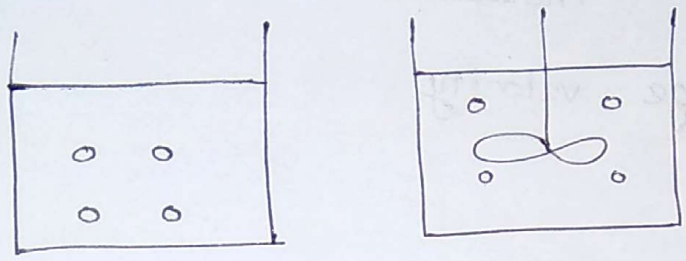
19/07/17
SN

1) Why mass transfer occurs?
→ Principles, mechanisms, driving force

2) Seperation process.

3) Transport process

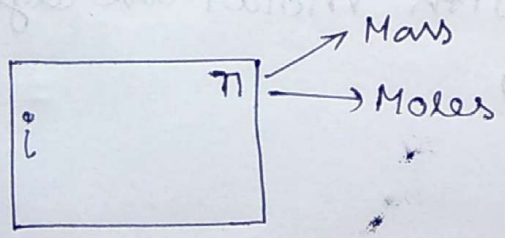


- Domain is discretized (Diffusion occurs in small areas)
- Localized diffusion/ Eddy diffusion

- path in between consecutive collisions is shorter compared to molecular diffusion
- convective mass transfer

- molecular diffusion
- occurs in entire domain
- on imposing external velocity, molecular diffusion becomes Eddy diffusion
e.g stirrer movement

In Isothermal, isobaric condition, concentration difference is major driving force in diffusion



⇒ ρ_i = mass concentration of ith component = $\frac{\text{Mass}}{\text{vol.}}$

$c_i = \frac{\text{mole}}{\text{volume}}$ = mole concentration of ith component

$\omega_i = \frac{\rho_i}{\sum \rho_i}$ = mass fraction of ith component

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$x_i, y_i = \frac{c_i}{\sum c_i}$ = mole fraction

$\sum w_i = 1, \quad \sum x_i, \sum y_i = 1$

$c_i \Leftrightarrow P_i, P, \quad y_i \Leftrightarrow P_i, P$

u_i = velocity of ith molecule

u = mass average velocity

$$= \frac{\sum \rho_i u_i}{\sum \rho_i}$$

U = molar average velocity $= \frac{\sum c_i u_i}{\sum c_i}$

Flux $= \frac{\text{Rate}}{\text{area}}$

Mass Mole

Reference → stationary

→ moving with mass average velocity u

→ moving with molar average velocity U

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Flux related to mole/mass

Molar Flux

Ref velocity

- $0 \rightarrow N_i$
- $U \rightarrow J_i$
- $u_i \rightarrow I_i$

Mass Flux

Ref. velocity

- $0 \rightarrow n_i$
- $U \rightarrow j_i$
- $u_i \rightarrow i_i$

Total flux of ith component

$$N_i = C_i (u_i - 0)$$

$$J_i = C_i (u_i - U)$$

$$I_i = C_i (u_i - u)$$

$$n_i = \rho_i (u_i - 0)$$

$$j_i = \rho_i (u_i - U)$$

$$i_i = \rho (u_i - u)$$

$$J_i = C_i (u_i - U) = C_i u_i - C_i \left(\frac{\sum C_i u_i}{\sum C_i} \right)$$

$$\boxed{J_i = N_i - \left(\frac{C_i}{C} \sum N_i \right)}$$

$\sum N_i \rightarrow$ convective flux

$\sum N_i \rightarrow$ Total flux of all component

$J_i \Rightarrow$ diffusive flux

$$\boxed{A + B}$$

$$U = \frac{C_A u_A + C_B u_B}{C = (C_A + C_B)}$$

$A \longrightarrow A + B, B$

$$u = \frac{\rho_A u_A + \rho_B u_B}{\rho}$$

$$N_A = C_A u_A$$

$$J_A = N_A - \frac{C_A}{C} (N_A + N_B)$$

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1) Molecular Diffusion

2) Driving force : chemical potential

3) i) $\rho_i, C_i, \omega_i, x, y$

ii) u_i, u, U

iii) $[N_i, J_i, I_i]$

(n_i, j_i, i_i)

iv) $J_i = N_i - \frac{C_i}{C}(\sum N_i)$

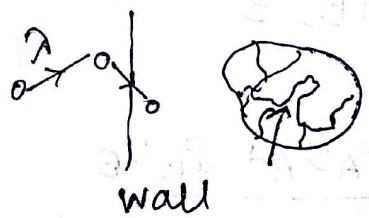
$$J_A = N_A - \frac{C_A}{C}(\sum N_A) = N_A - \frac{C_A}{C}(N_A + N_B)$$

<u>Diffusion in homogeneous binary system</u>

in single phase

- Molecular Diffusion
- Pore/Nano channel diffusion (in case of narrow channel, catalyst)
- Eddy Diffusion (Convective mass transfer)
- Surface Diffusion
- Knudsen Diffusion

movement along surface



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Molecular Diffusion : Single phase homogenous binary system

Fick's Law

flux $\propto$ concentration gradient

$$J_A = -(D_{AB})\frac{dC_A}{dx}$$

$$J_B = -(D_{BA})\frac{dC_B}{dx}$$

$$D_{AB} = \frac{J_A}{\frac{dC_A}{dx}} = \frac{mol/m^2 \cdot s}{\frac{mol/m^3}{m}} = \frac{m^2}{s}$$

$$N_A = -\frac{dC_A}{dx} + \frac{C_A}{C_B}(N_A + N_B)$$

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$$\cancel{N_A = -\frac{dC_A}{dx} + \frac{C_A}{C_B}(N_A + N_B)}$$

$$N_A = -D_{AB}\frac{dC_A}{dx} + \frac{C_A}{C}(N_A + N_B)$$

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$$N_A = -D_{AB}\frac{dC_A}{dx} + \frac{C_A}{C}(N_A + N_B)$$

$$+ \quad N_B = -D_{BA}\frac{dC_B}{dx} + \frac{C_B}{C}(N_A + N_B)$$

$$(N_A + N_B) = -\left(D_{AB}\frac{dC_A}{dx} + D_{BA}\frac{dC_B}{dx}\right) + \left(\frac{C_A + C_B}{C}\right)(N_A + N_B)$$

$$0 = D_{AB}\frac{dC_A}{dx} + D_{BA}\frac{dC_B}{dx}$$

Binary closed sol^n $\quad C = C_A + C_B$

[const. conc.]

$$\cancel{\frac{dC}{dx}}^{\,0} = \frac{dC_A}{dx} + \frac{dC_B}{dx}$$

$$\frac{dC_A}{dx} = -\frac{dC_B}{dx}$$

$$D_{AB}\frac{dC_A}{dx} = D_{BA}\frac{dC_A}{dx} \Rightarrow \boxed{D_{AB} = D_{BA}}$$

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$$\mu_A = \mu_A^\circ + RT \ln a_A$$

$$= \mu_A^\circ + RT \ln (\gamma_A C_A)$$

$$\frac{d\mu_A}{dx} = 0 + \frac{RT}{\gamma_A C_A} \cdot \gamma_A \frac{dC_A}{dx}$$

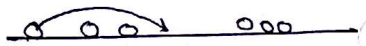
$$\boxed{\frac{dC_A}{dx} = \frac{C_A}{RT} \frac{d\mu_A}{dx}}$$

$$\boxed{J_A = -D_{AB} \frac{dC_A}{dx} = -\frac{D_{AB} C_A}{RT} \frac{d\mu_A}{dx}}$$

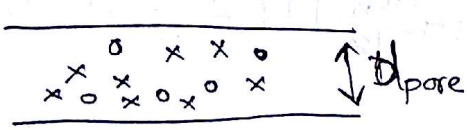
Surface diffusion

Diffusivity in surface

$$J_A = -D_S \frac{dC_A}{dx}$$



Knudsen diffusion



$d_{pore} < \lambda \Leftarrow$ condition for Knudsen diffusion

mean free path

$$K_n = \text{Knudsen Number} = \frac{\lambda}{d_{pore}}$$

$K_n > 1 \Rightarrow$ Pore diffusion / Knudsen diffusion occurs

Sometimes, it is hard to segregate molecular & porous diffusion.

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$$J_A = -\frac{D_{KA}}{\tau}\varepsilon\frac{dC_A}{dx}$$

Knudsen diffusivity of A

porous volume = total volume × porosity

$\varepsilon \rightarrow$ porosity correction factor, $V_{eff} = \varepsilon V_T \Rightarrow \varepsilon = \frac{V_{eff}}{V_T}$

$\tau \rightarrow$ tortuosity $= \frac{\text{torturous length}}{\text{~~total~~ actual length}}$

$$\boxed{J_A = -\frac{D_{KA}}{\tau}\varepsilon\frac{dC_A}{dx}}$$

$\Rightarrow$ In presence of only Knudsen diffusion

For both molecular & Knudsen diffusion are present then

$$\frac{1}{D} = \frac{1}{D_{KA}} + \frac{1}{D_{AB}}$$

Effective

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Diffusivity

- D_{AB}
- D_{KA}
- D_S (evaluated experimentally)

D_{AB} → Correlations

D_{KA} → Correlations, experiments

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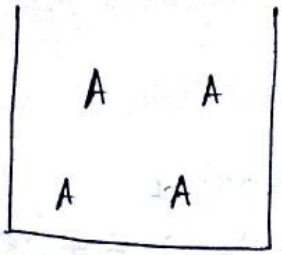
Gas phase



$$D_{AA} = \frac{1}{3}\lambda u$$

λ → mean free path, m

u → average molecular velocity

$$\lambda = \frac{kT}{\sqrt{2}\,\pi\,\sigma_A^2\,P} \qquad u = \sqrt{\frac{8kNT}{\pi M_A}}$$

k → Boltzman const.

σ_A → Diameter of the molecule

$$D_{AA} = \frac{\frac{2}{3}\left(\frac{k}{\pi}\right)^{3/2} N^{1/2}\, T^{3/2} \left[\frac{1}{M_A}\right]^{1/2}}{P\,\sigma_A^2}$$

$$D_{AB} = \frac{\frac{2}{3}\left(\frac{k}{\pi}\right)^{3/2} N^{1/2}\, T^{3/2}}{P\,\sigma_{AB}^2} \left[\frac{1}{2M_A} + \frac{1}{2M_B}\right]^{1/2}$$

$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$

i) Simplest of correlations

ii) ideal binary mixture

→ no intermolecular interaction

iii) Non polar system

For real gases

$$D_{AB} = \frac{\frac{2}{3}\left(\frac{k}{\pi}\right)^{3/2} N^{1/2}\, T^{3/2}}{\Omega_D\, P\,\sigma_{AB}^2} \left[\frac{1}{2M_A} + \frac{1}{2M_B}\right]^{1/2}$$

Ω_D → Leonard Jones parameter

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$$D = \frac{1.8\times10^{-7}\, T^{3/2}}{P\,\sigma_{AB}^2\,\Omega_D}\left[\frac{1}{2M_A}+\frac{1}{2M_B}\right]^{1/2}$$

in $\frac{m^2}{s}$

$$f\left(\frac{kT}{\varepsilon_{AB}}\right)$$

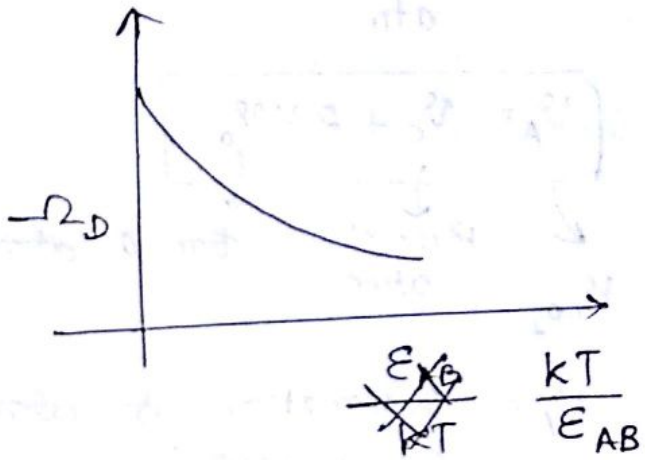
$$\Omega_D = \cancel{f\left(\frac{\varepsilon_{AB}}{kT}\right)}$$

$$\varepsilon_{AB} = (\varepsilon_A \varepsilon_B)^{1/2}$$

Tabulated data

$\frac{\varepsilon_{AB}}{kT}$	σ_D

or, graphical data



Ω_D, σ_A, σ_B

$$\Omega_D = f\left(\frac{kT}{\varepsilon_{AB}}\right)$$

$$\sigma = 1.18\, V_b^{1/3}$$

Molar volume at normal boiling point.

$$= 0.841\, V_c^{1/3}$$

critical volume

$$= 2.44\left(\frac{T_c}{P_c}\right)^{1/3}$$

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$\varepsilon_A / (k) = 0.77\, T_c$

Boltzman const.

$$D_{AB} = \frac{10^{-3}\, T^{1.75} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2}}{P\left[(\Sigma v_A)_A^{1/3} + (\Sigma v_B)_B^{1/3}\right]^2 \sigma}$$

$D_{AB} \rightarrow \frac{cm^2}{s}$, $P \rightarrow$ atm

$$\boxed{v_A = v_c + 2 \times v_o}$$

$v_A \rightarrow v_{CO_2}$; $v_c \rightarrow$ for 'c' atom; $v_o \rightarrow$ for 'o' atom

v_A = summation of atomic volume of components

$$D_{AB} = \frac{10^{-3}\, T^{1.75} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2}}{P\left[V_A^{1/3} + V_B^{1/3}\right]^2}$$

$\rightarrow$ Depends on T, P, nature of components

$$\frac{(D_{AB})_{T_1}}{(D_{AB})_{T_2}} = \frac{T_1^{3/2} P_2}{T_2^{3/2} P_1} \frac{(\Omega_D)_2}{(\Omega_D)_1}$$

from Harshfelder eqn

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Diffusivity (Molecular) 27/07/17

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- → Gas phase
- → liquid phase → Hydrodynamic Theory
  → Eyring Theory

Hydrodynamic Theory

$$\frac{D_{AB}\,\mu_B}{T} = \text{const.}$$

μ_B ← Viscosity of solⁿ

T ← system temperature

} applicable for dilute solution

Eyring Theory

$$\frac{D_{AB}\,\mu_B}{T} = f(V_A)$$

V_A ← ~~Molecular~~ Molar volume of solⁿ

Applicable for concentrated solⁿ also

Wilke-Chang ⇒ Majorly applicable ~~for~~ dil. solⁿ

$$\left[\frac{D_{AB}\,\mu_B}{T}\right] = \frac{7.4\times10^{-8}\,(\phi_B M_B)^{1/2}}{V_A^{0.6}} \quad \text{in c.g.s}$$

D_{AB} → cm^2/s; μ_B → g/m-s; ϕ_B ← Association factor

$$= \frac{1.73\times10^{-16}\,(\phi_B M_B)^{1/2}}{V_A^{0.6}} \quad \text{in S.I}$$

μ_B ← Solute viscosity for conc. solⁿ

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Haydak - Laudie

$$D_{AB}^{o} = 13.26 \times 10^{-5} \mu_B^{-1.14} V_A^{-0.589}$$

$$D_{BA}^{o} = 13.26 \times 10^{-5} \mu_A^{-1.14} V_B^{-0.589}$$

for dilute soln

$$D_{AB}\mu = (D_{AB}^{o}\mu_B)^{x_B}(D_{BA}^{o}\mu_A)^{x_A}$$ for conc. soln

For more than 2 component system in gas phase

A, B, C, D ..... n → $y_A, y_B, y_C, y_D, \ldots, y_n$

$D_{AB}, D_{AC}, D_{AD}, \ldots$

$$\frac{1}{D_{Am}} = \frac{y_B'}{D_{AB}} + \frac{y_C'}{D_{AC}} + \cdots \qquad y_i' = \frac{y_i}{\sum_{i \neq 1} y_i}$$

Knudsen Diffusivity

$$D_{AA} = \frac{1}{3}\lambda u$$ for ordinary gas phase

$\lambda = d_{pore}$ for Knudsen diffusion

$$D_{AA} = \frac{1}{3} d_{pore}\sqrt{\frac{8kNT}{\pi M_A}}$$

$$\boxed{D_{kA} = 4850\, d_{pore}\sqrt{\frac{T}{M_A}}}$$

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$$\frac{1}{D_{Ae}} = \frac{1-\alpha y_A}{D_{AB}} + \frac{1}{D_{KA}}$$

$$\left(\alpha = 1 + \frac{N_B}{N_A}\right)$$

D_{Ae} ↓

effective diffusivity when both molecular and Knudsen diffusion are present

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↓

effective diffusivity when both molecular and Knudsen diffusion are present

$$\left(\alpha = 1 + \frac{N_B}{N_A}\right)$$

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$D_{AB}|_{gas}$

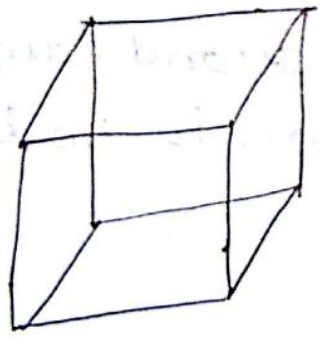
$D_{AB}|_{liquid} \rightarrow$ dil

$\rightarrow$ concentrated

D_{kA}

D_{AE} or $D_{Effective}$

$D_{AM} \rightarrow$ for multi component mixture



Rate of (moles in - moles out + moles generated)

= Rate of mole accumulation

$(0,0,0)$

$(\sigma^x, \sigma^y, \sigma^z)$

$$\left[N_{Ax}|_x - N_{Ax}|_{x+\sigma^x}\right]\sigma^y\sigma^z + \left[N_{Ay}|_y - N_{Ay}|_{y+\sigma^y}\right]\sigma^x\sigma^z$$

$$+ \left[N_{Az}|_z - N_{Az}|_{z+\sigma^z}\right]\sigma^x\sigma^y + R_A\,\sigma^x\sigma^y\sigma^z = \frac{d}{dt}(C_A\sigma^x\sigma^y\sigma^z)$$

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$$-\left(\frac{\partial N_{Ax}}{\partial x} + \cancel{\frac{\partial N_{Ay}}{\partial y}}^{\,0} + \cancel{\frac{\partial N_{Az}}{\partial z}}^{\,0}\right) + \cancel{R_A}^{\,0} = \cancel{\frac{dC_A}{dt}}^{\,0} = \frac{1}{M_A}\frac{d\rho^A}{dt}$$

for steady state, binary, non reacting system and constant area

$$-\frac{dN_A}{dx} + \cancel{R_A}^{\,0} = \cancel{\frac{dC_A}{dt}}^{\,0}$$

$$\frac{dN_A}{dx} = 0$$

$$J_A = C_A(u_A - U)$$

for ~~m~~ $U = 0$, there is no bulk convective transfer

$$J_A = N_A - \cancel{\left(\frac{C_A}{C}(N_A + N_B)\right)}^{\,0}$$

$$\frac{dJ_A}{dx} = 0 \Rightarrow \frac{d}{dx}\left(-D_{AB}\frac{dC_A}{dx}\right) = 0$$

$$\Rightarrow \boxed{\frac{d^2C_A}{dx^2} = 0}$$ ← Fick's second law when there is no bulk flow

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Steady State
Binary
homogeneous single phase
non reactive system
Molecular diffusion , 1 Dimensional

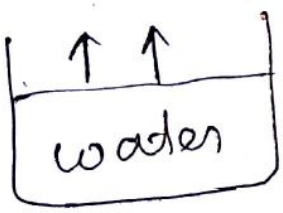
① <u>Fick's Law</u>

$$N_A = -D_{AB}\frac{dC_A}{dx} + \frac{C_A}{C}(N_A + N_B)$$

$$\frac{dN_A}{dx} = 0$$

A↑ B≠

air≠

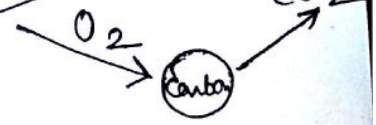


→ const. area

→ variable area

A↑ B↓

counter diffusion



$C + O_2 = CO_2$

Equimolar Diffusion

$C + O_2 \rightarrow CO_2$

non equimolar

$2C + O_2 \rightarrow 2CO$

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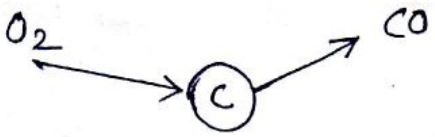
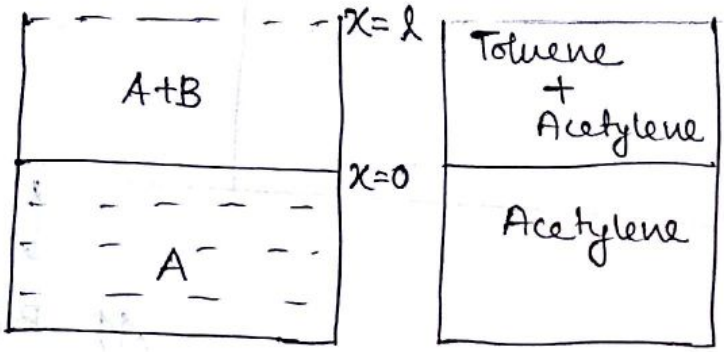


$N_A = -s\, N_B$

Case 1

$A\uparrow,\ B\neq$



$$N_A = -D_{AB}\frac{dC_A}{dx} + \frac{C_A}{c}(N_A+N_B)$$

$$\frac{d}{dx}(N_A) = 0 \Rightarrow N_A \neq f(x)$$

at $x=0$ $\quad C_A = C_{A_1}$

$x=l$ $\quad C_A = C_{A_2}$

$N_B = 0$

$$N_A = -D_{AB}\frac{dC_A}{dx} + \frac{C_A N_A}{c}$$

$$N_A\left(\frac{C_A}{c}-1\right) = D_{AB}\frac{dC_A}{dx}$$

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$$\frac{N_A \cancel{D_{AB}} dx}{D_{AB}\, C} = \frac{d C_A}{C_A - C}$$

$$N_A \int_0^{l} dx = -D_{AB} \cdot C \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{C - C_A}$$

$$N_A = \frac{D_{AB} \cdot C}{l} \ln\left(\frac{C - C_{A2}}{C - C_{A1}}\right)$$

$$= \frac{D_{AB} \cdot C}{l (C_B)_{lm}} (C_{A1} - C_{A2})$$

← Mass transfer coefficient

$$C = C_{B1} + C_{A1} = C_{B2} + C_{A2}$$

$$(C_B)_{lm} = \frac{C_{B2} - C_{B1}}{\ln\left(\frac{C_{B2}}{C_{B1}}\right)}$$

Mass flux = Mass transfer coefficient $\times$ Δ (driving force)

in reality

$N_A \rightarrow$ const

$l \rightarrow l >> \Delta l$

$$N_A = \frac{D_A C}{(C - C_A)} \frac{dC_A}{dx} \qquad \frac{d(N_A)}{dx} = 0$$

$$\frac{d}{dx}\left(\frac{D_A \cdot C}{(C - C_A)} \frac{dC_A}{dx}\right) = 0$$

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$C_A|_0 = C_{A1}$, $C_A|_l = C_{A2}$

$$\frac{dC_A}{dx\,(c-C_A)} = C_1$$

$$\ln (c - C_A) = C_1 x + C_2$$

$$\frac{c - C_A}{c - C_{A1}} = \left[\frac{c - C_{A2}}{c - C_{A1}}\right]^{x/l}$$

$$N_A = \frac{D_{AB} \cdot c}{l (C_B)_{lm}} \qquad y_A = \frac{C_{A1}}{c}$$

$$y_B = \frac{C_{A2}}{c}$$

<u>For gas</u>

(1)

$$N_A = \frac{D_{AB}\, c}{l}\left[\frac{y_{A1} - y_{A2}}{(y_B)_{lm}}\right], \quad (y_B)_{lm} = \frac{y_{B2} - y_{B1}}{\ln\left(\frac{y_{B2}}{y_{B1}}\right)}$$

(2) $$N_A = \frac{D_{AB}\, P}{RTl}\left[\frac{P_{A1} - P_{A2}}{(P_B)_{lm}}\right]; \quad (P_B)_{lm} = \frac{P_{B2} - P_{B1}}{\ln\left(\frac{P_{B2}}{P_{B1}}\right)}$$

