data plot.
3. Join FS_1 and locate M_1 corresponding to x_{M1} .

$$x_{M1} = \frac{Fx_F + y_S S_1}{F + S_1}$$

4. Draw the tie line that passes through the point M_1 .
5. Read the values of x_1 and y_1 on the terminals of this tie line.
6. Use the material balances to find R_1 and E_1 :

$$M_1 = F + S_1 = R_1 + E_1$$

$$M_1 x_{M1} = R_1 x_1 + E_1 y_1$$

7. Join $R_1 S_2$ and locate M_2 corresponding to x_{M2} where

$$x_{M2} = \frac{R_1 x_1 + y_2 S_2}{R_1 + S_2}$$

8. Draw the tie line that passes through the point M_2 and read the values of x_2 and y_2 on the terminals of this tie line.

9. Use the material balances to find R_2 and E_2

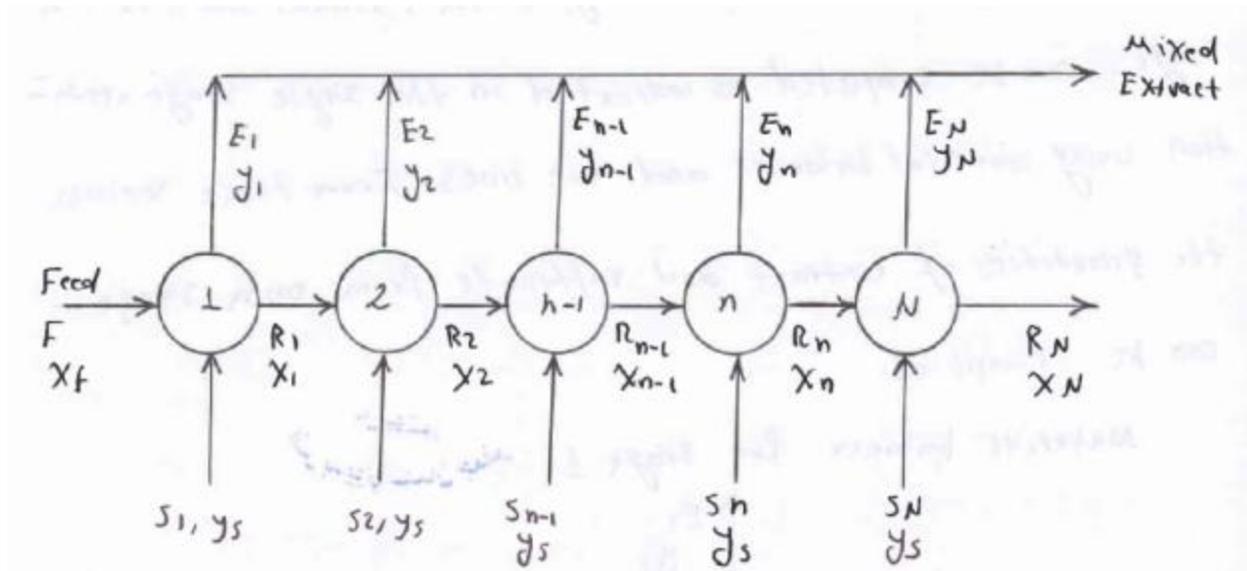
$$M_2 = R_1 + S_2 = R_2 + E_2 \dots\dots\dots (1)$$

$$M_2 x_{M2} = R_2 x_2 + E_2 y_2 \dots\dots\dots (2)$$

10. Repeat the procedure (from step 7 to step 9) for each stage until you reach the final stage.

Multistage cross-current operation

A typical flow diagram of a multistage cross-current operation is shown below:



Where:

F = feed

E = extract phase

R = raffinate phase

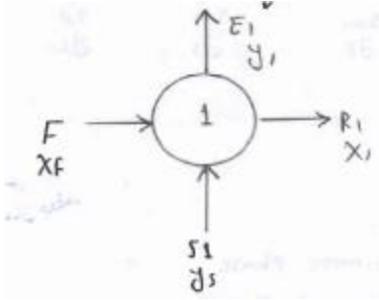
x = mass fraction in raffinate phase

y = mass fraction in extract phase

The feed enters the process at stage (1), and the raffinate successively passes from stage 1 to stage 2 to 3 and so on, until it leaves stage N. the solute concentration decreases gradually as long as the raffinate passes from stage to stage. Fresh or recovered solvent enters each stage. The solvent used could be of different concentration for each stage, but generally, it will have the same values as it enters either fresh or after recovery from extract.

The values of M_i , x_{Mi} , x_i and y_i where I stands for the i th stage can be computed as indicated in the single stage operation using material balances and tie lines. From these values, the quantities of extract and raffinate from each stage can be computed.

Material balance for stage 1

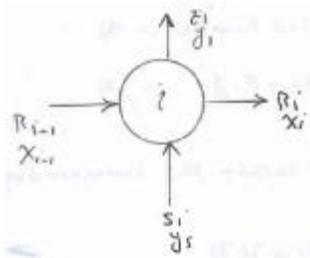


$$F + S_1 = R_1 + E_1 = M_1$$

$$Fx_F + S_1 y_S = R_1 x_1 + E_1 y_1 = M_1 x_{M1}$$

$$x_{M1} = \frac{Fx_F + y_S S_1}{F + S_1}$$

Similarly for any stage i



$$x_{Mi} = \frac{R_{i-1}x_i + y_S S_i}{R_{i-1} + S_i}$$

Or

$$x_{Mi} = \frac{R_{i-1}x_i + y_S S_i}{R_i + E_i}$$

Use the following steps to conduct the calculations of the multistage cross-current partially miscible extraction:

1. Plot the ternary data on a suitable plot.
2. Locate the feed point F and solvent S_1 on ternary data plot.
3. Join FS_1 and locate M_1 corresponding to x_{M1} .

$$x_{M1} = \frac{Fx_F + y_S S_1}{F + S_1}$$

4. Draw the tie line that passes through the point M_1 .
5. Read the values of x_1 and y_1 on the terminals of this tie line.
6. Use the material balances to find R_1 and E_1 :

$$M_1 = F + S_1 = R_1 + E_1$$

$$M_1 x_{M1} = R_1 x_1 + E_1 y_1$$

7. Join $R_1 S_2$ and locate M_2 corresponding to x_{M2} where

$$x_{M2} = \frac{R_1 x_1 + y_2 S_2}{R_1 + S_2}$$

8. Draw the tie line that passes through the point M_2 and read the values of x_2 and y_2 on the terminals of this tie line.

9. Use the material balances to find R_2 and E_2

$$M_2 = R_1 + S_2 = R_2 + E_2 \dots\dots\dots (1)$$

$$M_2 x_{M2} = R_2 x_2 + E_2 y_2 \dots\dots\dots (2)$$

10. Repeat the procedure (from step 7 to step 9) for each stage until you reach the final stage.