For liquid

$$N_A = \frac{D_{AB}\, c}{l}\left[\frac{x_{A1} - x_{A2}}{(x_B)_{lm}}\right], \quad (x_B)_{lm} = \frac{x_{B2} - x_{B1}}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)}$$

$$c = \frac{P}{RT} = \frac{\rho}{M_{average}}$$

For gas

For liquid

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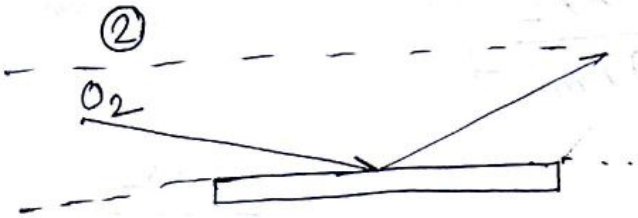
②



$C + O_2 = CO_2$

$N_A = N_B$

①

$$N_A = -\frac{D_{AB}\, dC_A}{dx} + \frac{C_A}{C}\cancel{(N_A + N_B)}^{\,0}$$

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

$$\frac{d(N_A)}{dx} = 0 \quad \Rightarrow N_A \neq f(x)$$

$$C_A = C_{A_1}, \quad C_A = C_{A_2}$$

$$N_A = -D_{AB}\frac{(C_{A_1} - C_{A_2})}{l}$$

$$\frac{d}{dx}(N_A) = 0$$

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

$$-D_{AB}\frac{dC_A}{dx} = C_1$$

$$C_A = -\frac{C_1}{D_{AB}}x + C_2$$

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$$N_A = \frac{D_{AB} \cdot C}{l} \left[\frac{x_{A1} - x_{A2}}{(x_B)_{lm}} \right]$$

03/08/17
SN

$N_A = -s N_B$
for $s \neq 1$

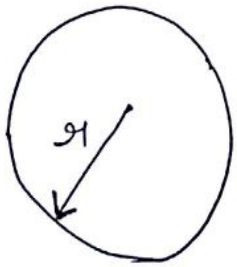
Variable Area

1. $A\uparrow$, $B \neq$
   a) Spherical geometry
   b) cylindrical geometry

2. $A\downarrow, B\uparrow$, $s = 1$
   a) Spherical geometry

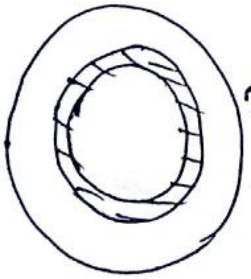
   b) Tappered tube

Spherical Geometry ($A\uparrow$, $B \neq$)



at,
$t = t$, $r = r$
$t = 0$, $r = R_{so}$
$t = t_f$, $r = R_{sf}$

$t = 0$ $r = r$, $C_A = C_{AS}$
$r = \infty$, $C_A = C_{A,\infty}$



$\Rightarrow$ From shell balance

$N_A \cdot A = \text{const.}$

$N_A \cdot 4\pi r^2 = \text{const.}$

$= W$ moles

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$$N_A = -\frac{D_{AB} \cdot C}{(C - C_A)} \frac{dC_A}{dr}$$

$N_B = 0$

$C \equiv$ conc. in gas phase

$$\int N_A \, dr = -D_{AB} \cdot C \int \frac{dC_A}{C - C_A}$$

$W =$ area $\times$ mole flux

$$\int_{r=r_s}^{\infty} \frac{\overset{N_A \cdot 4\pi r^2}{W}}{4\pi r^2} \, dr = -D_{AB} C \int_{C_{AS}}^{C_{A\infty}} \frac{dC_A}{C - C_A}$$

$$\left[-\frac{W}{4\pi r} \right]_{r}^{\infty} =$$

$$\frac{W}{4\pi r} = +D_{AB} \cdot C \left[\ln (C - C_A) \right]_{C_{AS}}^{C_{A\infty}}$$

$$\frac{W}{4\pi r} = +D_{AB} \cdot C \ln \left[\frac{C - \overset{0}{C_{A\cdot\infty}}}{C - C_{A\cdot S}} \right]$$

$$\frac{W}{4\pi D_{AB} C \cdot r} = \ln \left(\frac{C}{C - C_{A\cdot S}} \right)$$

$$C - C_{A\cdot S} = C \cdot e^{-4\pi D_{AB} C r}$$

$$C_{A\cdot S} = C \left(1 - e^{-4\pi D_{AB} \cdot C \cdot r} \right)$$

$$W = 4\pi D_{AB} C \left[\ln \left(\frac{C - C_{A\infty}}{C - C_{A\cdot S}} \right) \right] \cdot r$$

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$$\frac{d}{dt}\left[\frac{4}{3}\pi r^3 \left(\frac{\rho_A}{M_A}\right)\right] = -W$$

Gas phase conc.

$$= -4\pi D_{AB}\, C \cdot r \ln\left(\frac{C - C_{A\cdot\infty}}{C - C_{A\cdot s}}\right) = 4\pi \left(\frac{\rho_A}{M_A}\right) r$$

$$4\pi\left(\frac{\rho_A}{M_A}\right)\int_{r_{s0}}^{r_{sf}} r\, dr = -4\pi D_{AB} \cdot C \ln\left(\frac{C - C_{A\cdot\infty}}{C - C_{A\cdot s}}\right)\int_0^{t_f} dt$$

$$r_{s0}^2 - r_{sf}^2 = 2 D_{AB} \cdot C \left(\frac{M_A}{\rho_A}\right) \ln\left(\frac{C - C_{A\infty}}{C - C_{AS}}\right) \cdot t_f$$

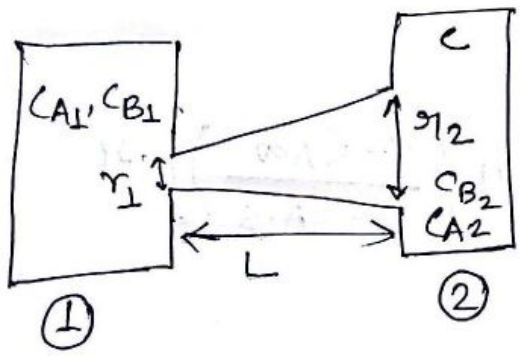
for 2(a)

Equimolar counter Diffusion

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

$$r_{s0}^2 - r_{sf}^2 = 2 D_{AB}\left(\frac{M_A}{\rho}\right)(C_{A\infty} - C_{A\cdot s})\, t_f$$

2(b) Tappered pipe



$C_{A1} > C_{A2} \Rightarrow$ A diffuse from 1 to 2 maintained at same temp. & pressure

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$$N_A \pi r^2 = W$$

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

Important

$$\frac{W}{\pi} \frac{dx}{r^2} = -D_{AB} dC_A$$

$$r = r_1 + \frac{x}{L}(r_2 - r_1)$$

$$\frac{W}{\pi} \int_0^L \frac{dx}{\left[r_1 + \frac{x}{L}(r_2 - r_1)\right]^2} = -D_{AB} \int_{C_{A1}}^{C_{A2}} dC_A$$

$$W = \pi D_{AB} \frac{r_1 r_2}{L} (C_{A1} - C_{A2})$$

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$$W = \pi D_{AB} \frac{r_1 r_2}{L} (C_{A1} - C_{A2})$$

07/08/17

Experimental measurement

Gas

1) Stefan tube / Arnold cell

2) Twin bulb

1) Diaphragm cell

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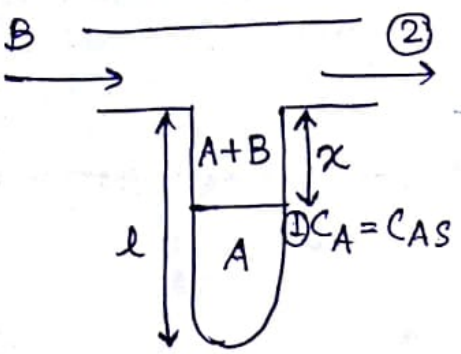
Stefan tube



B is not soluble in A

Flow rate of B is large

$A\uparrow,\ B \neq$

$N_B = 0$

$t=0,\ x=x_1 \quad \Big|\quad C_{A_1} = C_{A_S} = C_{A_1}$

$t=t_f,\ x=x_f \quad \Big|\quad C_{A_2} = 0 = C_{A_2}$

$$N_A = \frac{D_{AB}C}{C_{Blm}x}(C_{A_1} - C_{A_2})$$

$a \equiv$ cross sectional area of vertical tube

$$\frac{d}{dt}\left(a(l-x)\frac{\rho_A}{M_A}\right) = -N_A.a$$

$$\frac{\rho_A}{M_A}\int_{x_1}^{x_f} x\,dx = \frac{D_{AB}C}{C_{Blm}}(C_{A_1} - C_{A_2})\int_0^{t_f} dt$$

$$\cancel{\frac{\rho_A}{2M_A}(x_f^2 - x_1^2) = \frac{D_{AB}C}{C_{Blm}}(C_{A_1} - C_{A_2})t_f}$$

$$\frac{\rho_A}{2M_A}(x_f^2 - x_1^2) = \frac{D_{AB}C\,(C_{A_1} - C_{A_2})t_f}{C_{Blm}}$$

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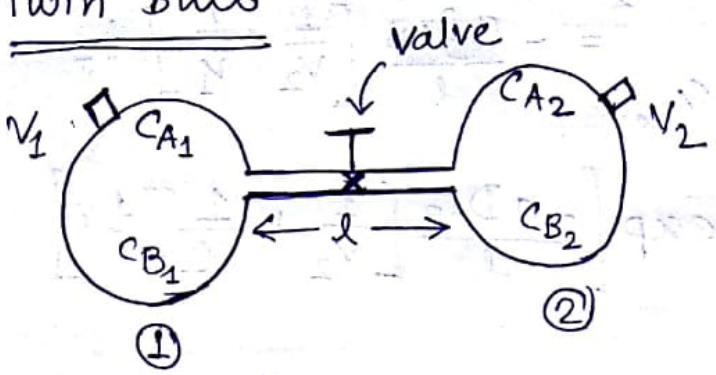
Twin Bulb



Equimolar counter diffusion as both of the bulbs are maintained at same pressure

t, C_{A_1}, C_{A_2}

$t = 0, \; C_{A_1} = C_{A_{1_0}}, \; C_{A_2} = C_{A_{2_0}}$

$t = t_f, \; C_{A_1} = C_{A_{f_1}}, \; C_{A_2} = C_{A_{f_2}}$

$$N_A = \frac{D_{AB}}{l_1}(C_{A_1} - C_{A_2}) = -N_B$$

$$\frac{d}{dt}(V C_{A_1}) = -N_A \cdot a$$

$$\frac{dC_{A_1}}{dt} = -\frac{a}{V_1}\frac{D_{AB}}{l}(C_{A_1} - C_{A_2}) \quad \text{--- (1)}$$

$$\frac{d}{dt}(V_2 C_{A_2}) = N_A \cdot a \quad ; \; [N_A = -N_B]$$

$$\frac{dC_{A_2}}{dt} = \frac{a}{V_2}\frac{D_{AB}}{l}(C_{A_1} - C_{A_2}) \quad \text{--- (2)}$$

$$\frac{dC_{A_1}}{dt} - \frac{dC_{A_2}}{dt} = -\frac{a\, D_{AB}(C_{A_1} - C_{A_2})}{l}\left[\frac{1}{V_2} + \frac{1}{V_1}\right]$$

$$\int \frac{d(C_{A_1} - C_{A_2})}{(C_{A_1} - C_{A_2})} = -\frac{a\, D_{AB}}{l}\left[\frac{1}{V_2} + \frac{1}{V_1}\right]\int_0^{t_f} dt$$

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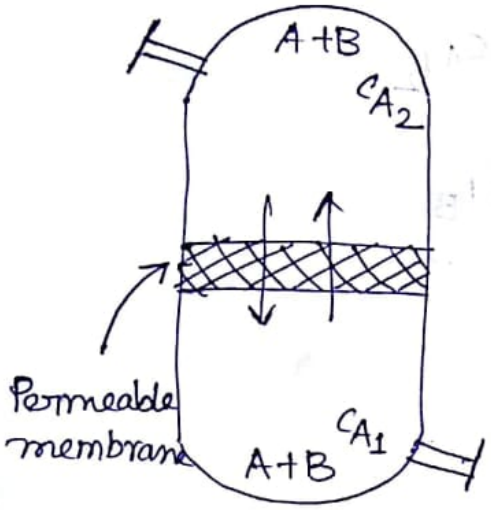
$$\left[\ln\left(C_{A_1} - C_{A_2}\right)\right]_{C_{A_{1_0}}, C_{A_{2_0}}}^{C_{A_1}, C_{A_2}} = -\frac{a D_{AB}}{l}\left[\frac{1}{V_2} + \frac{1}{V_1}\right] t_f$$

$$\frac{C_{A_1} - C_{A_2}}{C_{A_{1_0}} - C_{A_{2_0}}} = \exp\left[\frac{-a D_{AB}}{l}\left[\frac{1}{V_2} + \frac{1}{V_1}\right] t_f\right]$$

Diaphragm cell



$t=0,\ C_{A_1} = C_{A_{1_0}},\ C_{A_2} = C_{A_{2_0}}$

$A\uparrow\ B\downarrow$

$t = t_f,\ C_{A_1},\ C_{A_2}$

$$\int_{C_{A_{1_0}} - C_{A_{2_0}}}^{C_{A_{1f}} - C_{A_{2f}}} \frac{d(C_{A_1} - C_{A_2})}{(C_{A_1} - C_{A_2})} = -\frac{D_{AB}\, a\, \varepsilon}{l\, \tau}\left[\frac{1}{V_2} + \frac{1}{V_1}\right] t_f$$

$$= -D_{AB} K_{cell} t_f$$

$$K_{cell} = \frac{\cancel{D_{AB}}\, a\, \varepsilon}{l\, \tau}\left[\frac{1}{V_2} + \frac{1}{V_1}\right]$$

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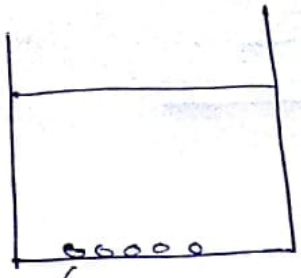
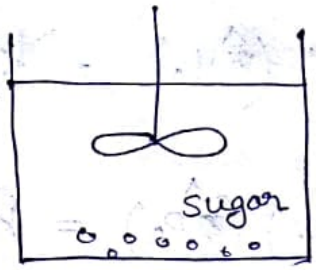
~~$y = 0.9 y_0$~~ 09/08/17





Convective mass transfer

i) Molecular diffusion

ii) Fick's Law

i) Eddy diffusion

ii) Fick's law is not applicable

iii) Additional effect of flow/velocity needs to be accounted

Mass flux $\propto \Delta\nabla$(driving force)

Mass flux = (constant) ($\nabla\Delta$(driving force))

M.T.C

$$\left.\begin{aligned} N_A &= k_c(\overset{\Delta}{\nabla} C_A) \\ &= k_y(\overset{\Delta}{\nabla} y_A) \\ &= k_G(\overset{\Delta}{\nabla} p_A) \end{aligned}\right\} \text{gases}$$

$$\left.\begin{aligned} N_A &= k_L(\overset{\Delta}{\nabla} C_A) \\ &= k_x(\overset{\Delta}{\nabla} x_A) \end{aligned}\right\} \text{liquid}$$

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$$N_A = k_c(\Delta C) = \frac{k_c \cdot C \, C_A}{C}$$

$$= (k_c C)(\Delta y_A) = k_y(\Delta y_A)$$

$$= \left(\frac{k_c}{RT}\right)(\Delta P_A) = k_G(\Delta P_A)$$

$\frac{1}{MTC}$ = Mass transfer resistance

MTC

- Analytically
  - Molecular
  - Theories for convective Mass transfer
    1) specific to simple cases
    2) Simplified Assumptions
    3) No direct accountability for velocity
- Correlations
- Direct experimental measurement

Theories

- i) Film theory
- ii) Penetration theory
- iii) Surface Renewal theory
- iv) Boundary layer theory

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Gas phase

	situation	k_c	k_y	k_g

liquid phase

Variable Geometry

	Situation	k_{L_A}	k_{y_A}	k_{g_A}
1)	Cylindrical			
2)	Spherical			

In case of variable geometry k changes with area.

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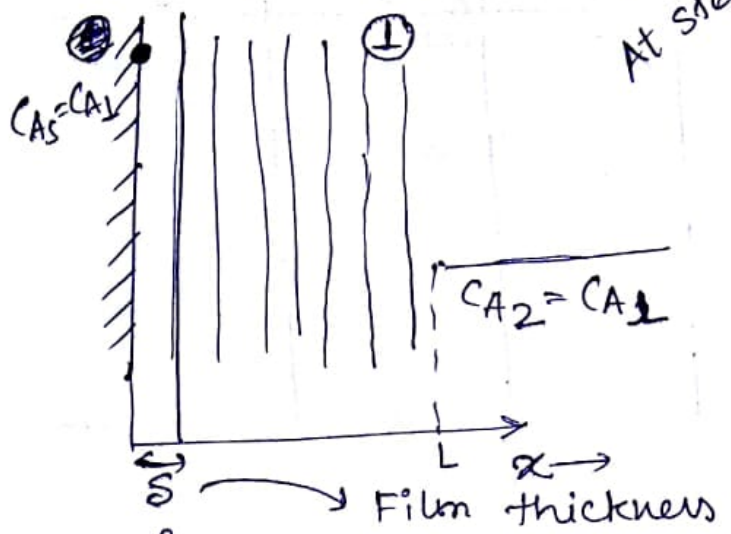
Film Theory

At steady state



$$\frac{d^2 C_A}{dx^2} = 0$$

$$C_A|_{x=0} = C_{A_1} = C_{A_s}$$

$$C_A|_{x=\delta} = C_{A_2} = C_{A_l}$$

⇓

All the mass transfer takes place within this filmthickness

$$\frac{dC_A}{dx} = k_1$$

$$C_A = k_1 x + k_2$$

Neglect bulk flow $(N_A + N_B) = 0$

$$C_{A_1} = 0 + k_2 = C_{A,s}$$

$$C_{A_l} = k_1 l + C_{A,s}$$

$$k_1 = \frac{C_{A,l} - C_{A,s}}{l}$$

$$C_A = \left(\frac{C_{A,l} - C_{A,s}}{\delta}\right) x + C_{A,s}$$

$$\frac{dC_A}{dx} = \frac{(C_{A,l} - C_{A,s})}{\delta}$$

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$$N_A = -\frac{D_{AB}}{\delta}(C_{A,2} - C_{A,1})$$

$\downarrow$ MTC

$\delta \equiv$ hypothetical parameter

higher falling rate

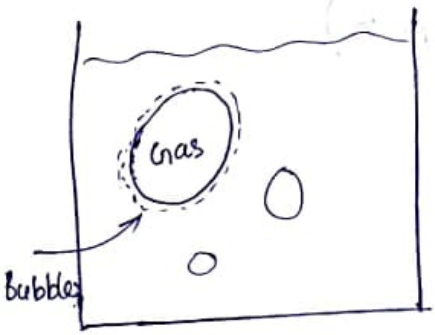
$\Rightarrow$ higher M.T rate

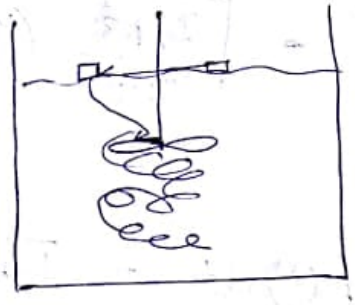
$\Rightarrow$ lower δ

$$K_c = (D_{AB})^n$$

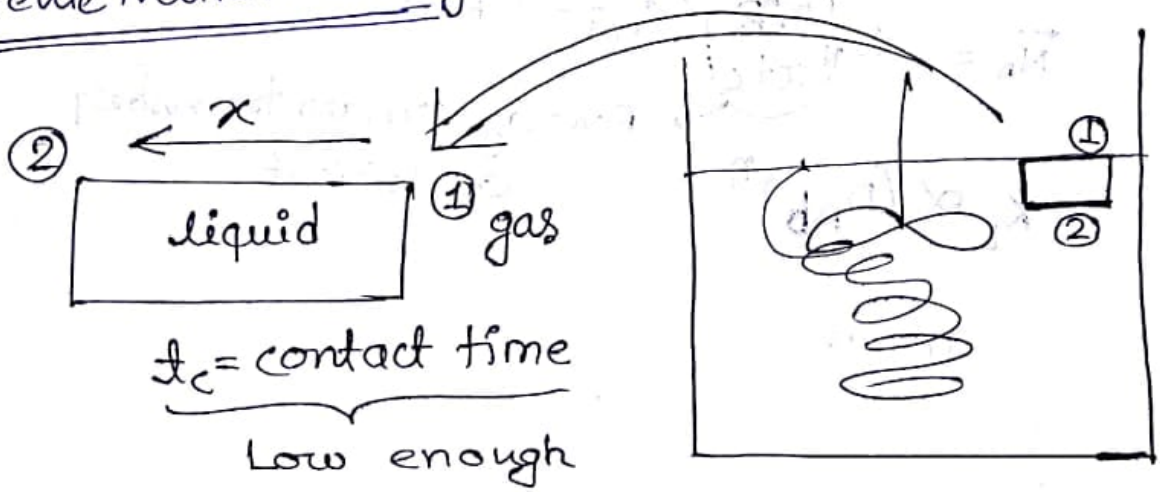
$n < 1$

10/08/17





Penetration Theory



t_c = contact time

Low enough so that diffusing ~~element~~ component never reaches other end of the element

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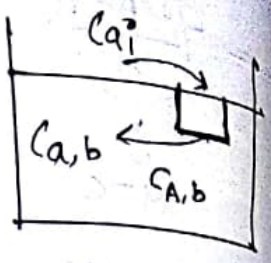
$$-D_{AB}\frac{d^2C_A}{dx^2} = \frac{\delta C_A}{\delta t}$$



$t=0, \quad C_A(x) = C_{A,b}$

$t>0, \quad C_A(0) = C_{A,i}$

$C_A(\infty) = C_{A,b}$

$$\frac{C_A - C_{A,b}}{C_{Ai} - C_{A,b}} = 1 - \text{erf}\,\eta \quad , \quad \cancel{\eta = \frac{x}{2\sqrt{D_{AB}t}}}$$

$$\eta = \frac{x}{2\sqrt{D_{AB}t}}$$

$$N_A(t) = \sqrt{\frac{D_{AB}}{\pi t}}\,(C_{A,i} - C_{A,b})$$

$$\frac{1}{t_c}\int_0^{t_c} N_A(t)\,dt = \overline{N}_A$$

$$\overline{N}_A = 2\sqrt{\frac{D_{AB}}{\pi t_c}}\,(C_{A,i} - C_{A,b})$$

Average mass transfer coefficient

$$k_L \propto (D_{AB})^n$$

$n = 0.5$

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Film theory

Vel ↑ N_A ↑, k_c ↑, δ ↓

Penetration theory

vel ↑ N_A ↑, k_l ↑, t_c ↓

Surface Renewal Theory:

$$N_A = \sqrt{D_{A,B}\, S}\,(C_{A,i} - C_{A,b})$$

S = surface renewal ~~theory~~ rate

vel ↑, N_A ↑, k_l ↑, S ↑

Does not account for velocity profile (Bulk motion)

$$J_A = -D_{AB}\frac{dC_A}{dx}$$

$$q'' = -\frac{k}{\rho C_p}\frac{d(T\rho C_p)}{dx}$$

$$\tau = -\frac{\mu}{\rho}\frac{d(V\rho)}{dx}$$

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14/08/17

$$J_A = -D_{AB}\frac{dC_A}{dx}$$ → Mass diffusivity

$$q = -\left(\frac{k}{\rho c_p}\right)\frac{d(\rho c_p T)}{dx}$$ → $\frac{1}{\text{Thermal diffusivity}(\alpha)}$

$$\tau = -\left(\frac{\mu}{\rho}\right)\frac{dv}{dx}$$ → Kinematic viscosity or Momentum diffusivity (ν)

$$D_{AB} \Leftrightarrow \frac{1}{\alpha} \Leftrightarrow \nu$$

$$Nu = \frac{\text{Heat transfer due to convection}}{\text{Heat transfer due to conduction}}$$

$$= \frac{hA\Delta T}{K.A\frac{\Delta T}{L}} = \frac{hL}{K}$$

$Sh \equiv$ Sheerwood Number

$$= \frac{\text{Mass transfer due to convective mass transfer}}{\text{" " " " molecular diffusion}}$$

Ignoring bulk flow $N_A + N_B = 0$

$$Sh = \frac{K_c A \Delta C_A}{\frac{D_{AB}}{l} A \Delta C_A} = \frac{K_c l}{D_{AB}} = \frac{K_L l}{D_{AB}}$$

For $N_A + N_B \neq 0$

$$Sh = \frac{K_c l}{D_{AB}}\left[\frac{C}{(C_B)_{lm}}\right]$$

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$$Re = \frac{\rho V D}{\mu} = \frac{G D}{\mu}$$

$$Pr = \frac{\nu}{\alpha} \Leftrightarrow Sc \equiv \text{Schmidt Number} = \frac{\nu}{D_{AB}}$$

$$Pe_H = Re \cdot Pr \qquad St_H = \frac{Nu}{Pe}$$

$$Pe_M = Re \cdot Sc \qquad St_M = \frac{Sh}{Pe_M}$$

For mass transfer

Boundary layer thickness depends on Schimdt & Prandtl number.

$$\frac{K_L \cdot x}{D_{AB}} = 0.332 \left(\frac{x V_\infty \rho}{\mu}\right)^{1/2} \left(\frac{\nu}{D_{AB}}\right)^{1/3}$$

$$Sh_x = 0.332 (Re_x)^{1/2} (Sc)^{1/3}$$

$$Sh_x \propto Re^n$$
$$\propto Sc^m$$

$$\frac{\int_0^L Sh_x dx}{\int_0^L x dx} = \overline{Sh_L} = 0.664 (Re_L)^{1/2} (Sc)^{1/3} = \frac{K_L \cdot L}{D_{AB}}$$

Average Sheerwood number

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$K_L \propto D_{AB}$ film theory

$\propto D_{AB}^{1/2}$ Penetration theory

$\propto D_{AB}^{1/2}$ Surface Renewal "

$\propto D_{AB}^{2/3}$ Boundary Layer theory

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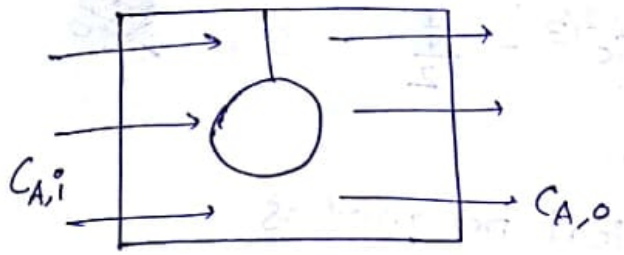
16/08/17

$N_A = (MTC)\, D.F$

MTC
- Analytical
- Experimental
- Correlation



$W = k_c \Delta C_A$

$k_c = f(Sh, Re, Pr)$

Boundary Layer theory

$Sh = f(Re, Sc)$

Analogous correlations

① Heat, mass & momentum

Correlations

→ analogy : Reynold's Analogy
Applicable for
→ Laminar flow
→ $Sc = Pr \approx 1$
→ $(St)_H = (St)_M = f/2$

→ Experimental data

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Analogy

→ Laminar flow

→ $Sc = Pr \simeq 1$

→ $St_H = St_M = \frac{f}{2}$

$$\frac{Nu}{Re \cdot Pr} = \frac{Sh}{Re \cdot Sc} = \frac{f}{2}$$

Coulburn - Chilton : Correction for turbulent flow

$$St_H \, Pr^{2/3} = St_M \, Sc^{2/3} = \frac{f}{2}$$

$Sc < 3000$

$Pr < 60$

1) Match the situation
2) Match process critical parameters

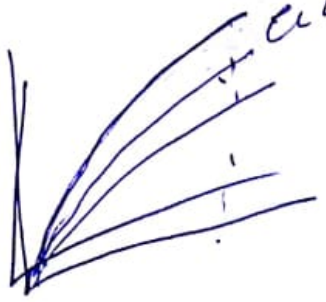
   Sc, Re

3) Find suitable correlations
4) If no correlation is available, look for analogy.
5) Use analogous correlation from heat transfer

e.g $Nu = 2 + 0.3 \, Re^{0.5} \, Pr^{0.33}$

$Sh = 2 + 0.3 \, Re^{0.5} \, Sc^{0.33}$

6) Still not available, use boundary layer theory



$Pr = \frac{\mu}{\rho} \; m^2/s$

$Sc = \frac{\mu}{\rho D_{AB}} \; m^2/s$

$\frac{Sc}{Pr} =$

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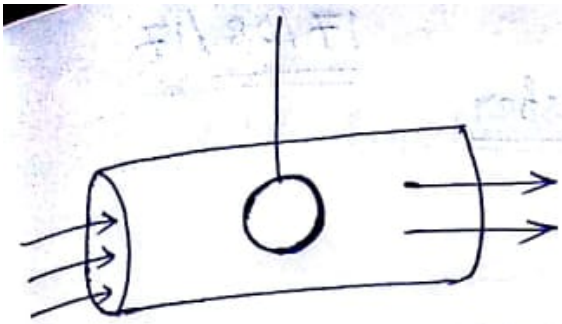

from $W \Rightarrow NA$

	W	ΔC	
D_i			
μ			
ρ			
V			
D_{AB}			

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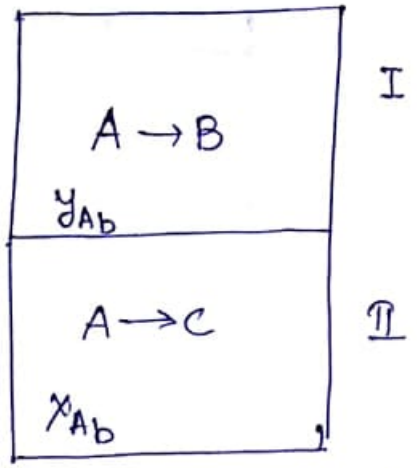
17/08/17

Inter Phase Mass Transfer

→ Binary system

→ Non reactive

→ Two phases - Gas liq.



1) Is there any transfer of A? for $\mu_1 \neq \mu_2$

2) From which phase to which? from higher to lower chemical potential

3) How long?
untill equilibrium reached

$$y_{Ab} > f(x_{Ab})$$

$$y_{Ab} < f(x_{Ab})$$

Mass transfer between two phases occur when

1) $y_{AB} \neq y_A^*$

$$y_A^* = f(x_{Ab})$$

2) $y_{AB} > f(x_{AB})$

Mass transfer occurs from gas phase to liq phase

⇒ Absorption

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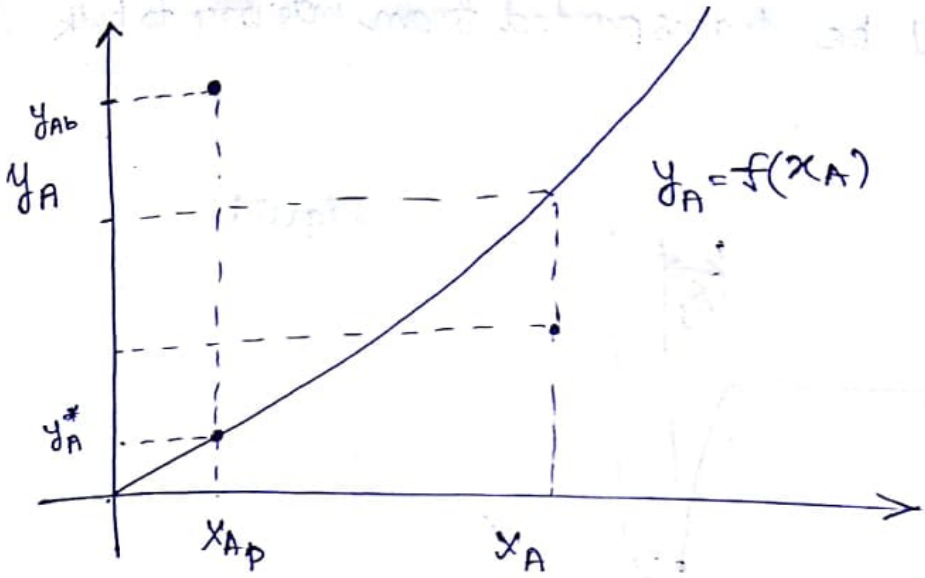
8/17

$y_{AB} < f(x_{AB}) \Rightarrow$ stripping

from liquid phase to gas phase



$\mu_1 \neq \mu_2$

n higher to
er chemical
potential

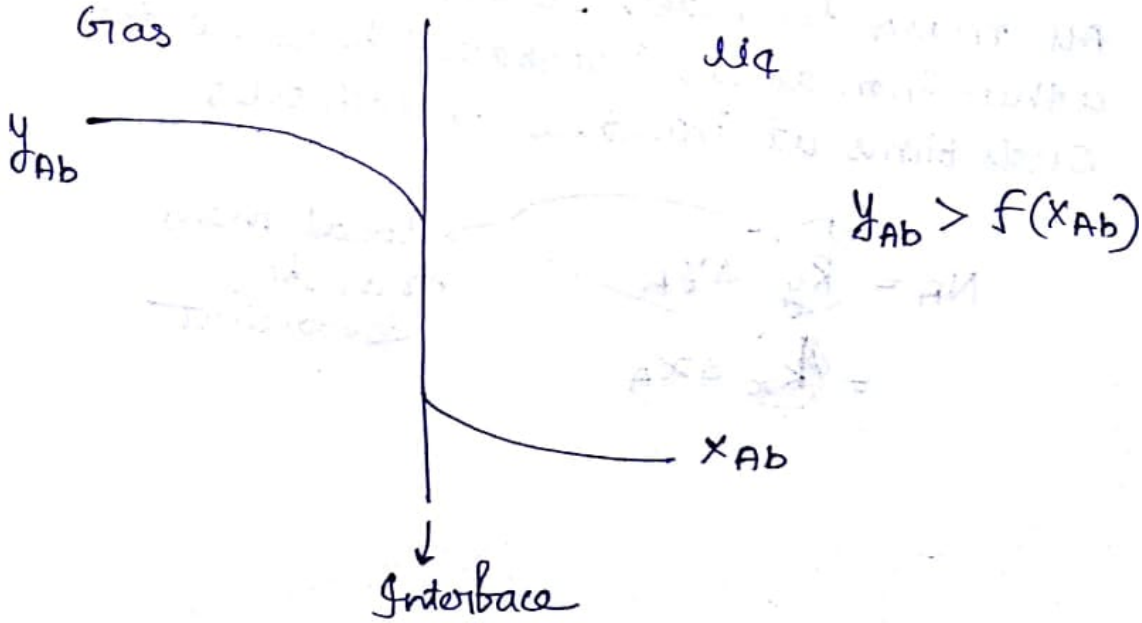
$y_A = f(x_A)$

$P_A = x_A P_A^S \Rightarrow$ Raoult's Law

$y_A = k_H x_A \Rightarrow$ Henry's Law

} Suitable for ideal gases

when



e to liq
hase

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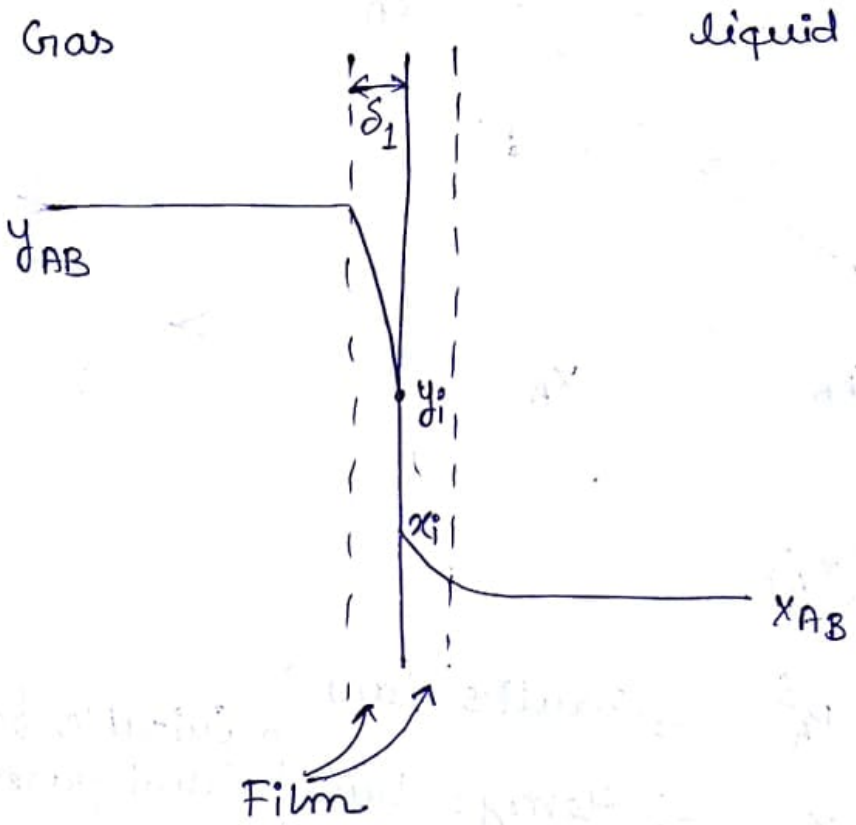
1) Transport of A from bulk to interface
2) At interface equilibrium will be established
3) A will be transported from interface to bulk



All mass transfer resistance exists in a thin film at the interface. There are two such films at interface on both sides.

$$N_A = k_y \, \Delta y_A$$
$$= k_x \, \Delta x_A$$

→ Local mass transfer coefficient

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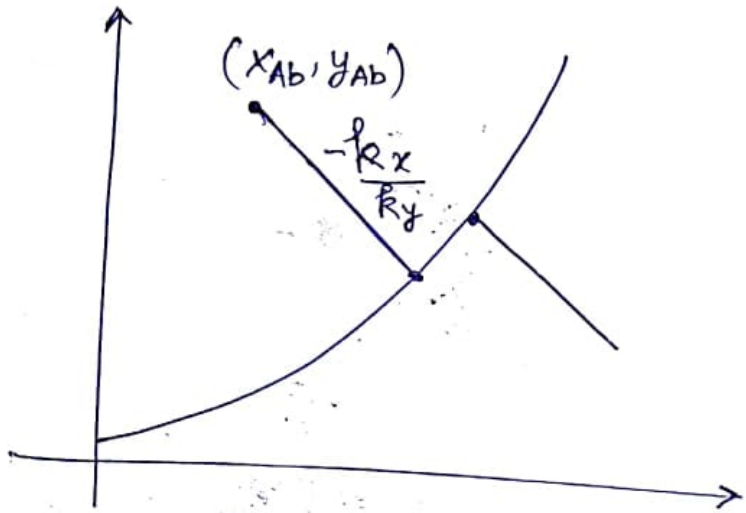
Absorbtion

$$N_A = k_y (y_{Ab} - y_i)$$

$$N_A = k_x (x_{Ab} - x_i)$$

$$k_y (y_{Ab} - y_i) = k_x (x_i - x_{ab})$$

$$-\frac{k_x}{k_y} = \frac{y_{Ab} - y_i}{x_{Ab} - x_i}$$



Stripping

$$N_A = k_y (y_i - y_{Ab})$$

$$N_A = k_x (x_{Ab} - x_i)$$

$$-\frac{k_y}{k_x} = \frac{x_{Ab} - x_i}{y_{Ab} - y_i}$$

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$$\frac{N_A}{K_x} = \frac{N_A}{k_x} + \frac{N_A}{m_2 k_y}$$

$$\boxed{\frac{1}{K_x} = \frac{1}{k_x} + \frac{1}{m_2 k_y}}$$

23/08/17

For Henry's law $y = Hx$

$\Rightarrow m_1 = m_2$

$\frac{1}{K_y}$ = total M.T resistance based on overall gas phase driving force

$\frac{1}{K_x}$ = total M.T resistance based on liquid phase driving force.

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{m_1}{k_x}$$

$\frac{m_1}{k_x}$ → Liq phase mass t.r. based on ~~liq~~ gas phase driving force

$\frac{1}{k_y}$ → Gas phase mass transfer resistance to the overall resistance based on gas phase driving force

$\frac{1}{m_2 k_y}$ = gas phase m.t.r. to overall m.t.r based on liquid phase driving

$\frac{1}{k_x}$ = liq phase ——— " ———

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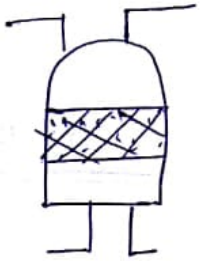
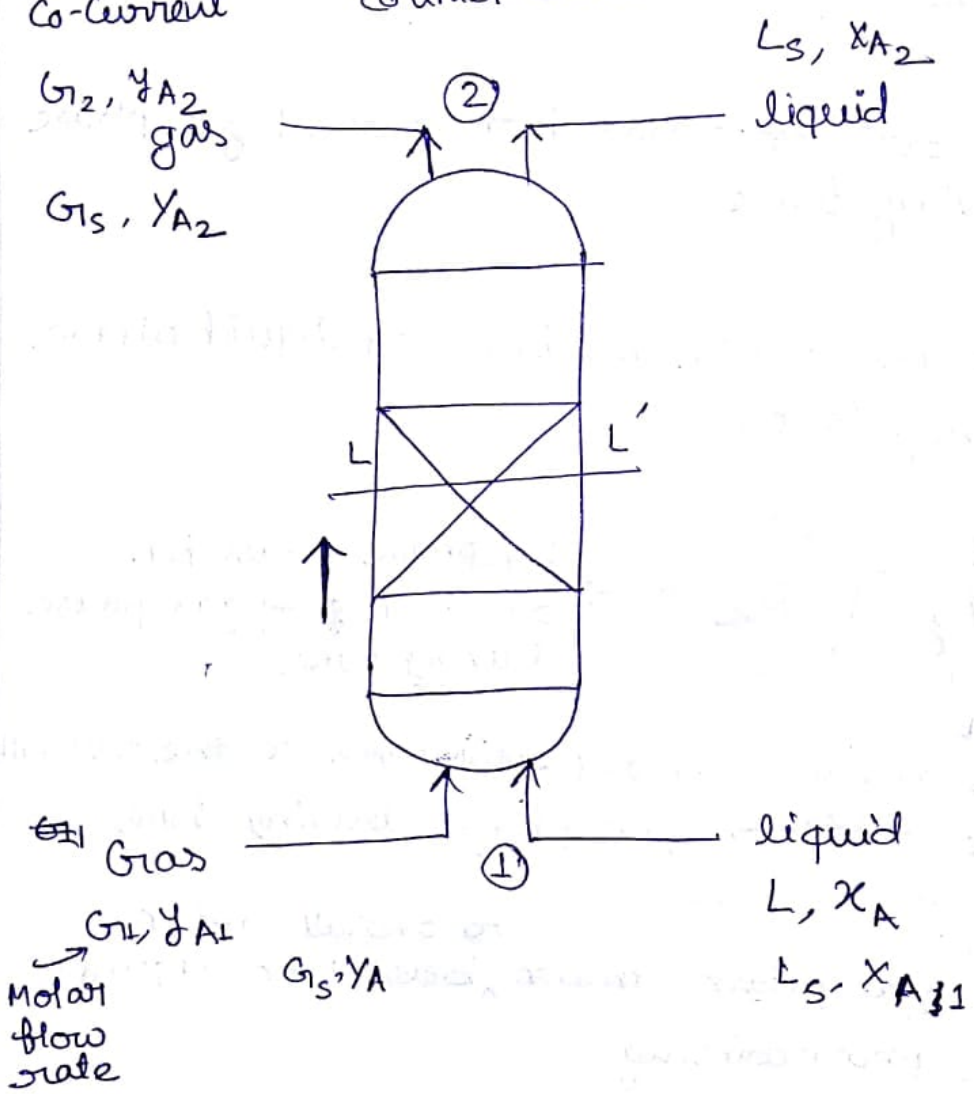
Mass Transfer Equipments

- Continuous
  - → Packed bed



  - Co-current
  - Counter-current

- Stage wise (distillation) column



Flow rate → Solute free basis

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$$Y_A = \frac{y_A}{1 - y_A}$$

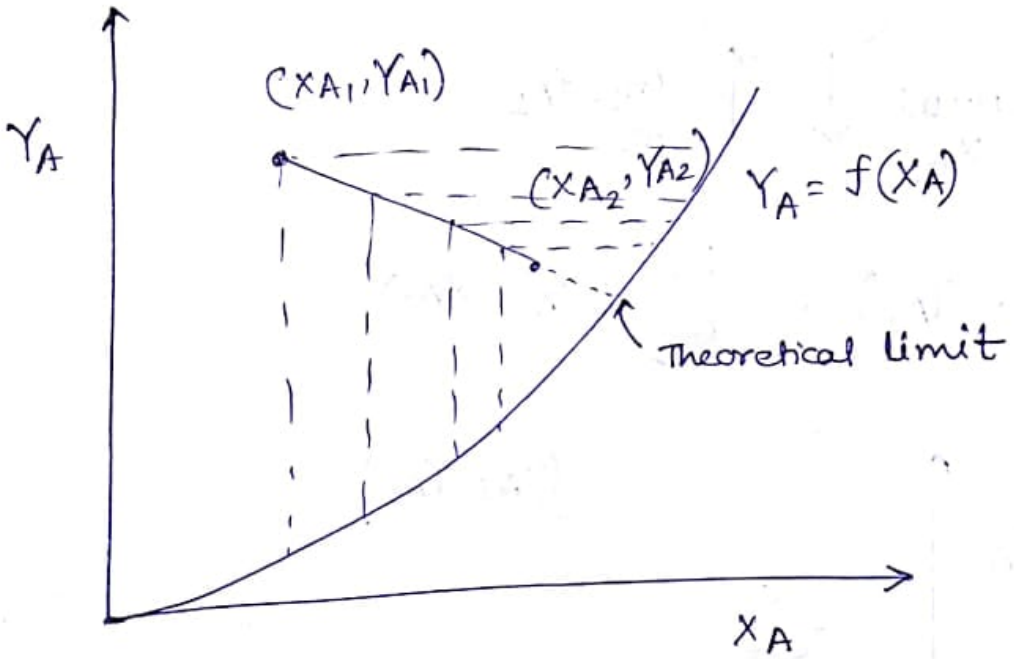
$$X_A = \frac{x_A}{1 - x_A}$$

$$y_A = f(x_A) \quad \text{--} \quad (1)$$

Given in mole fraction basis, to be converted in to mole ratio basis

$$G_S Y_{A1} + L_S X_{A1} - G_S Y_{A2} - L_S X_{A2} = 0 \quad \text{--} \quad (2)$$

$$(Y_{A1} - Y_{A2}) = -\frac{L_S}{G_S}(X_{A1} - X_{A2})$$



$$G_S Y_{A1} + L_S X_{A1} - G_S Y_A - L_S X_A = 0$$

$$\boxed{(Y_A - Y_{A1}) = -\frac{L_S}{G_S}(X_A - X_{A1})}$$

⇒ operating eqn

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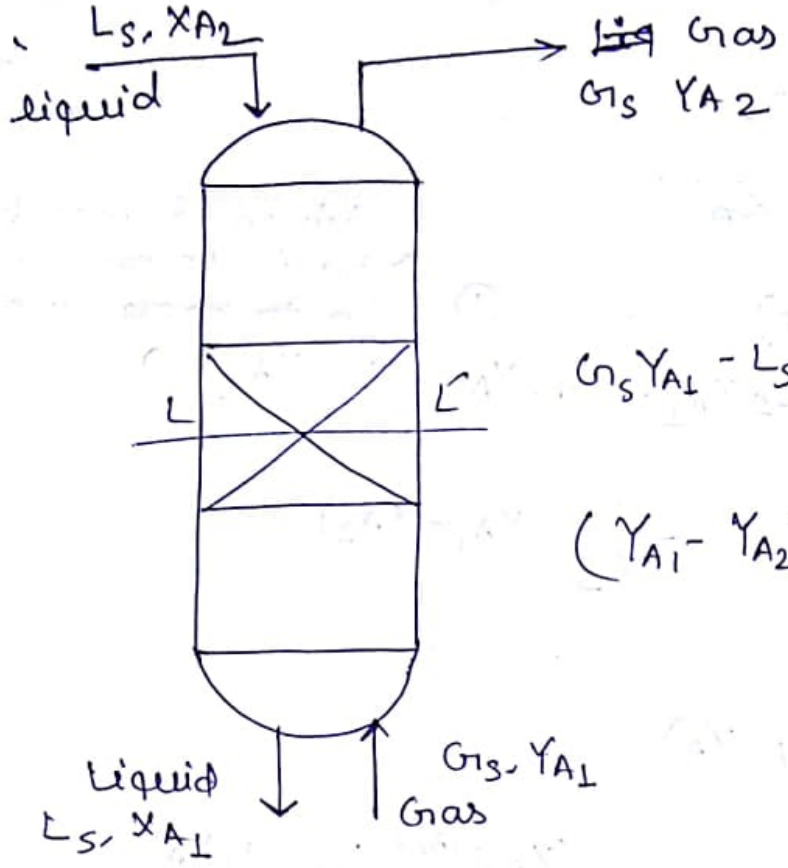
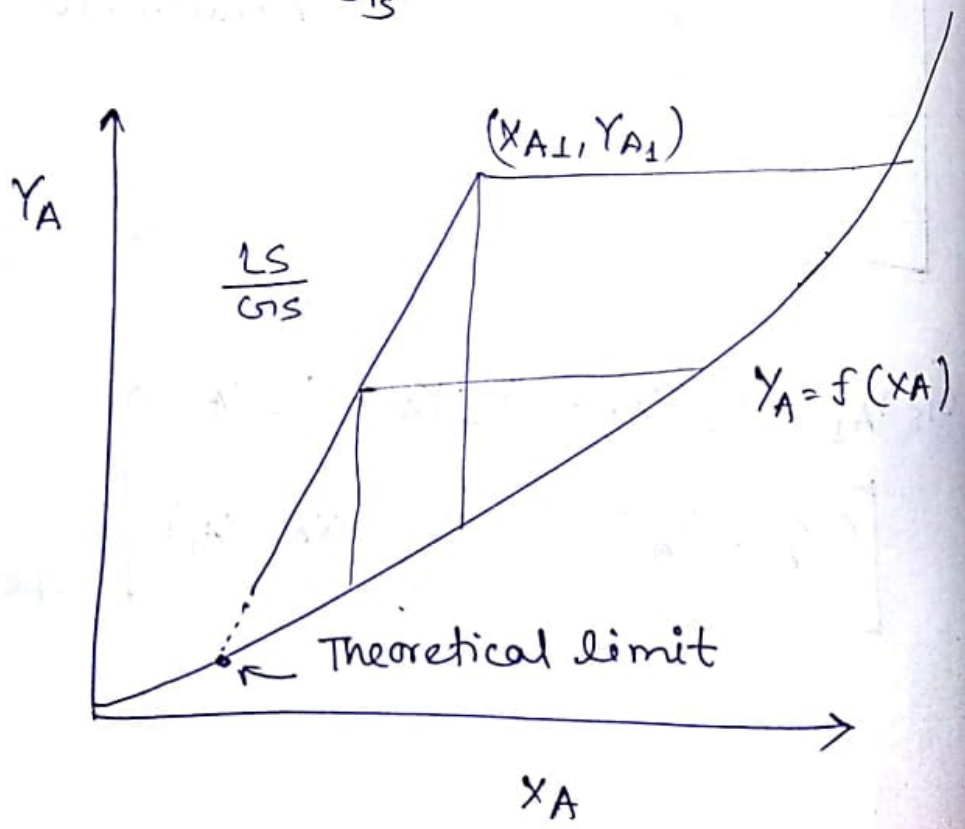


$$G_s Y_{A1} - L_s X_{A1} - G_s Y_{A2} + L_s X_{A2} = 0$$

$$(Y_{A1} - Y_{A2}) = \frac{L_s}{G_s}(X_{A1} - X_{A2})$$

$$(Y_A - Y_{A1}) = \frac{L_s}{G_s}(X_A - X_{A1})$$



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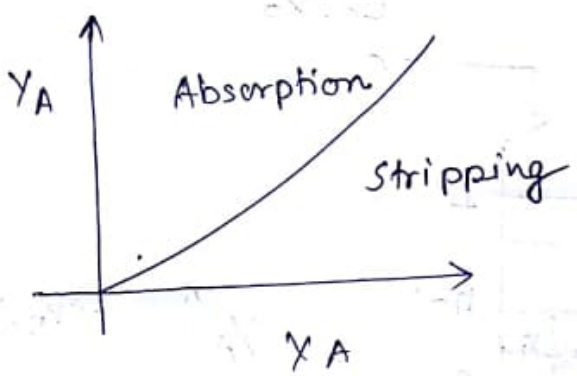
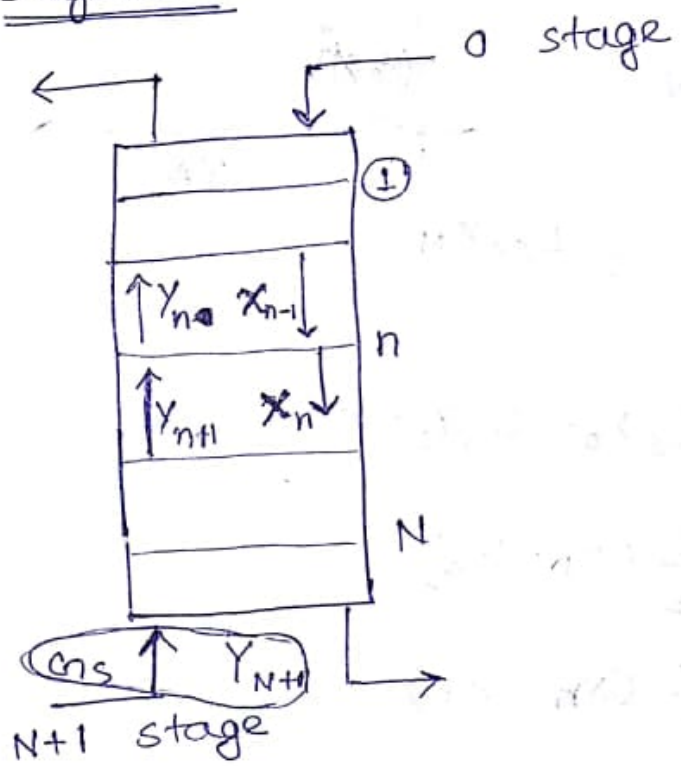


Stage wise



24/08/17

Flash distilation
≡ one stage co-current distilation

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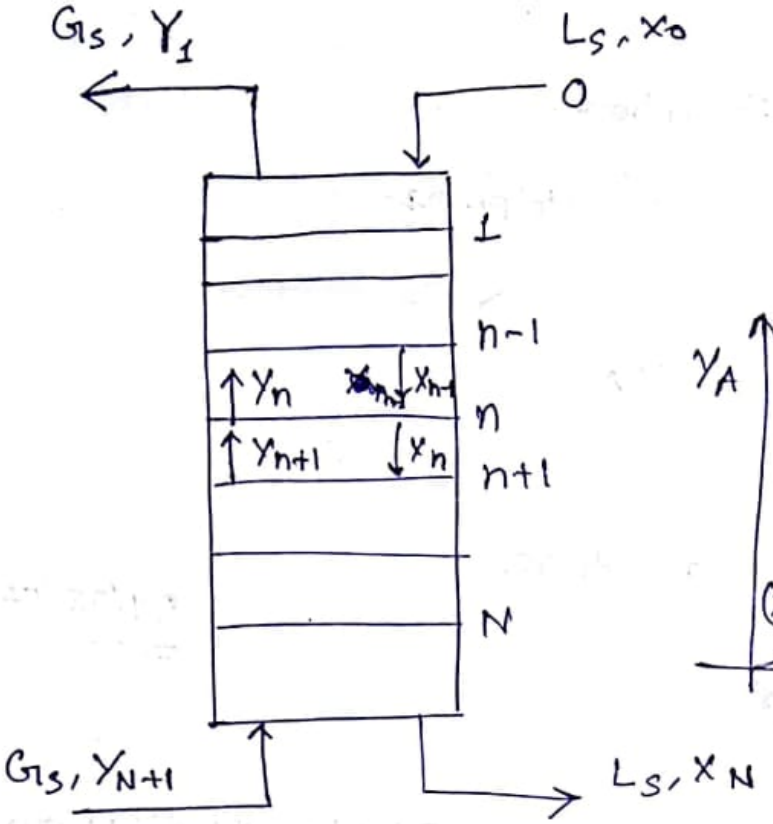
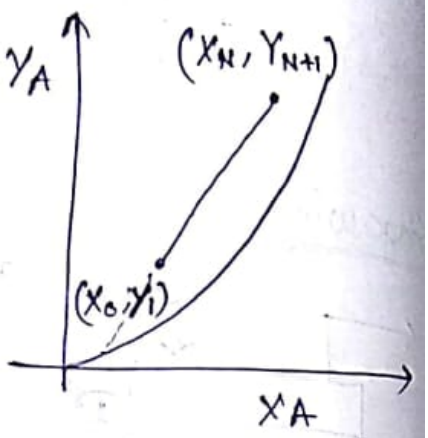
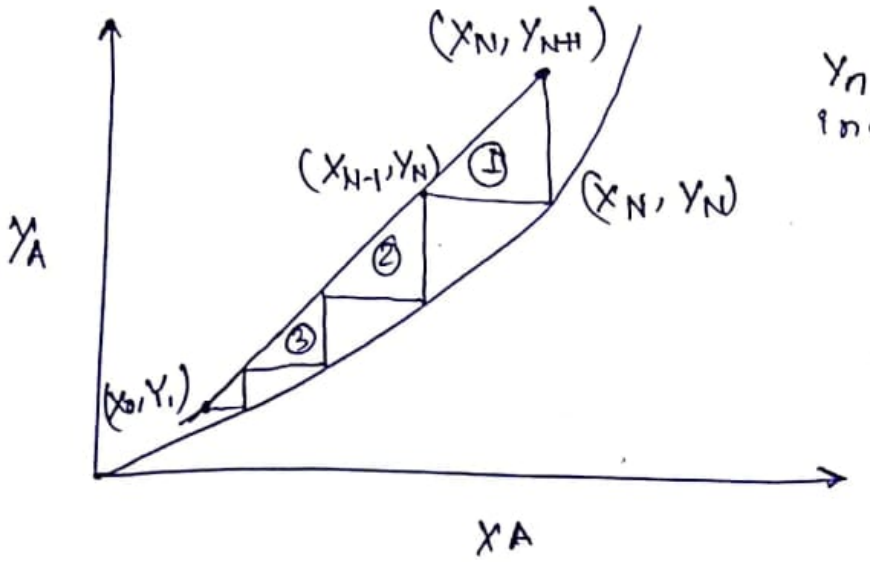




$$G_s Y_{N+1} - L_s X_N + L_s X_0 - G_s Y_1 = 0$$

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

$$(Y_{n+1} - Y_1) = \frac{L_s}{G}(X_n - X_0)$$



$Y_n = X_n$ = are in equilibri

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B.K. Dutta Page - 145 onwards

$$\left.\begin{aligned}(Y_{n+1} - Y_1) &= \frac{L_s}{G_s}(X_n - X_0)\\ Y_n = f(X_n) &= \alpha X_n\end{aligned}\right\}$$

$$\boxed{Y_{n+1} - \bar{A}Y_n = Y_1 - \bar{A}\alpha X_0} \qquad \bar{A} = \frac{L_s}{G_s \cdot \alpha}$$

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

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

$$N = \frac{\log\left[\left(\frac{Y_{N+1} - \alpha X_0}{Y_1 - \alpha X_0}\right)\left(1 - \frac{1}{\bar{A}}\right) + \frac{1}{\bar{A}}\right]}{\log \bar{A}} \qquad \text{for } \bar{A} \neq 1$$

for $y_n = \frac{L_s}{G_s} X_n$

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

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For stripping

$$N = \frac{\log\left[\left(\frac{x_0 - y_{N+1}/\alpha}{x_N - y_{N+1}/\alpha}\right)(1-\bar{A}) + \bar{A}\right]}{\log(1/\bar{A})}$$

$\bar{A} \neq 1$

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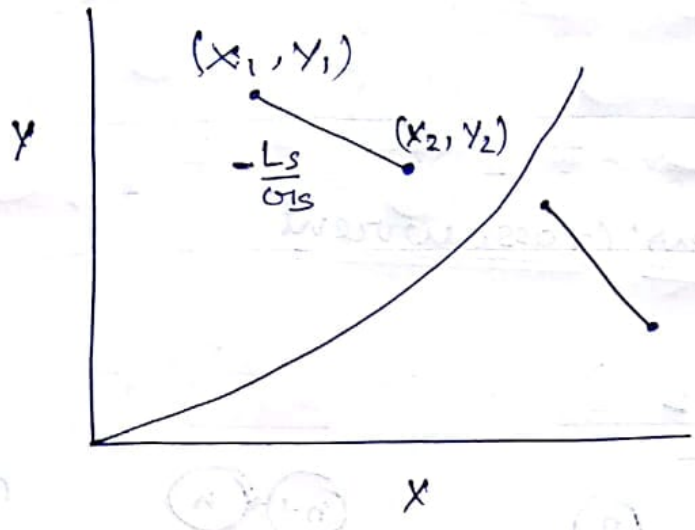
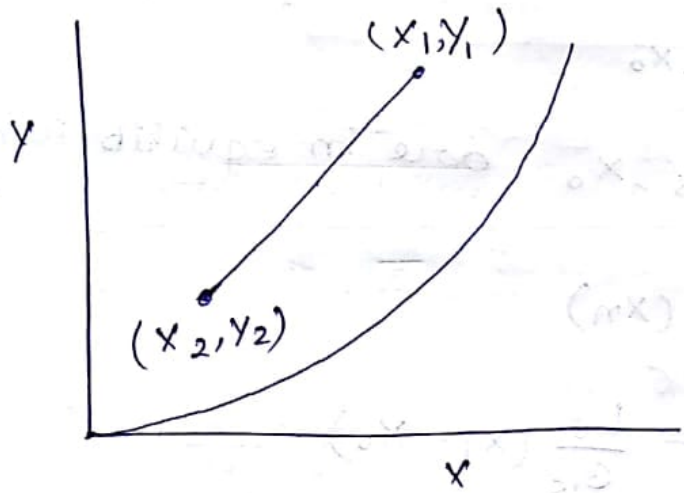
1. Cocurrent continious operation 25/08/17

$$Y_2 - Y_1 = -\frac{L_s}{G_s}(x_2 - x_1)$$

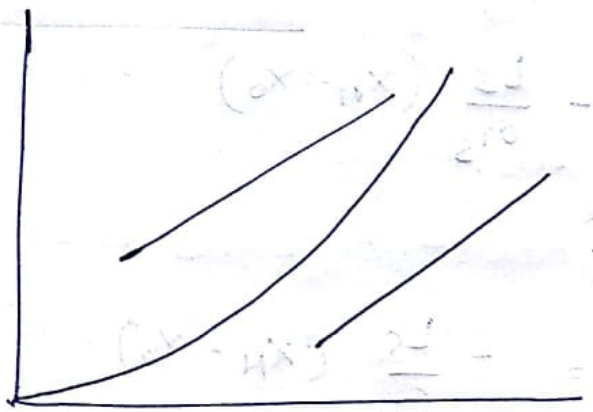


2. Counter-current continious flow



$$Y_2 - Y_1 = \frac{L_s}{G_s}(x_2 - x_1)$$

3. Stagewise counter current



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

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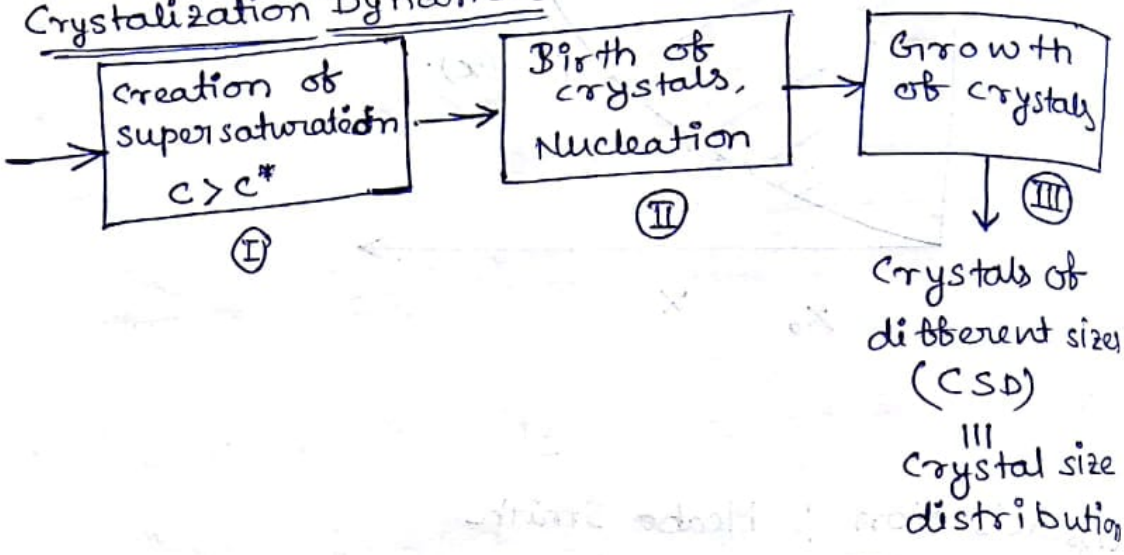
Crystalization

30/08/17

Separation of solute in solid form from a solution.

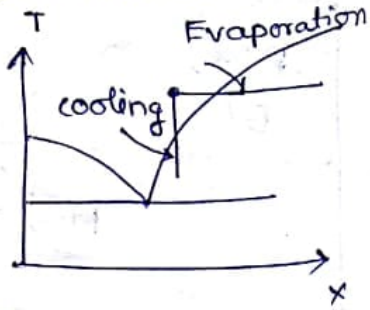
Crystalization Dynamics



I) Creation of supersaturation:

$$\frac{c - c^*}{c^*} = s \equiv \text{Degree of supersaturation}$$

$(c - c^*) \equiv$ Extenst of supersaturation



→ By cooling
→ Evaaporation } Industrial methods

→ Addition of solute or solvent may shift the equilibrium curve.

II) Birth of crystals / Nucleation

Rate of generation of crystals of zero size.

$= B_0$

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Characteristic length of crystal = L

$$B_0 = \lim_{L \to 0} \frac{d(N/V)}{dt}$$

$A_a = \phi_a L^2$

$V = \phi_v L^3$

Nucleation

- Primary
  - Homogeneous
  - Heterogeneous
- Secondary

Occurs due to storage or prolonged action of impellers

Homogeneous ≡ No addition of fine crystals. Occurs without any external interuption

Heterogeneous ≡ Seeds (small fine crystals) are added to fascilitate formation of crystals

For primary nucleation: (crystal size)

$$B_0 = A' \exp\left[\frac{16\pi \sigma^3 v_m^2}{3 k^3 T^3 [\ln(S+1)^2]}\right]$$

(k = Boltzmann const.)

For ~~secondary~~ Heterogeneous nucleation:

$$B_0 = K_1 M_T S^n$$

(M_T = Mass of suspension)

K_1, n } Experimentally determined

n = order ≃ 0-5

$\boxed{n=2}$ if nothing mentioned

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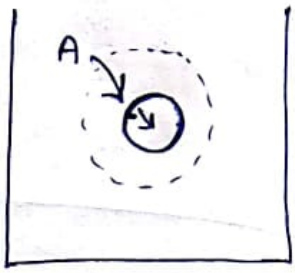
III) Growth of crystals:

m_c = mass of crystal

$$\text{Growth rate} = \frac{dL}{dt} = G$$



1) Transfer of solute molecules from bulk to top of surface.

$$\frac{dm_c}{dt} = k_c A_c (c - c_i)$$

2) Integration of solute in the bulk of crystal

$$\frac{dm_c}{dt} = k_r A_c (c_i - c^*)$$

$$K_L = \frac{1}{\frac{1}{k_c} + \frac{1}{k_r}}$$

$$m_c = V_c \rho_c$$

$$= \phi_v L^3 \rho_c$$

$$A_c = \phi_a L^2$$

$$\frac{dm_c}{dt} = K_L A_c (c - c^*)$$

$$\frac{d}{dt}(\phi_v L^3 \rho_c) = K_L A_c (c - c^*)$$

$$\cancel{dm_c}\ \frac{dL}{dt} = K_L \left(\frac{\phi_a c^*}{3\phi_v \rho_c}\right)\left(\frac{c - c^*}{c^*}\right)$$

$$\frac{dL}{dt} = k' s$$

$$G = k' s$$

$$\boxed{G = k' s^n}$$ In general, determined exp...

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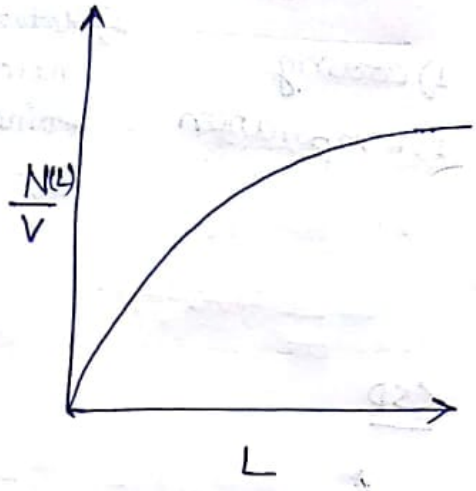
$$B_0 = k_1 M_T s^n$$
$$G = k' s^n$$

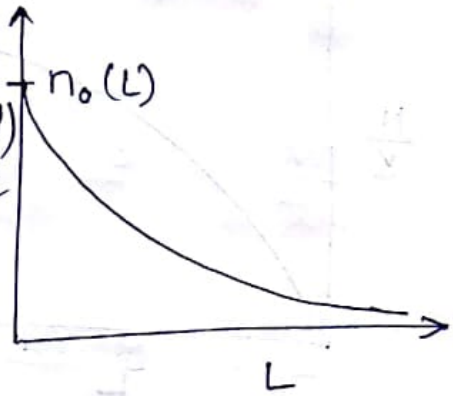
Competetive process, nucleation and growth of crystals

CSD Crystal size distribution

$n(L)$ -



$n_0(L) \equiv$ crystal size distribution of vanishingly small size



$$n(L) = \frac{d\left(\frac{N(L)}{V}\right)}{dL}$$

$$n_0(L) = \lim_{L \to 0} \left[\frac{d\left(N(L)/V\right)}{dL}\right]$$

$$= \frac{\frac{d\left(\frac{N(L)}{V}\right)}{dt}}{\lim_{L \to 0} \frac{dL}{dt}}$$

$$n_0(L) = \frac{B_0}{G}$$

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31/08/17

→ [Creation of Supersaturation] → [Nucleation] → [Growth of Crystal] → CSD

$S = \frac{C - C^*}{C^*}$

1) cooling
2) Evaporation

$B_0 = \lim_{L \to 0} \frac{d(N(0)V)}{dt}$

1) Heterogeneous nucleation (fine crystals)

$B_0 = k_1 M_T S^n$

$G = \frac{dL}{dt}$

$G = k_1 S^n$

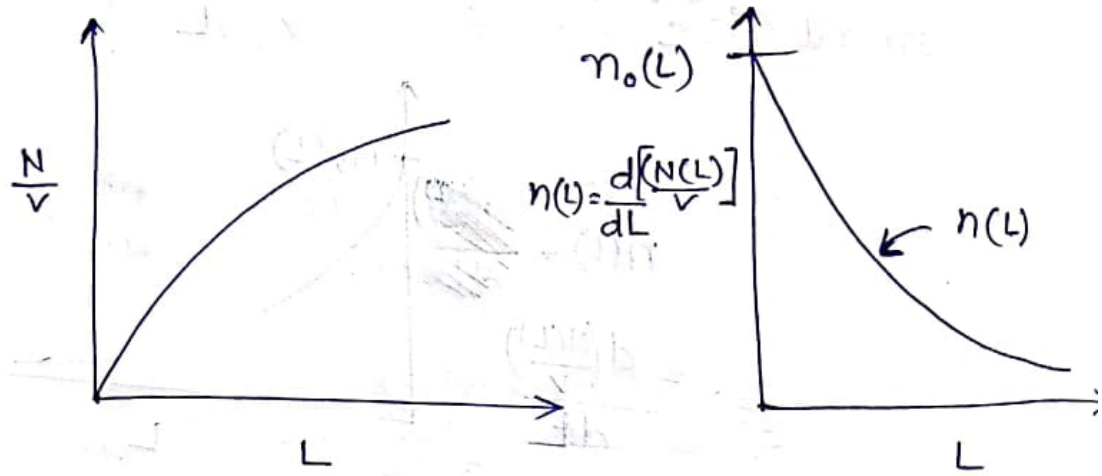
According to hypothesis

$G = k_1 S$

k_1, n are to be determined from experiment

$n(L) = \frac{d}{dL}\left[\frac{N(L)}{V}\right]$

CSD



~~N_T~~ avg

$$\frac{N_T}{V} = \int_{L_1}^{L_2} n(L)\,dL$$

$$A_c = \int_{L_1}^{L_2} n(L)\,\phi_a L^2\,dL$$

$$V_c = \int_{L_1}^{L_2} n(L)\,\phi_v L^3\,dL$$

$$M_c = V_c \rho_c = \rho_c \int_{L_1}^{L_2} n(L)\,\phi_v L^3\,dL$$

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Crystallizer

1) Supersaturation to be created and maintained.
   Degree of supersaturation to be maintained.

2) Nucleation → slurry containing fine crystals

3) Time

McCale 'ΔL' Law

$$G = \frac{dL}{dt} \neq f(L)$$

Crystallizer

- Batch
  - Evaporative crystallizer (continuous evaporation)
  - Cooling Crystallizer
- continuous
  - Mixed slurry mixed product removal ≡ MSMPR
    |||
    ~~Multiple slurry multiple product~~

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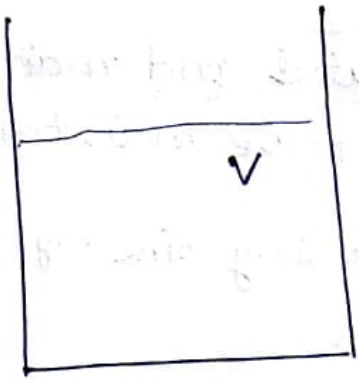

$\frac{dV}{dt} = ?$ $\Rightarrow S = \text{const.} = \frac{C_{-}}{C_{+}}$

$t = 0$, $L = L_s$, $M_s = N \phi_v L_s^3 \rho_c$

$t = t$, $L = L$, $M = N \phi_v L^3 \rho_c$

at $t = t$, $L = Gt + L_s$

$$\cancel{\frac{d}{dt}(VC\rho)} \quad \frac{d}{dt}(VCM_w) = -\frac{dM_c}{dt}$$

$$\frac{d}{dt}(VCM_w) = -\frac{d}{dt}(N\phi_v L^3 \rho_c)$$

$$C\frac{dV}{dt} = \frac{3N\phi_v L^2 \rho_c}{M_w}\frac{dL}{dt}$$

$$C\frac{dV}{dt} = \frac{3N\phi_v L_s^3 (L_s + Gt)^2 G \rho_c}{M_w L_s^3}$$

$$C\frac{dV}{dt} = \frac{3M_s}{M_w}\left(\frac{L_s + Gt}{L_s}\right)^2 \frac{G}{L_s}$$

$L_f = L_s + G t_b$ ← Batch time

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04/09/17

1. Crystallization dynamics
2. CSD
3. Crystallizers → Batch
   → Continious

i) Creates supersaturation and maintains degree of supersaturation
ii) Time for crystal growth
iii) Size, size distribution

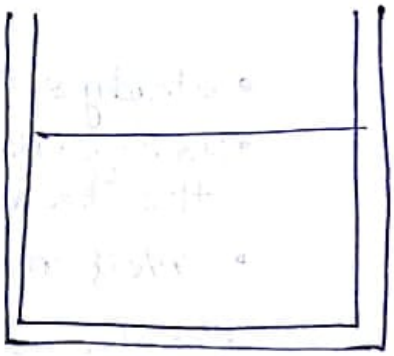
Batch crystallizer

→ Evaporative crystallizer

$\frac{dV}{dt} = \text{const}, \quad L_f = L_s + Gt_b$

→ Cooling crystallizer

$\frac{dT}{dt}$ ~~const~~, $\quad L_f = L_s + Gt_b$



$t = 0, \; L = L_s, \; M_s = N \phi_v L_s^3 \rho_c$

$t = t, \; L = L, \; M_c = N \phi_v L^3 \rho_c$

$\frac{d(M_c)}{dt} = -\frac{dM_c}{dt}$

$V \frac{dc}{dt} = -3N\phi_v L^2 \rho_c \frac{dL}{dt}$

$S = \frac{C - C^*}{C^*}$

→ with temp c^* varies

$V\frac{dc}{dt} = 3N\phi_v L^2 \rho_c G = 3N\phi_v (L_s + Gt_b)^2 \rho_c G$

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$$V\frac{dc}{dt} = 3M_s\left(\frac{L_s+Gt}{L_s}\right)^2\frac{G}{L_s}$$

Now,

$$s = \frac{c-c^*}{c^*} = \frac{c}{c^*} - 1$$

$$c = c^*(s+1) = f(T)(s+1)$$

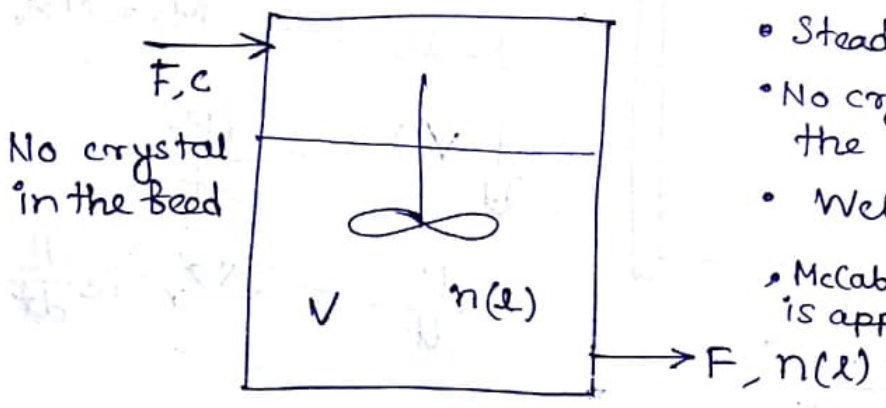
$$\frac{dc}{dT} = f'(T)(s+1)\frac{dT}{dt}$$

$$V\frac{dT}{dt} = \frac{3M_s}{f'(T)(s+1)}\left(\frac{L_s+Gt}{L_s}\right)^2\frac{G}{L_s}$$

$G \rightarrow$ to be determined from kinetic data
k, n are system dependent parameters

Continuous Crystallizer

1) Mixed slurry mixed product removal type (MSMPR)



- Steady state
- No crystals in the feed
- Well mixed
- McCabe 'ΔL' law is applicable

$$n(L) = \frac{d(N/V)}{dL}$$

$$n_0(L) = \lim_{L\to 0}\frac{d(N/V)}{dL}$$

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No. of crystals with size L in

0

- No. of crystals with size L out

$F \Delta t \; n(L) \; \Delta L$

+ No. of crystals ~~with~~ grown to size L

$n(L) \; v \; \Delta L$

- No. of crystals grown to size $L + \Delta L$

$n(L+\Delta L) \; v \; \Delta L$

$= 0$

$$F \, n(L) \, \Delta L = n(L) \, v \frac{\Delta L}{\Delta t} - n(L+\Delta L) \, v \frac{\Delta L}{\Delta t}$$

$$F n(L) \Delta L = n(L) \, v \, G - n(L+\Delta L) \, v G$$

$$\lim_{\Delta L \to 0} \frac{n(L) - n(L+\Delta L)}{\Delta L} = \frac{F}{v \cdot G} n(L)$$

$$-\frac{d\,n(L)}{dL} = \frac{F}{v \cdot G} n(L)$$

$$\frac{dn(L)}{dL} = -\frac{F}{vG} n(L) = -\frac{n(L)}{G\tau}$$

$$\int_{n_0(L)}^{n(L)} \frac{dn(L)}{n(L)} = -\int_0^L \frac{1}{G\tau} dL$$

$$\ln\left(\frac{n(L)}{n_0(L)}\right) = -\frac{L}{G\tau}$$

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$$n(L) = n_0(L) \exp\left(-L/G\tau\right)$$

$$n_0(L) = \frac{B_0}{G}$$

$$n(L) = \frac{B_0}{G} \exp\left(-L/G\tau\right)$$

$$M_c = \int_0^{n(L)} n(L)\, \phi_v L^3 dL\, \rho_c$$

06/09/17

$n(L)$

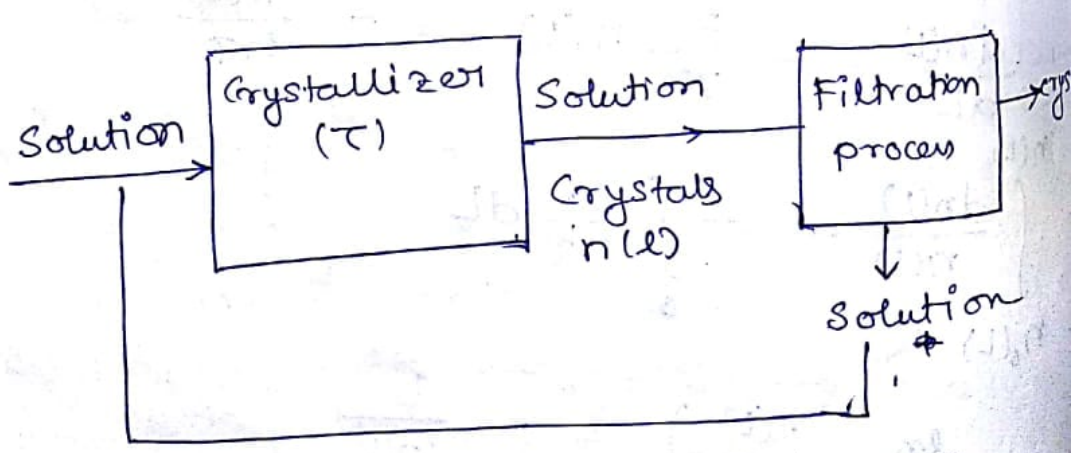
A_c/V, N/V, V_c/V, m_c/V

$B_0 = k_1 S^n$ $\quad G = k_2 S^m$ $\quad n_0(l)$

$$\left.\frac{dV}{dt}\right|_t = M_s \cdot L_s G_s$$

$$\left.\frac{dT}{dt}\right|_t = M_s L_s \cdot G_s$$

Crystallizer



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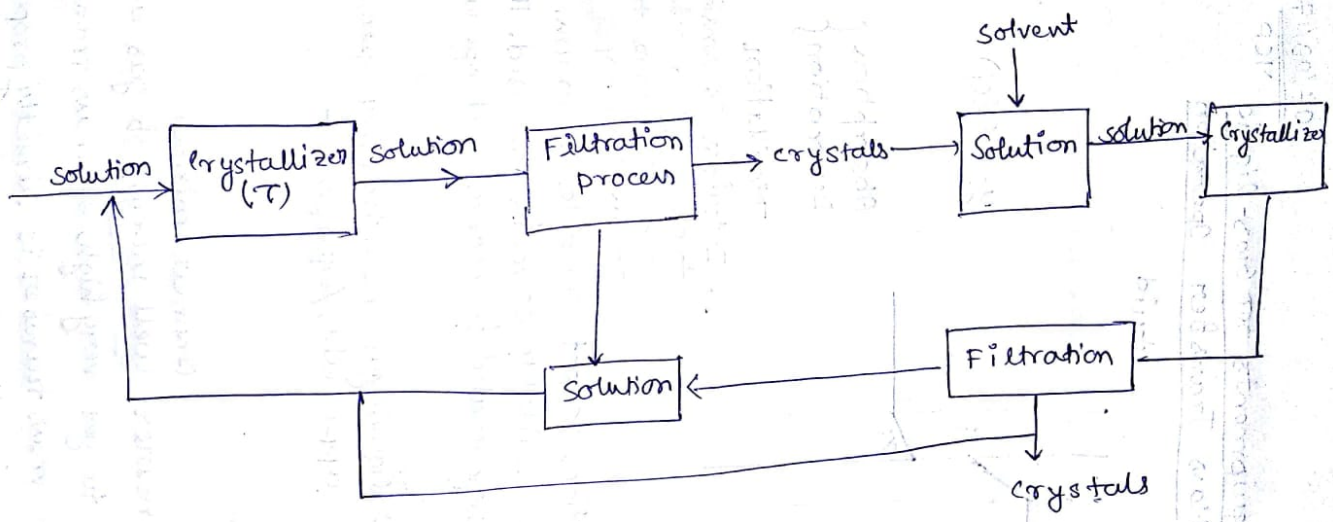

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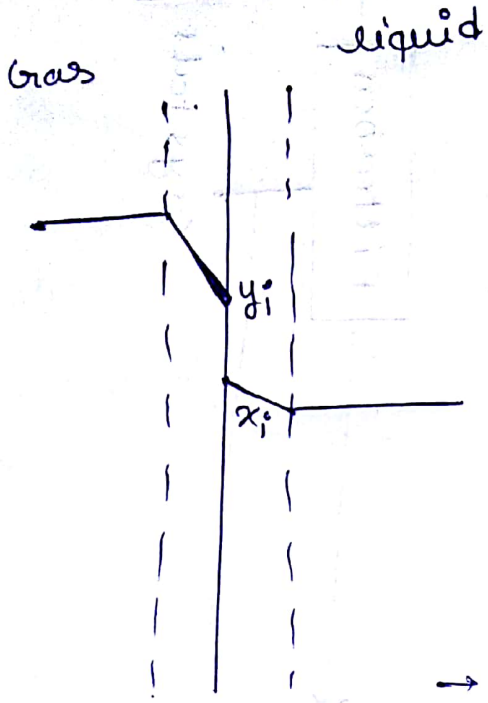
NCP

Equipments for Gas-liquid Mass Transfer Operation



$y_i = f(x_i)$

Absorption
Desorption
Distillation

→ Interface is considered to be very thin, offering no resistance to mass transfer

→ In extraction, to get suitable optimum mass transfer rate, suitable solvents are used. These solvents are regenerated for economical operation

→ Contactor ⇒ liquid-gas mass transfer operation apparatus/equipment

$$R = k_L a \Delta c$$

→ Contactor ensures well mixing (Intimate mixing) of gas and liquid phase to get very high of mass transfer area. Rate of mass transfer is directly proportional to interface area. Very high flow rate is maintained in interest to do this. Usually Counter flow is preferred over co-current flow

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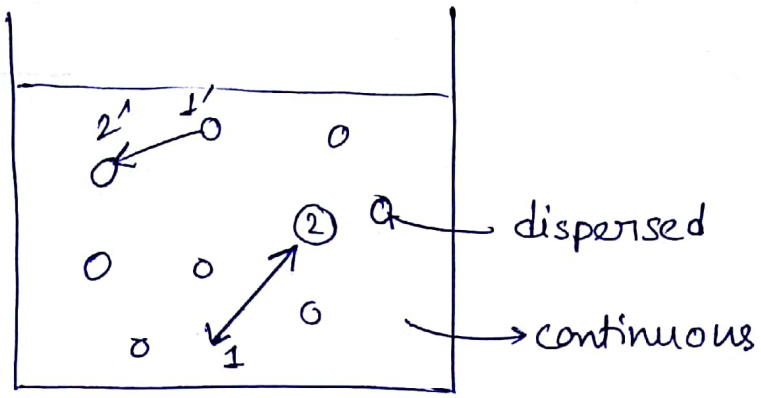
Mixing

- → Fine droplets of liquid in gas phase
- → Bubbling the gas through liquid

One phase is dispersed in other continuous phase.



Dispersed phase is that phase for which we need to cross boundary of two phases to travel from one place to another in that phase

Gas-liquid Contactors

- Gas dispersed
  - → Mechanically agitated Contractors (MAC)
  - → Sparged Vessels (Bubble column)
  - → * Tray towers
    - Sieve Tray
    - valve Tray
    - Bubble-cap tray
- Liquid dispersed
  - → Venturi Scrubber (Chemical Rkn with MT)
  - → Wetted-wall Towers
  - → Spray Towers
  - → Packed Towers
    - Randomly packed
    - Regularly packed

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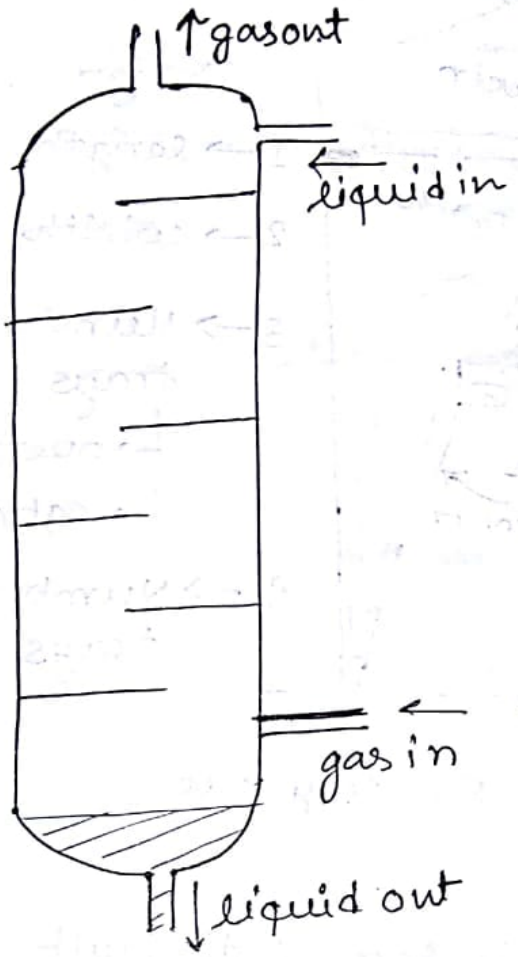
13/09/17

Tray Towers



Selection of Trays

	Bubble caps	Valves	Sieves
Relative cost	2.0	1.2	1.0
pressure drop	highest	intermediate	Lowest
Efficiency	highest	highest	lowest
Vapor capacity	Lowest	highest	highest
Typical turndown ratio	5	4	2

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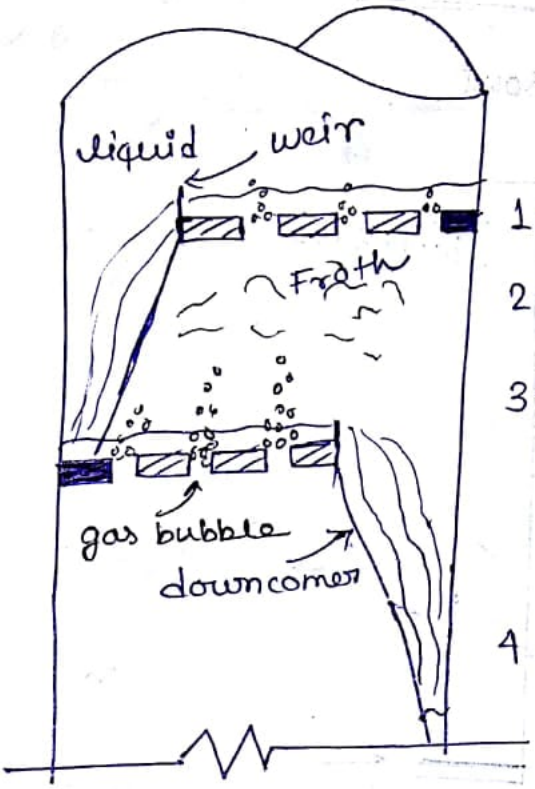
Turn down ratio → ~~least~~ Maximum to least feed ratio



Design

1 → length

2 → width

3 → Number of ideal trays
- → operating line
- → eqbm. relationship

4 → Number of real trays

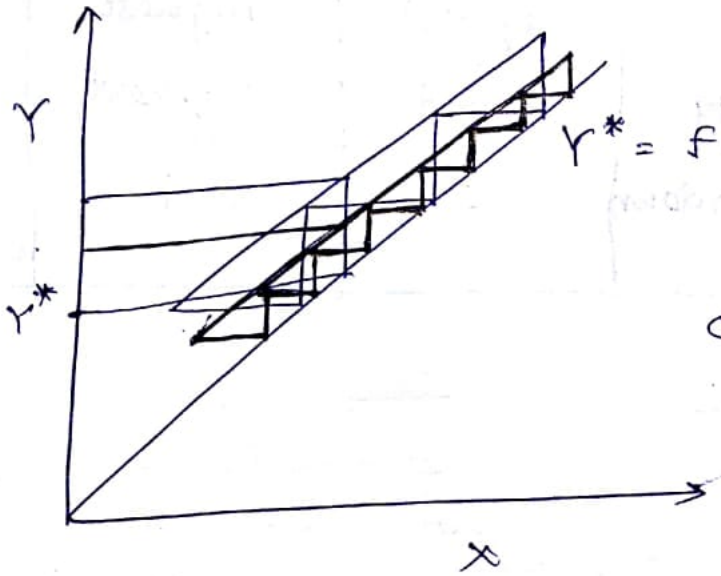
Gas-liquid Sive tray tower

Difficulty level

→ Driving force is less ⇒ difficult

→ Driving force is more ⇒ easier

Lesser driving force ⇒ Lesser separation between equilibrium line & operating line



Real trays can not deliver ~~at~~ eqbm at each stage

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) number of real trays

$$= \frac{\text{number of ideal trays}}{\text{fractional efficiency}}$$

5) Tray spacing 6″ – 36″

depends on diameter length, diameter
usually 24″ spacing is required

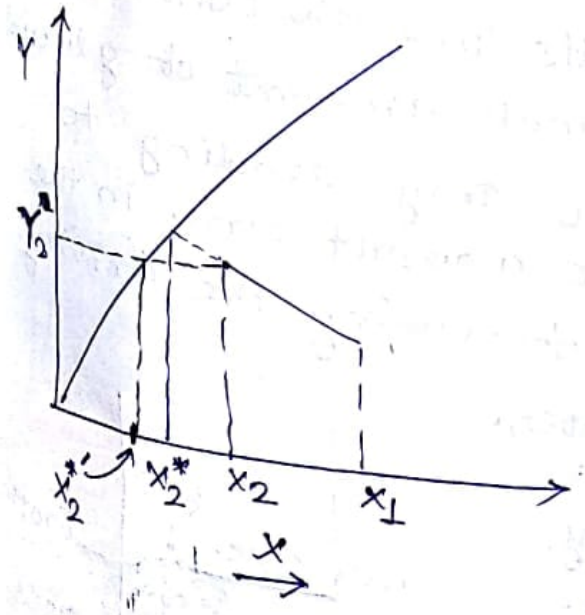
6) Length = {(number of total real trays − 1) × Spacing} + {15 to 20%}

→ Account for holdups

7) Diameter ⇒ depends on volume of feed to be processed

· Efficiency of such towers ~ 50 – 60%

· Efficiency:



$$E_L = \frac{x_1 - x_2}{x_1 - x_2^*}$$

$$E_{ML} = \frac{x_1 - x_2}{x_1 - x_2^{*\prime}}$$

Murphrus Efficiency

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Efficiency ↑ increased with

- → Mass Transfer rate higher
  - → ~~Good~~ Large contact time
  - → Higher surface area
  - → Higher mass transfer coefficient with higher turbulence

Large contact time

→ Higher depth of liquid pool in tray

Higher surface area

→ Smaller bubbles by high gas flow velocity

→ Higher velocity increases turbulence in the liquid pool

Operating Difficulty

- Heavy agitation results in froth formation. Bubbles take away small amount of liquid from lower to higher tray, leading to liquid entrailment. As a result conc. in the upper tray ↑ increases, decreasing the driving force for mass transfer.

- For high flow velocity, pressure drop is ~~low~~ high. Thus pressure at bottom is very high at low at top. Operational cost increases

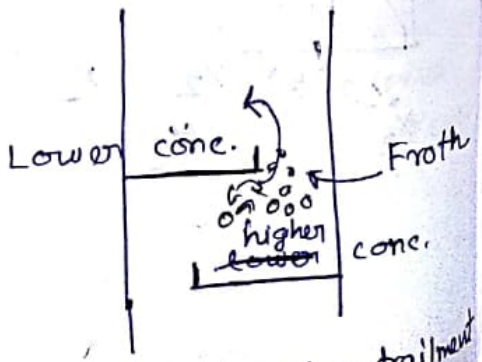

Fig: Liquid entrailment

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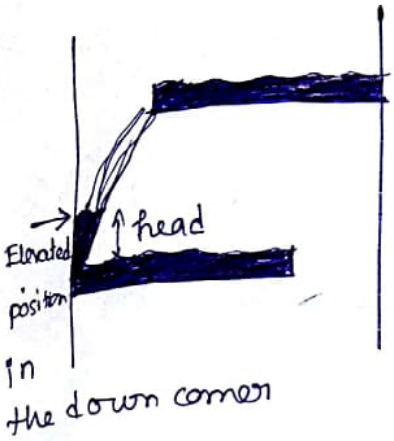
- Hydrostatic head is required for the liquid to flow ~~fi~~ lower to higher pressure zone in the down comer.

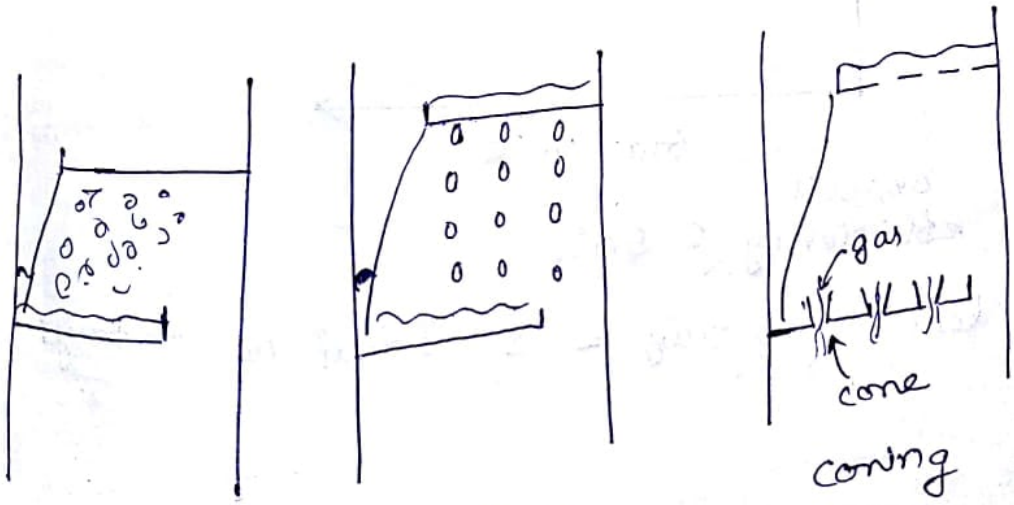


- A situation may arise when the required head ~~lea~~ reaches the upper tray leading to flooding of tower.

<u>Priming</u>: Excessive entrainment in forming liquid leads to high pressure drop

<u>Dumping</u>: Due to low flow velocity, liquid will start weeping. At further low velocity the liquid do not go to down comer and come down directly through holes

<u>Coning</u>: high velocity of gas, Low liquid flow rate



priming Dumping coning

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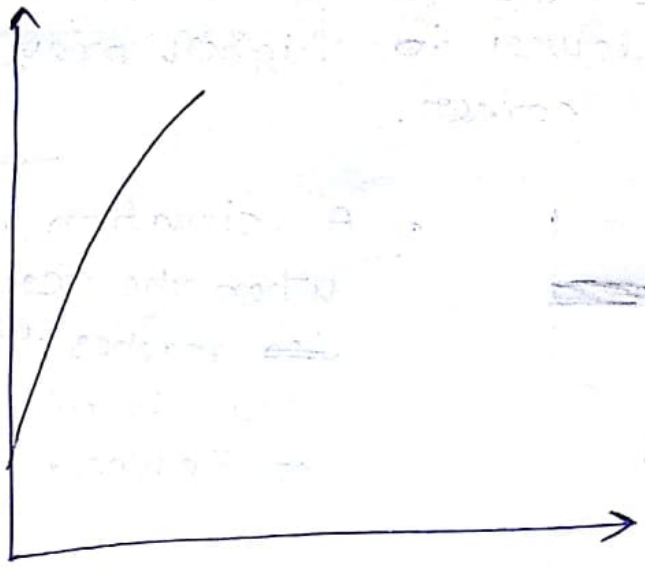

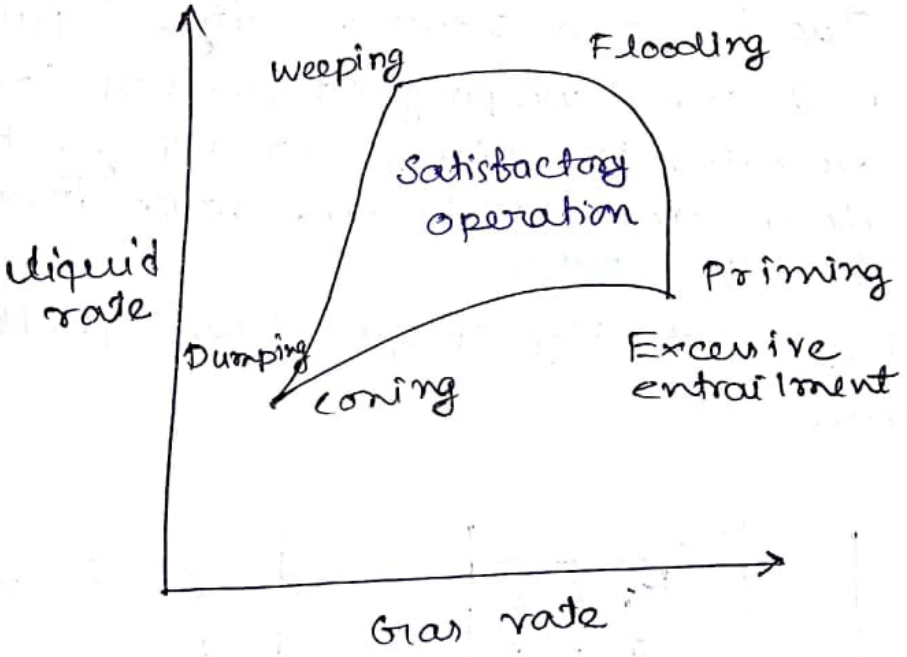

overall efficiency $\simeq 50\%$

Real no. of trays = 2× Ideal no. of trays

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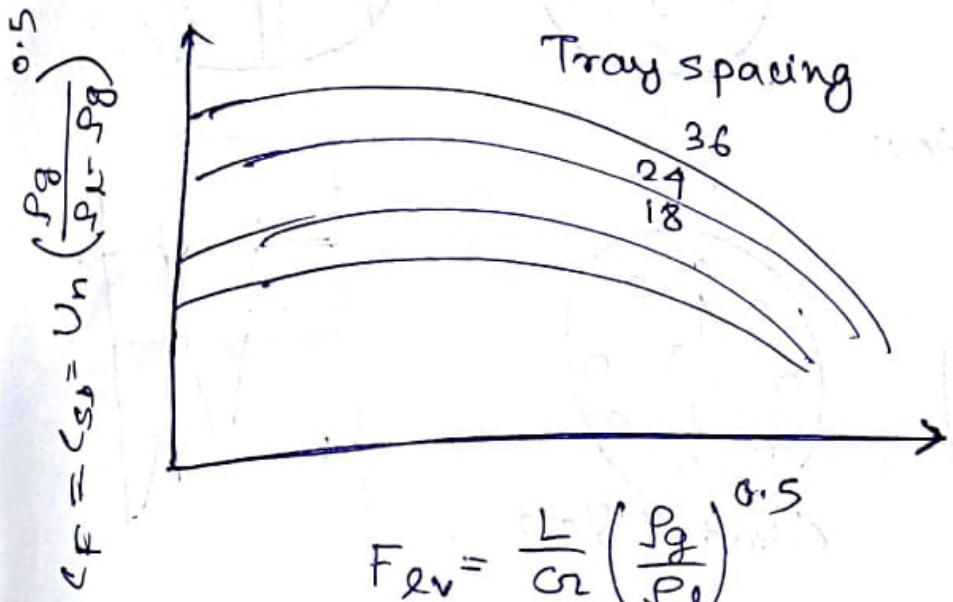
Correlation of flooding velocity in bubble-cap column and perforated column by Fair and matthews



Actualy velocity < flooding velocity

For nonforming liquid

Actual velocity ≃ 85% of flooding velocity

For forming liquid

Actual velocity ≲ 75% of flooding velocity

Gas flow rate ⇒ Area required

design area ≃ 1.2 calculated area

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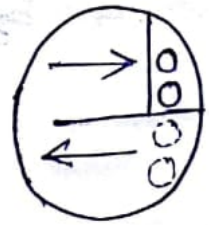
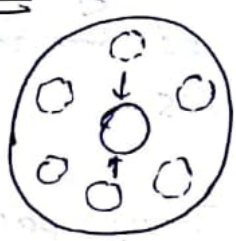
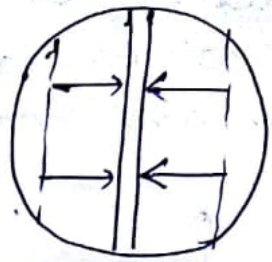
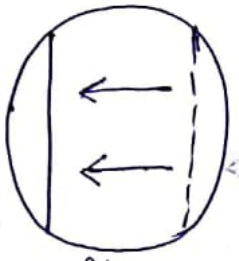
Tray Arrangements



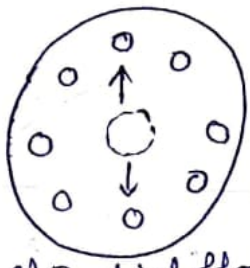
a) Reversible flow



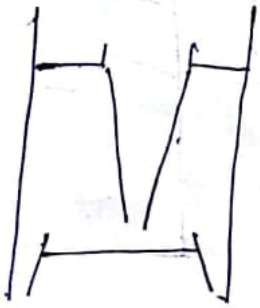


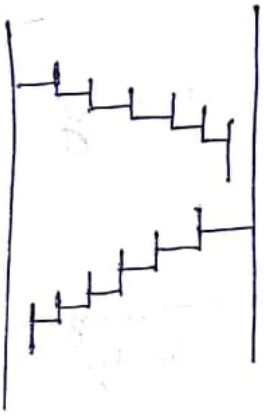


b) Cros flow



c) Radial flow





(e) Cascad trays

d) Split flow

Cascade trays are used to maintain almost equal liquid level. In a single tray, the height of liquid varies resulting in non uniform gas distribution.

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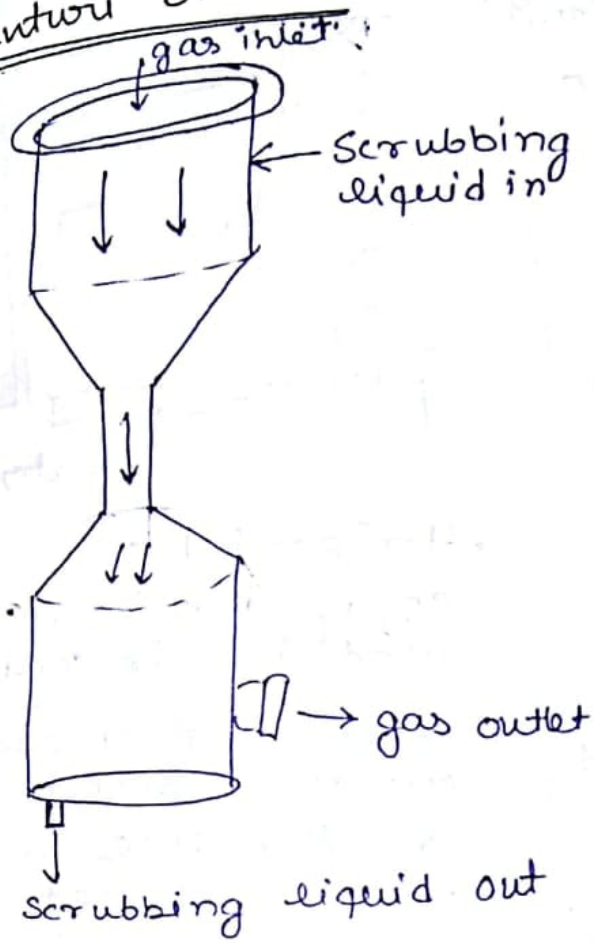
Liquid Dispersed type gas-liquid contractor

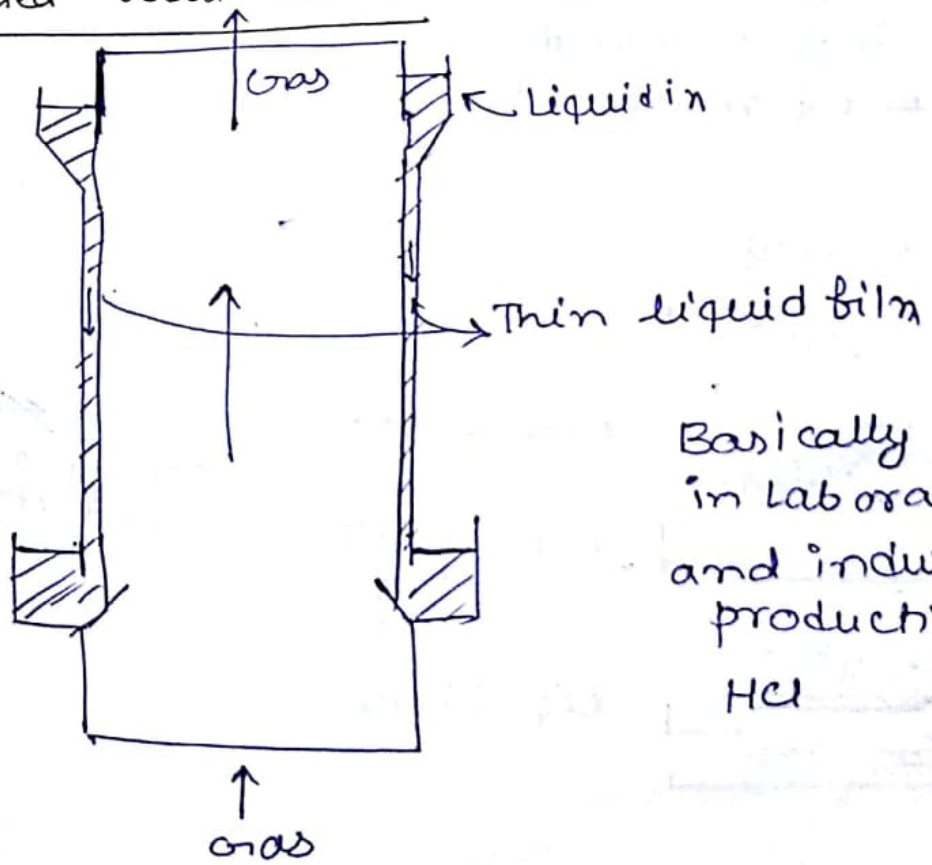
Venturi Scrubber



reaction + mass transfer

e.g SO_2 adsorption.

Wetted - wall column



Basically used in laboratory and industrial production of HCl

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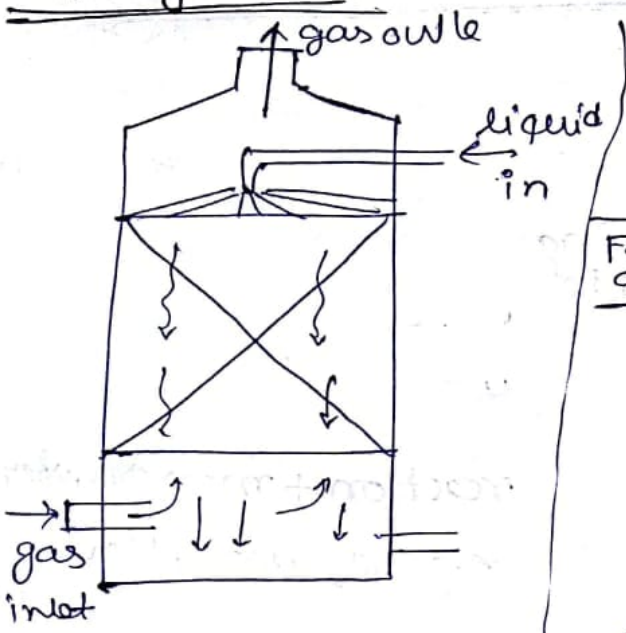
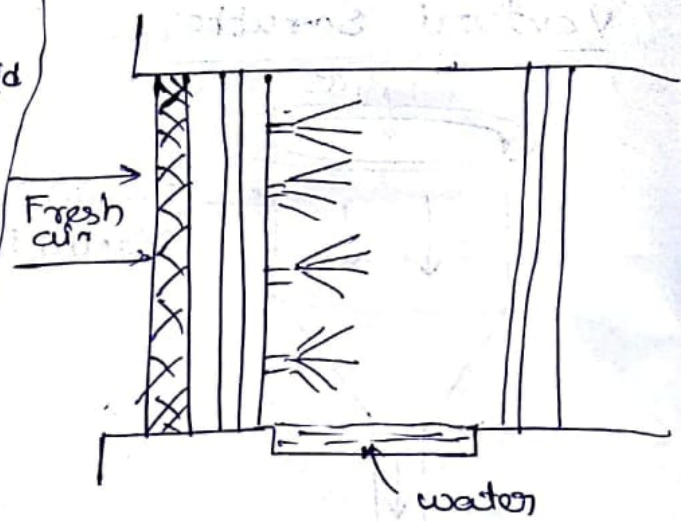
Spray Tower



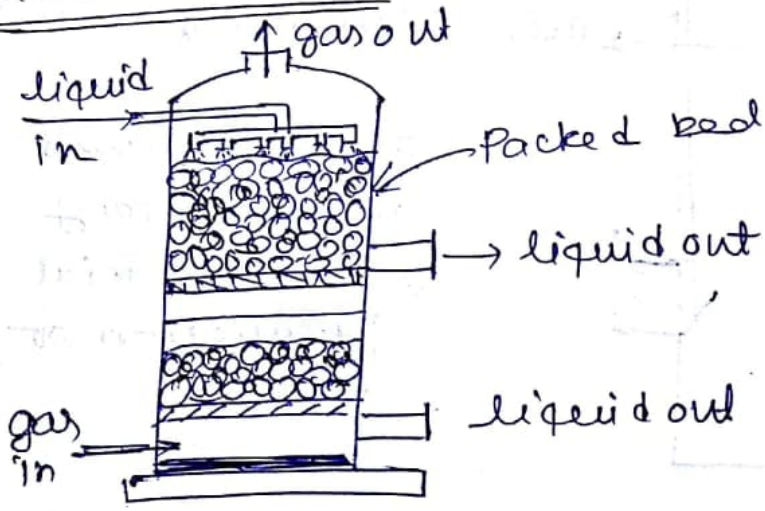
- For large diameter tower there is batch mixing, reducing counter-current benefit
- For very low diameter, the liquid drops will come very fast to wall and the flow downward in ~~dropwise~~ filmwise manner

Spray chamber



- Horizontal co-current spray chambers are used in air conditioning
- Co-current or counter-current effect makes no difference as pure liquid is used

Packed towers



continuous contactor

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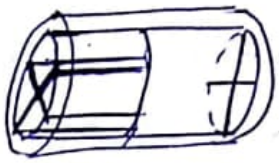
Packing Material

Rasching Ring

Lessing Ring

Cross partition ring 

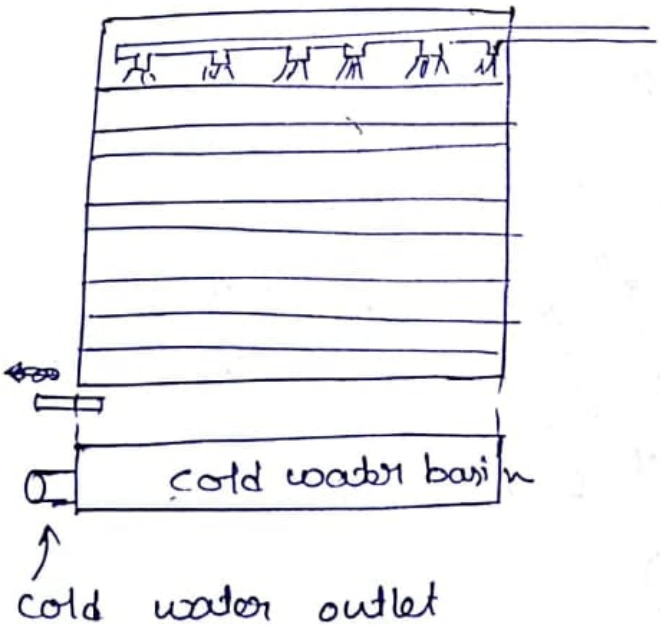
&

Pall ring

Saddles.

Tellerettes → Metal
→ Plastic

Cooling Towers



Regularly packed

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Tower packing characteristic

→ Provide large interfacial surface between liquid and gas. The surface of packing per unit volume (a_p) should be zero

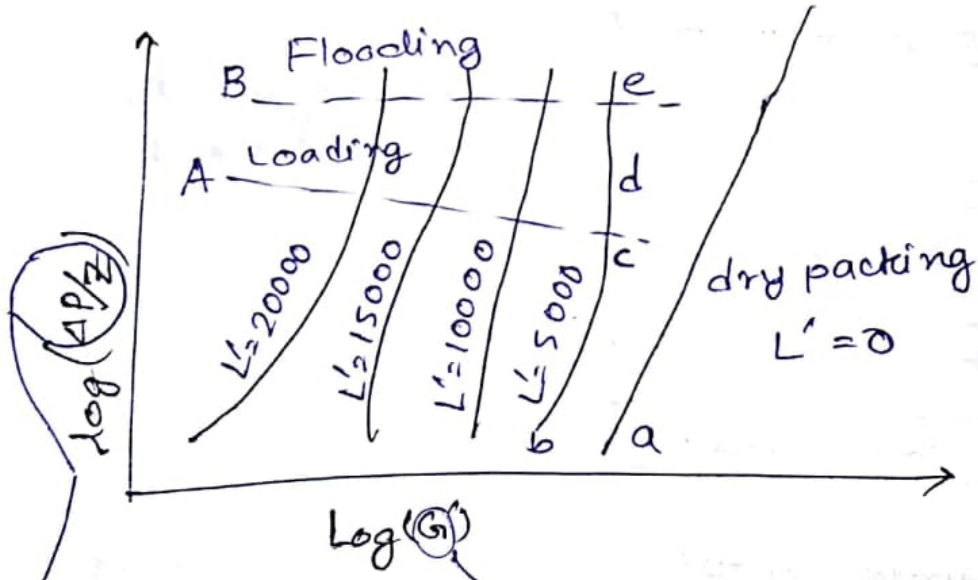
→ Void volume, or fraction should be large to allow flow of gas & liquid without ~~enough~~ high pressure drop

→ Chemically inert to the fluids to be processed

→ Having structural strength to permit easy handling and installation

→ Represent low cost

Loading and flooding in packed Towers



Gas pressure drop per unit height

Superficial gas mass velocity

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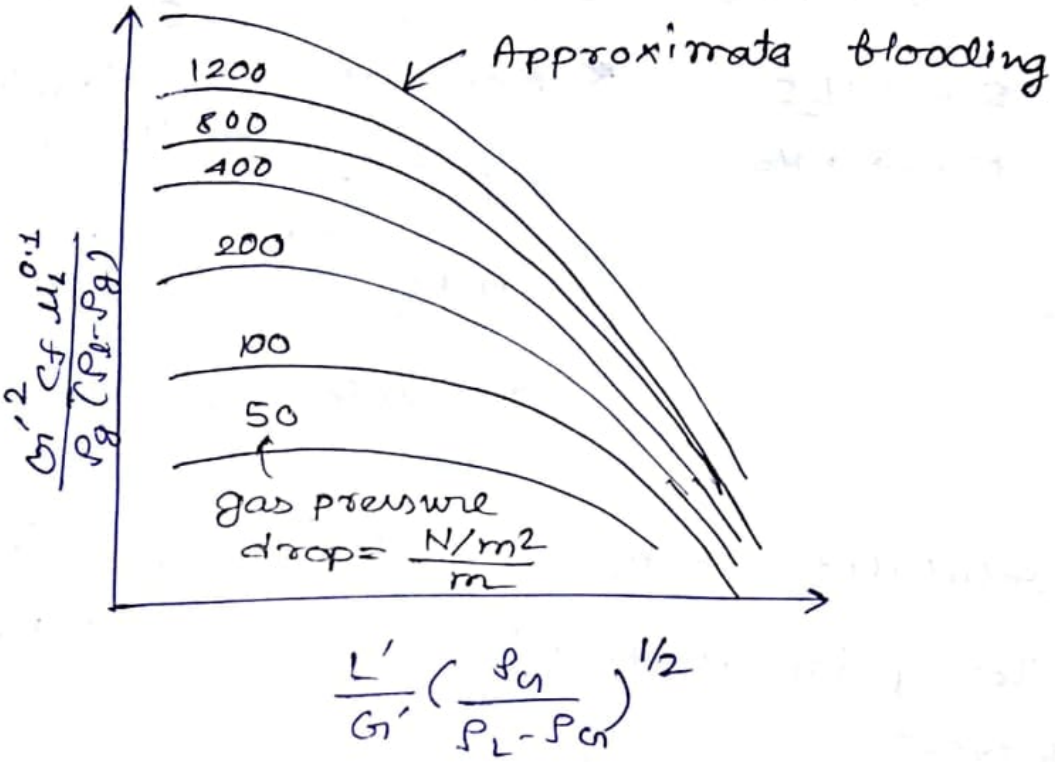
liquid hold up beyond ~~point~~ line A increases leading to higher pressure drop. When there is 100% flooding, gas becomes dispersed phase insted of liquid



Plot: ~~Dr~~ Pressure Drop and flooding in random-packed towers

Tray tower vs. Packed tower.

- ~~Small~~ Packed towers require smaller pressure drop
- Packed towers provide substantially smaller liquid hold up
- Low L/G best suited in tray towers
  higher L/G " " " packed "
- Tray towers ~~and~~ suitable ~~from~~ for cooling
- Tray towers suitable for side streams
- Foaming suitable ~~for~~ Packed
- Corrosion - packed tower
- Cleaning - tray towers

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04/10/17

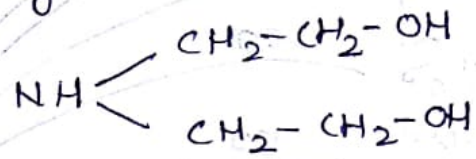
Gas Absorption & Desorption or stripping

* Hydrotreating is used to remove sulphur from crude diesel fraction by reacting with hydrogen

$S \longrightarrow H_2S$

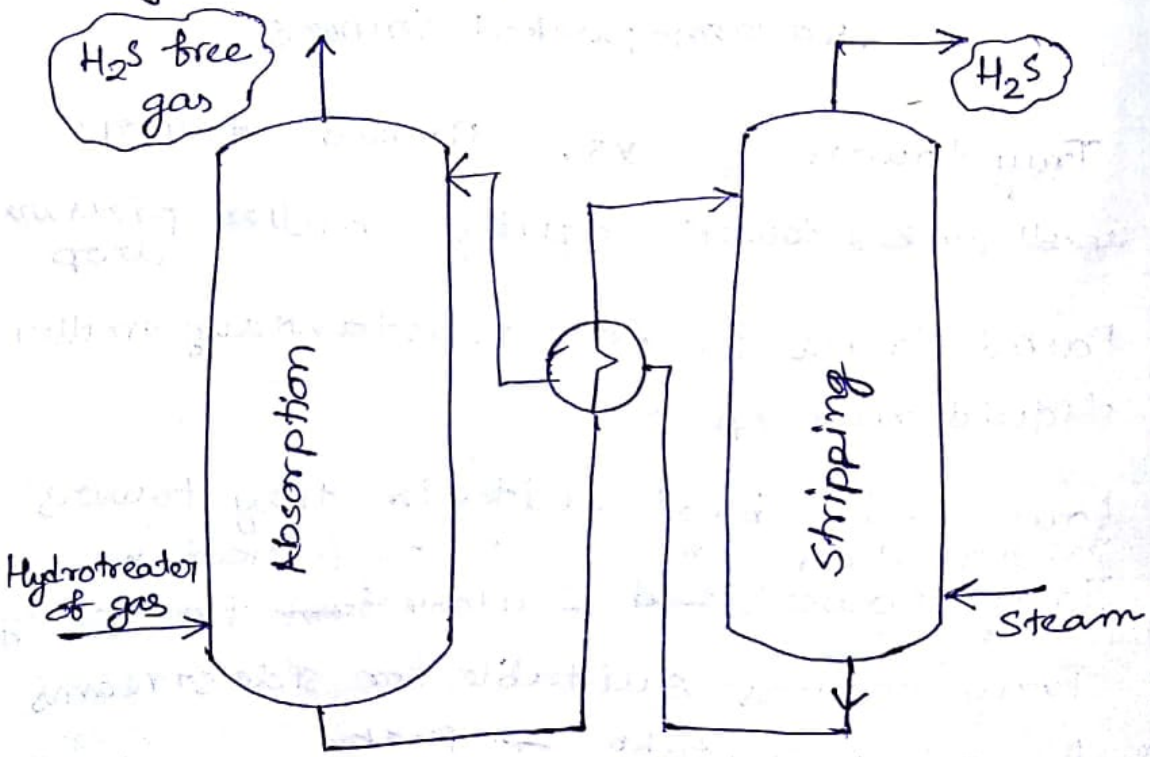
$N \longrightarrow NH_3$

* Aqueous alkanolamine solvents are used, e.g DEA



for selective removal of H_2S

* solubility of H_2S in DEA is very high
* Desorption is required to regenerate the ~~absorb~~ solvent
* They (Absorption as well as desorption) are performed side by side in two columns



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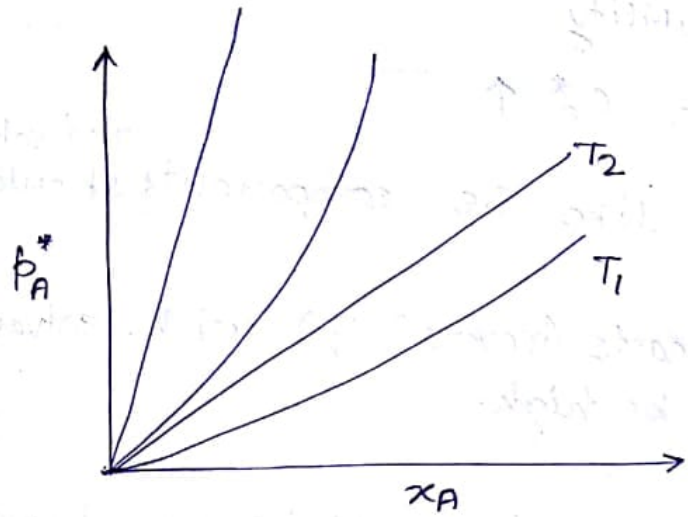
$$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$$

$$H_2S + NH(C_2H_4OH)_2 \rightleftharpoons [(C_2H_4OH)_2\overset{+}{N}H_2]_2 S^{-2}$$

* Further the phases are away from equilibrium higher will be the mass transfer rate.

*



$T_2 > T_1$

Equilibrium Relationship

* gas adsorption is accompanied with generation of heat. With increasing temperature, solubility decreases

* For ideal solⁿ and ideal gas system Raoult's law is used $p_A^* = P_A x_A$

* For dilute solution, Henry's Law is used

$$y_A^* = \frac{p_A}{P_t} = m_A x_A$$

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Properties of Absorbent solvent

1) **Solubility** of the component to be removed should be high.

$$\text{Rate} = k_L a \underbrace{(C_A^* - C_{A,b})}_{\text{Solubility}}$$

rate ↑ with C_A^* ↑

* like dissolves like i.e components and solvent should be of same kind

* If solute reacts (reversibly) with solvent, solubility will be high.

2) **Volatility** of solvent should be low to prevent solvent loss. The solvent should not be perfectly non-volatile as that will result in higher boiling point leading to low solubility,

Gas processing unit: Solvent should be of higher volatility, e.g Dehexanized naptha. In this case loss of solvent due to evaporation is high. There is a need of solvent recovery section in the section

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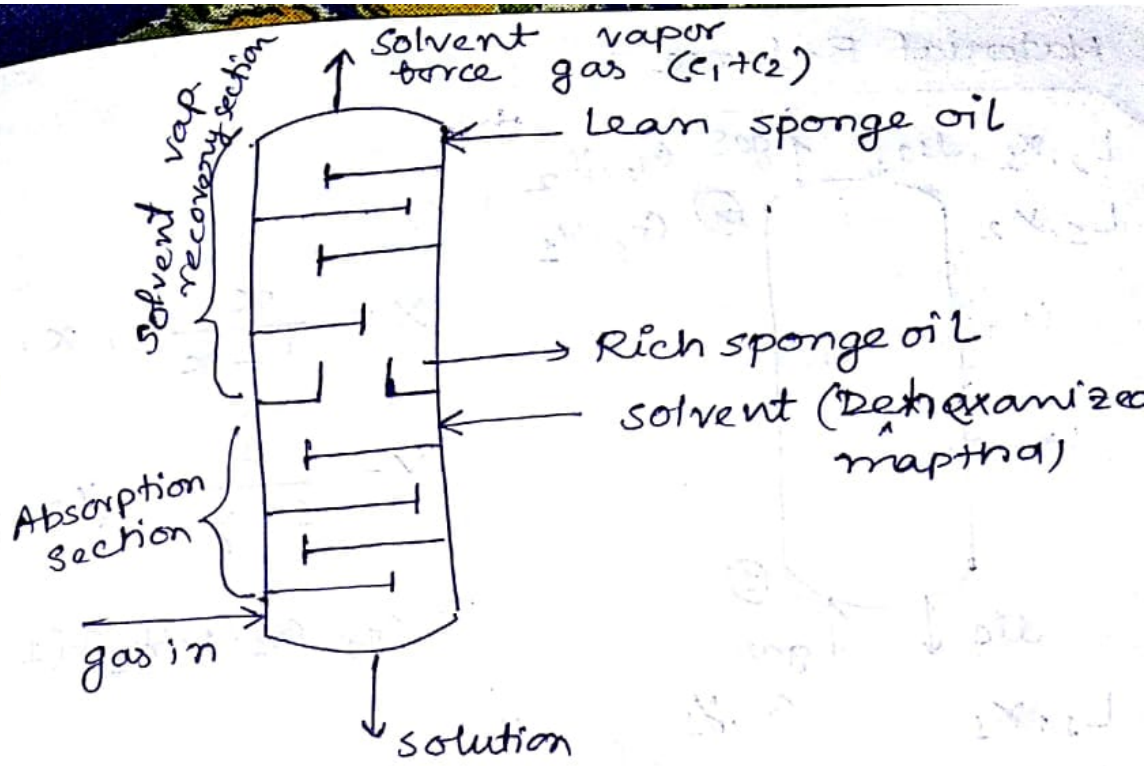

③ Corrosiveness
Solvent should not be corrosive

④ Viscosity of solvent should be low

⑤ Freezing point of the solvent should be low

⑥ Cost

⑦ Miscellaneous

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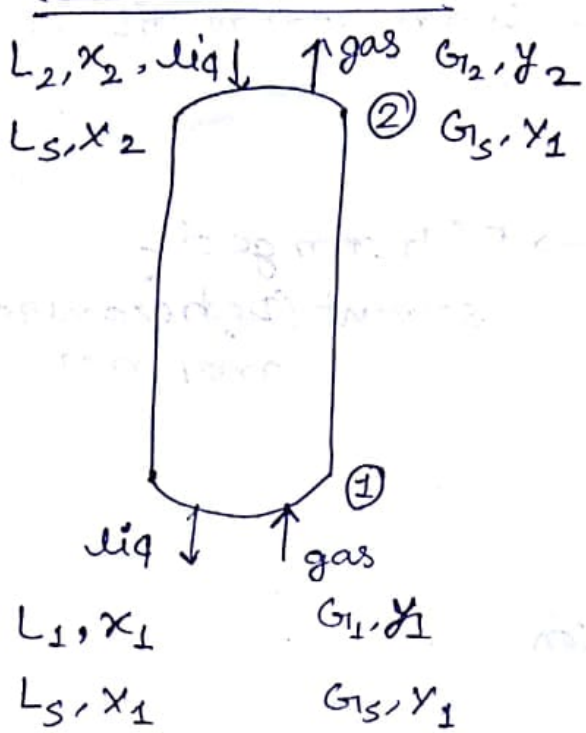
Material Balance



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

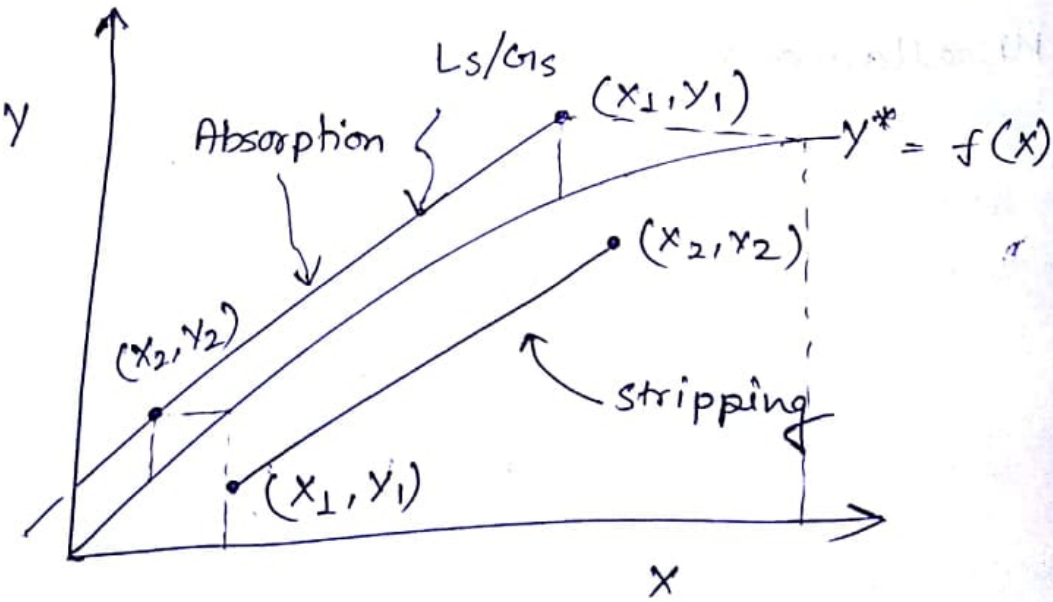
$$Y = \frac{y}{1-y} \; ; \; y = \frac{Y}{1+Y}$$

$$G_s = G_1(1-y_1) = (1-y_2)G_2$$

$$G_s Y_1 + L_s X_2 = G_s Y_2 + L_s X_1$$

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

$$Y_1 - Y_2 = \frac{L_s}{G_s}(X_1 - X_2)$$



$$(Y_1 - Y) = \frac{L_s}{G_s}(X_1 - X)$$

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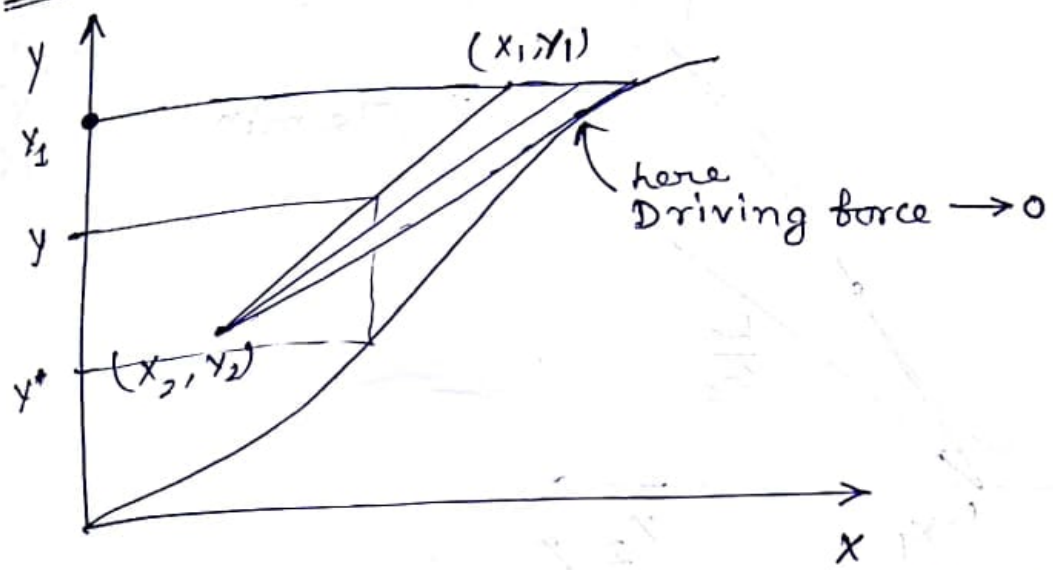
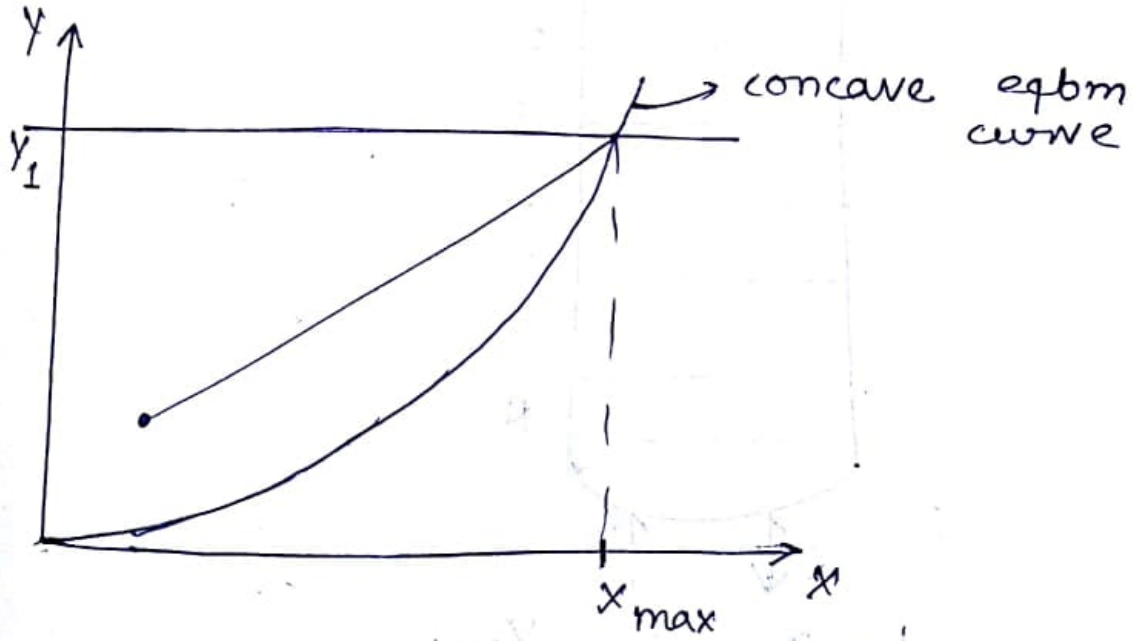
05/10/17

Absorption



* The liquid rate at which the operating line touches the equilibrium curve, is called minimum liquid rate

* $\boxed{L_{s,min} \times (1.2 \text{ to } 2) = L_s}$ ✓ Actual liquid rate



$$G_s(Y_1 - Y_2) = L_s(X_{max} - X_2)$$

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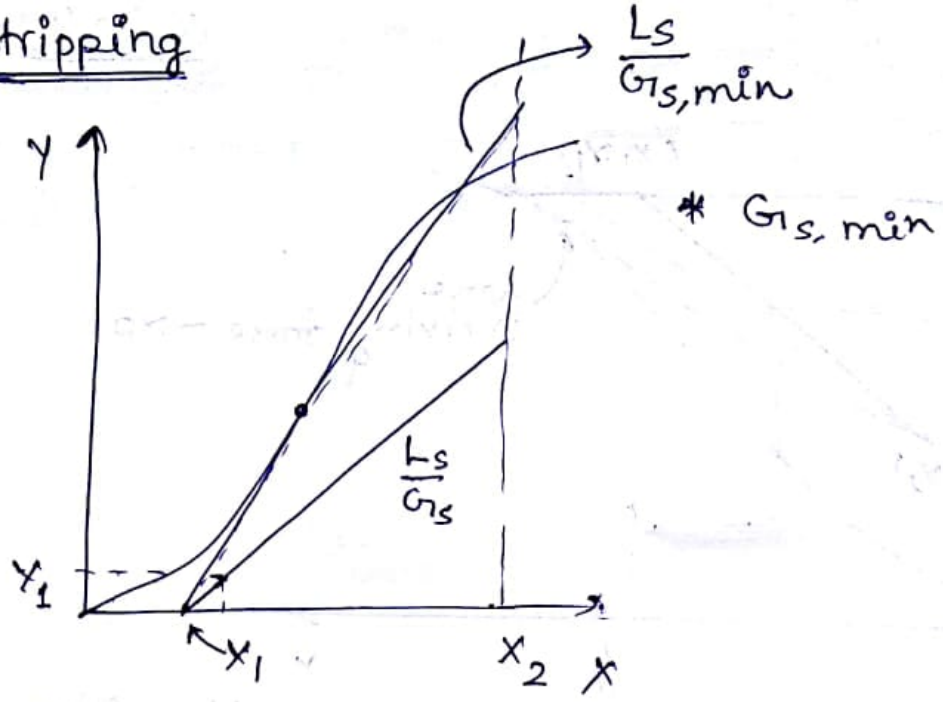
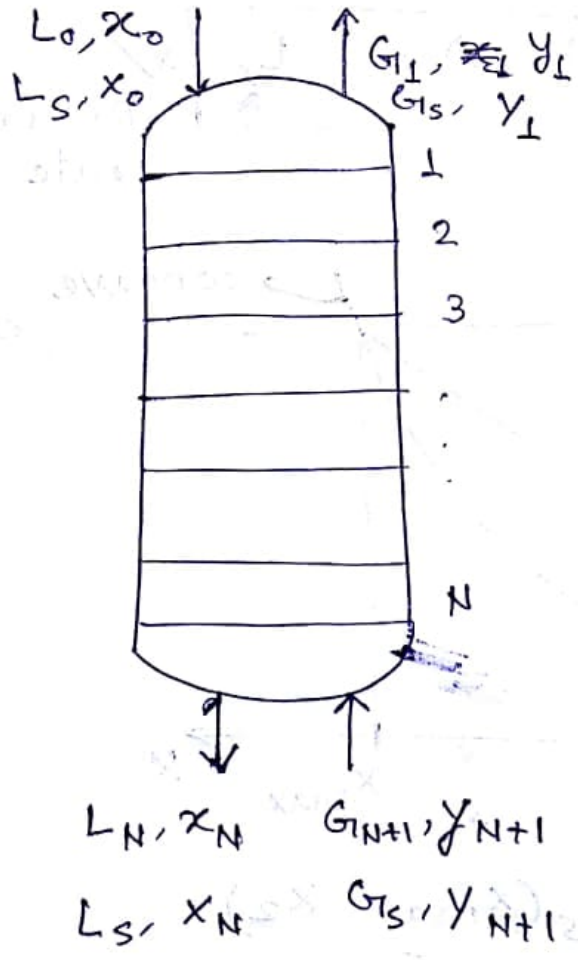
Stripping



* co-current process is preferred in case of pure gas and reversible reaction or fast reaction



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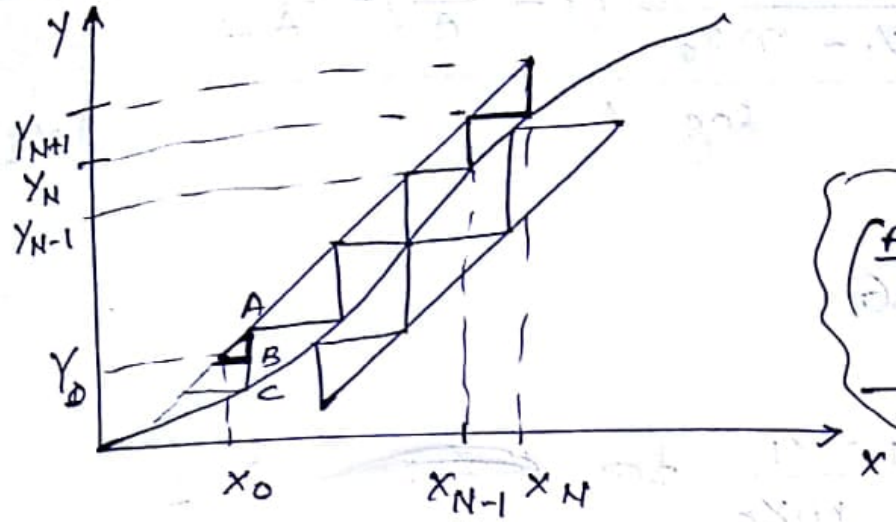


$$\left(\frac{AB}{AC} + \text{no of stages with full operation}\right) \div \text{efficiency}$$

$\Downarrow$

Roundup to next whole no.

For dilute system

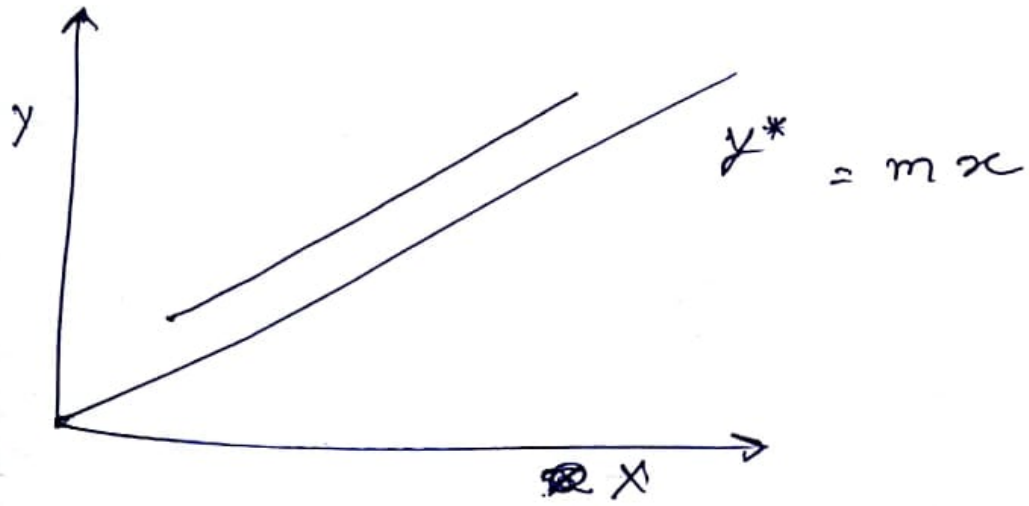
$$Y = \frac{y}{1-y} \simeq y$$

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

$$L_1 \simeq L_2 = L$$

$$G_1 \simeq G_2 = G$$

Use Kremsor's eq^n



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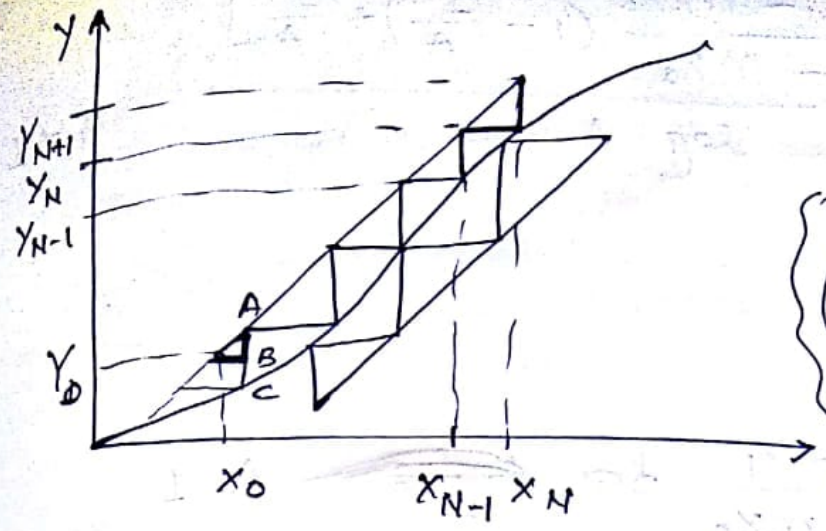


$$\left(\frac{AB}{AC} + \text{no of stages with full operation}\right) \Big/ \text{efficiency}$$

$\Downarrow$

Roundup to next whole no.

For dilute system

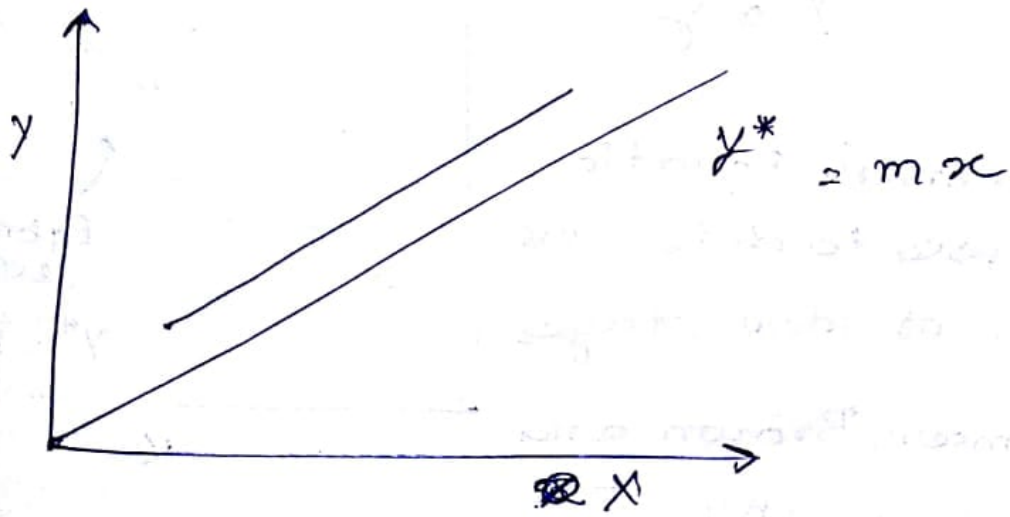
$$Y = \frac{y}{1-y} \simeq y$$

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

$$L_1 \simeq L_2 = L$$

$$G_1 \simeq G_2 = G$$

Use Kremsor's eq^n



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$$N = \frac{\log\left[\frac{y_{n+1} - m x_0}{y_1 - m x_0}\left(1 - \frac{1}{A}\right) + \frac{1}{A}\right]}{\log A} \qquad A \neq 1$$

$$A = \frac{L}{mG}$$

$$N = \frac{y_{n+1} - y_1}{y_1 - m x_0} \quad \text{for } A = 1$$

09/10/17

Design of Tray Tower for Dilute Gas

→ Operating line is straight line (both y vs. x and Y vs. X)

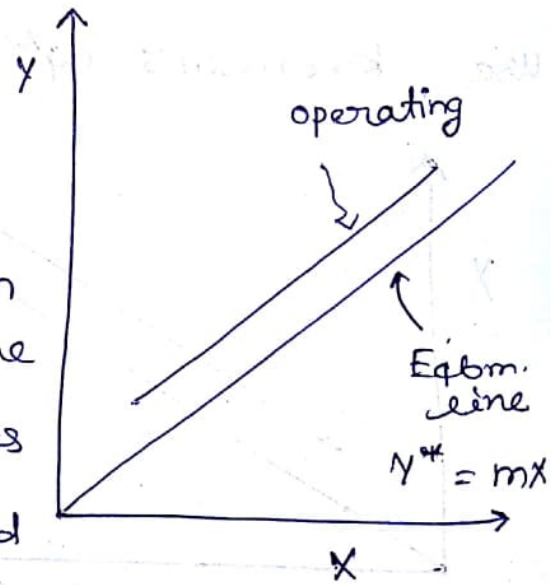
→ For concentrated gas operating line is not st. line

→ Dilute gas will follow Henry's Law

$$y^* = mx$$

where $X \simeq x$

$Y \simeq y$



→ Kremser's Equation is used to determine no. of ideal stages

[Kremser, Brown and Sonder's Eq^n]

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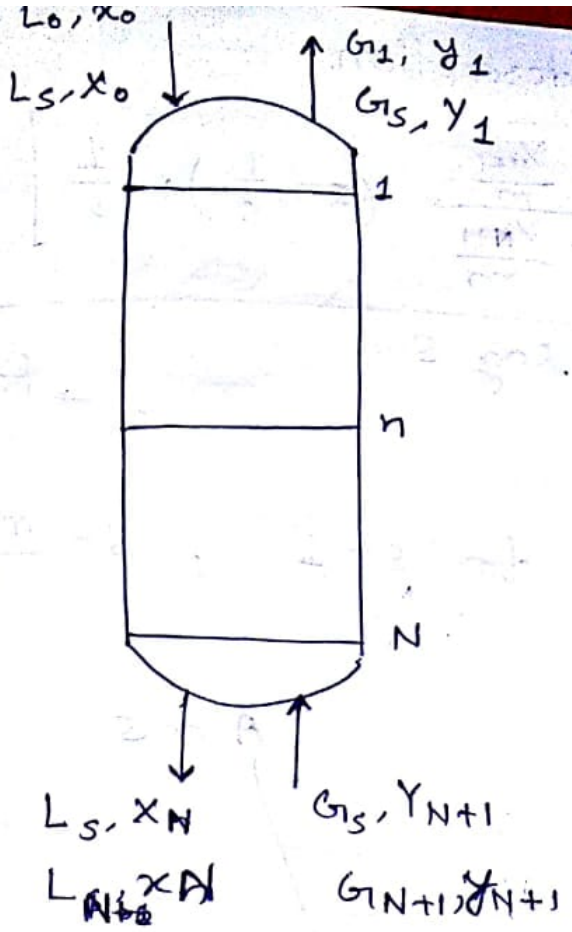

For absorption:

$$N = \frac{\log\left[\frac{Y_{N+1} - m x_0}{Y_1 - m x_0}\left(1 - \frac{1}{A}\right) + \frac{1}{A}\right]}{\log A}$$

for $A \neq 1$

$$A = \frac{L}{mG}$$

For $A = 1$

$$N = \frac{Y_{N+1} - Y_1}{Y_1 - m x_0}$$ for $A = 1$

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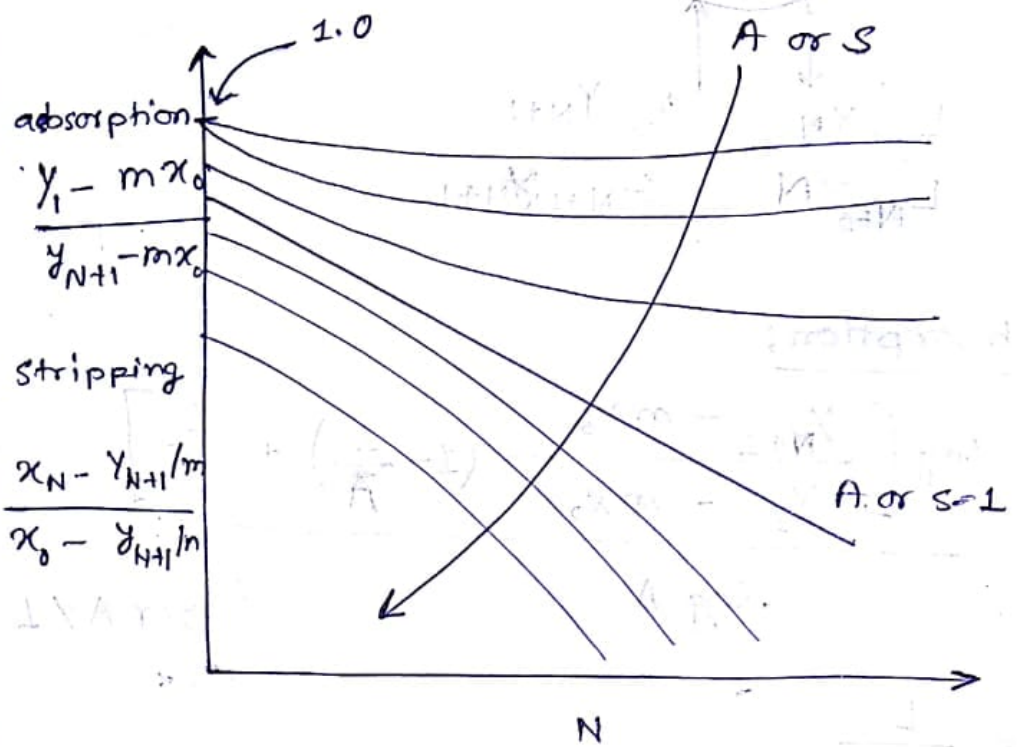
For stripping / desorption

$$N = \frac{\log\left[\dfrac{x_0 - \frac{y_{N+1}}{m}}{x_N - \frac{y_{N+1}}{m}}\left(1 - \frac{1}{S}\right) + \frac{1}{S}\right]}{\log S}$$

for $S \neq 1$

$$N = \frac{x_0 - x_N}{x_N - \frac{y_{N+1}}{m}} \quad \text{for } S = 1 \quad , \quad S = \frac{mG}{L}$$



→ For A or S < 1, the upper part of operating line can be approximated as the eqbm. curve.

→ For increased value of A, solution will be dilute i.e L will be high. So, regeneratio of solvent from dilute sol^n is harder and economically not feasible.

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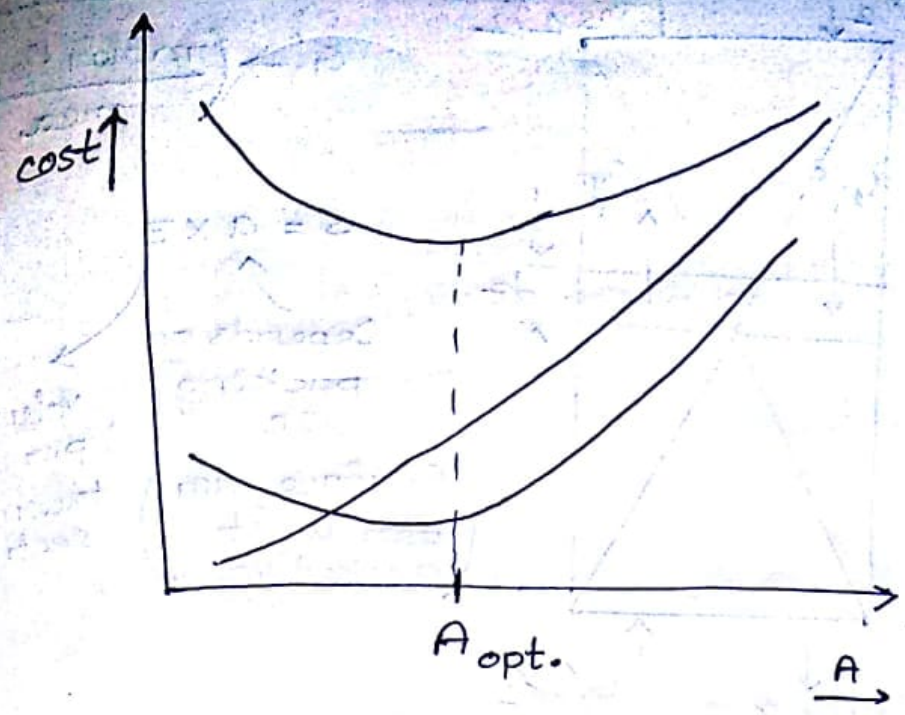

→ In general, $A_{opt} \in (1.25, 2.0)$

11/10/17

Design of continuous contact Equipment

(Packed Tower)

→ In reality, there is change in concentration in trays, discontinuously

→ In continuous cotactor, there is continuous change in concentration of both gas and liquid.

→ HETP (Height equivalent theoretical plates) method is used to ~~constr~~ design a packed bed contactor

→ HETP does not consider the difference between operations of stage wise and continuous contact equipment.

→ Transfer Unit ~~is~~ was introduced by Coulburn in 1939

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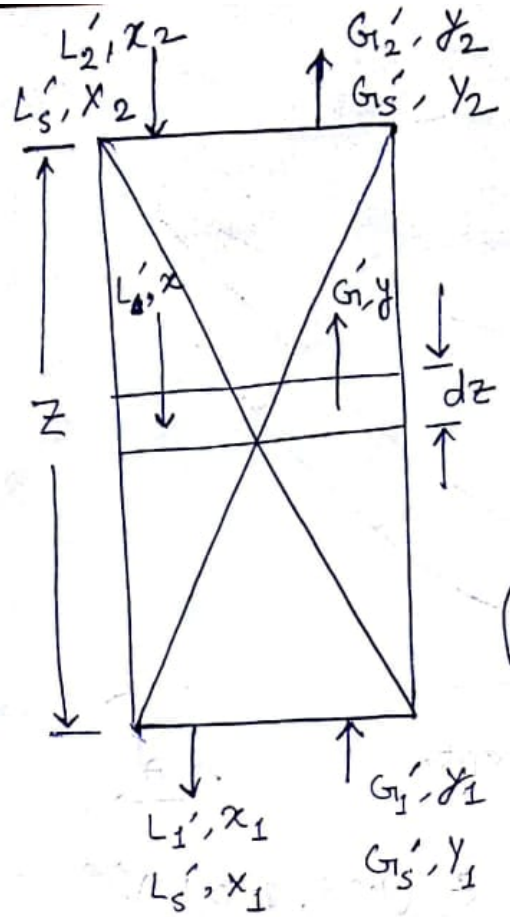
TRANSFER UNIT



$G' \rightarrow \left(\frac{\text{molar flowrate}}{\text{area}}\right)$

$S = a \times Z$

Depends on packing size (Surface area per unit packed volume)

volume per unit tower cross section

$ds = a\,dz$

$-d(G'y) = N_A ds = N_A a\,dz$

or, $-G'dy - y\,dG' = N_A a\,dz$

or, $-G'dy - y N_A a\,dz = N_A a\,dz$

or, $-G'dy = (1-y) N_A a\,dz$

or, $\frac{-G'dy}{1-y} = N_A a\,dz$

$-dG' = N_A a\,dz$

$\cancel{-d(G'y) = d\left(\frac{G_s'y}{1}\right)}$

$-d(G'y)$

$= -d\left(\frac{G_s'y}{1-y}\right)$

$= -G_s' \, d\left(\frac{y}{1-y}\right)$

$= -\frac{G_s' \, dy}{(1-y)^2}$

$= -\frac{G_s'}{(1-y)} \frac{dy}{1-y}$

$= -G' \frac{dy}{1-y}$

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$$-\frac{G' dy}{(1-y)} = k_y a (y - y_i) dz$$

$$\Rightarrow \int_0^z dz = -\int_{y_1}^{y_2} \frac{G' dy}{k_y a (1-y)(y-y_i)}$$

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

$\frac{G'}{k_y a y_{BM}}$ → almost constant throughout the tower

$$y_{BM} = \frac{(1-y_i) - (1-y)}{\ln\left(\frac{1-y_i}{1-y}\right)}$$

$$z = \underbrace{\frac{G'}{k_y a y_{BM}}}_{H_{tg}} \underbrace{\int_{y_2}^{y_1} \frac{y_{BM}\, dy}{(1-y)(y-y_i)}}_{N_{tg}} = H_{tg} \times N_{tg}$$

$$= \frac{G'}{k_y a y_{BM}} \int_{y_2}^{y_1} \frac{\cancel{(y-y_i)}}{\left[\ln\left(\frac{1-y_i}{1-y}\right)\right]\left[(1-y)\cancel{(y-y_i)}\right]} dy$$

$$= \frac{G'}{k_y a y_{BM}} \int_{y_2}^{y_1} \frac{dy}{(1-y)\ln\left(\frac{1-y_i}{1-y}\right)}$$

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Usually, $G' = \frac{(G_1' + G_2')}{2}$

$$y_{BM} = \frac{(y_{BM_1} + y_{BM_2})}{2}$$

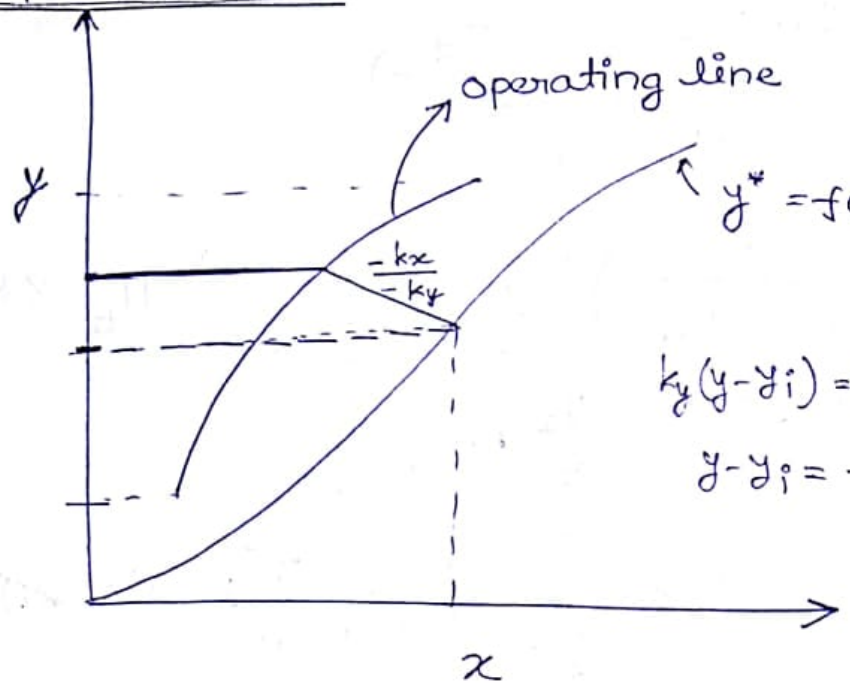
$H_{tg} \rightarrow$ Height of gas phase transfer unit

$N_{tg} \rightarrow$ Number of gas phase transfer unit

$H_{tg} \rightarrow$ Relative ease of mass transfer operation

$N_{tg} \rightarrow$ Difficulty involved in achievement of desired degree of seperation

Graphical Method



$$k_y(y - y_i) = k_x(x_i - x)$$

$$y - y_i = -\frac{k_x}{k_y}(x - x_i)$$

$$\rightarrow Z = \underbrace{H_{tog} \times N_{tog}}_{\text{Based on overall transfer coefficient}}$$

$$= \frac{G'}{K_y a\, y_{BM}^*} \int_{y_2}^{y_1} \frac{y_{BM}^*\, dy}{(1-y)(y-y^*)}$$

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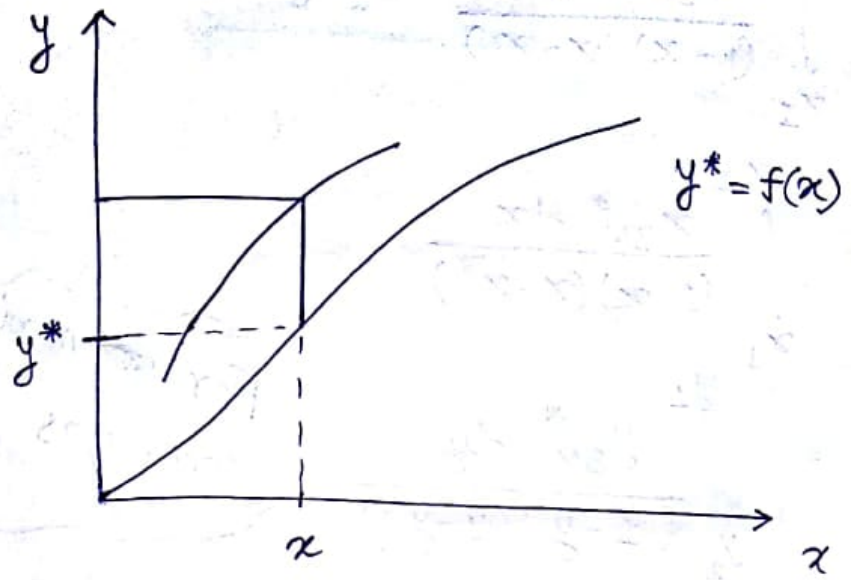
$$y_{BM}^{*} = \frac{(1-y^{*}) - (1-y)}{\ln \frac{(1-y^{*})}{(1-y)}}$$



$$Z = H_{tL} \times N_{tL} = H_{toL} \times N_{toL}$$

$$H_{tL} = \frac{L'}{k_x a\, x_{BM}} \qquad N_{tL} = \int_{x_2}^{x_1} \frac{x_{BM}\, dx}{(1-x)(x_i - x)}$$

$$H_{toL} = \frac{L'}{k_x a\, x_{BM}^{*}} \qquad N_{toL} = \int_{x_2}^{x_1} \frac{x_{BM}\, dx}{(1-x)(x^{*}-x)}$$

Stripper

$$N_{tg} = \int_{y_2}^{y_1} \frac{y_{BM}\, dy}{(1-y)(y-y_i)} \qquad y_{BM} \simeq 1 \qquad 1-y \simeq 1$$

$$\simeq \int_{y_2}^{y_1} \frac{dy}{y-y_i} = \frac{y_1 - y_2}{(y-y_i)_{av}}$$

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$N_{tg} = 1, \quad y_1 - y_2 = (y - y_i)_{av}$

Stripper

$$N_{tL} = \int_{x_1}^{x_2} \frac{x_{BM}\, dx}{(1-x)(x-x_i)}$$

$$N_{toL} = \int_{x_1}^{x_2} \frac{x_{BM}^{*}\, dx}{(1-x)(x-x^{*})}$$

$$N_{tog} = \int_{y_2}^{y_1} \frac{y_{BM}^{*}\, dy}{(1-y)(y-y^{*})}$$

For moderately conc. gas

$$y_{BM}^{*} = \frac{(1-y) + (1-y^{*})}{2}$$

$$y_{BM}^{*} = \frac{2(1-y) + (y-y^{*})}{2}$$

$$N_{tog} = \int_{y_2}^{y_1} \frac{dy}{y-y^{*}} + \frac{1}{2}\int_{y_2}^{y_1} \frac{dy}{1-y}$$

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

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For dilute Gas (system)

$$N_{tG} = \int_{y_2}^{y_1} \frac{dy}{y - y_i}$$

$$N_{toG} = \int_{y_2}^{y_1} \frac{dy}{y - y^*}$$

→ In this range of y_1 to y_2 eqbm. line may be considered as straight line given by

$$y^* = mx + r$$

$$y = \frac{L}{G}(x - x_2) + y_2$$

$$y - y^* = \left(\frac{L}{G} - m\right)x + \left(y_2 - \frac{L}{G}x_2 - r\right)$$

$$= qx + s$$

$$N_{toG} = \int_{y_2}^{y_1} \frac{dy}{qx + s} = \frac{L}{G}\int_{y_2}^{y_1} \frac{dx}{qx + s}$$

$$= \frac{L}{Gq} \ln\left(\frac{qx_1 + s}{qx_2 + s}\right)$$

$$= \frac{L}{Gq} \ln\left(\frac{y_1 - y_1^*}{y_2 - y_2^*}\right)$$

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$$\frac{L}{Gq} = \frac{y_1 - y_2}{x_1 - x_2} \cdot \frac{1}{\left(\frac{y_1 - y_2}{x_1 - x_2} - m\right)} \qquad q = \frac{L}{G} - m$$

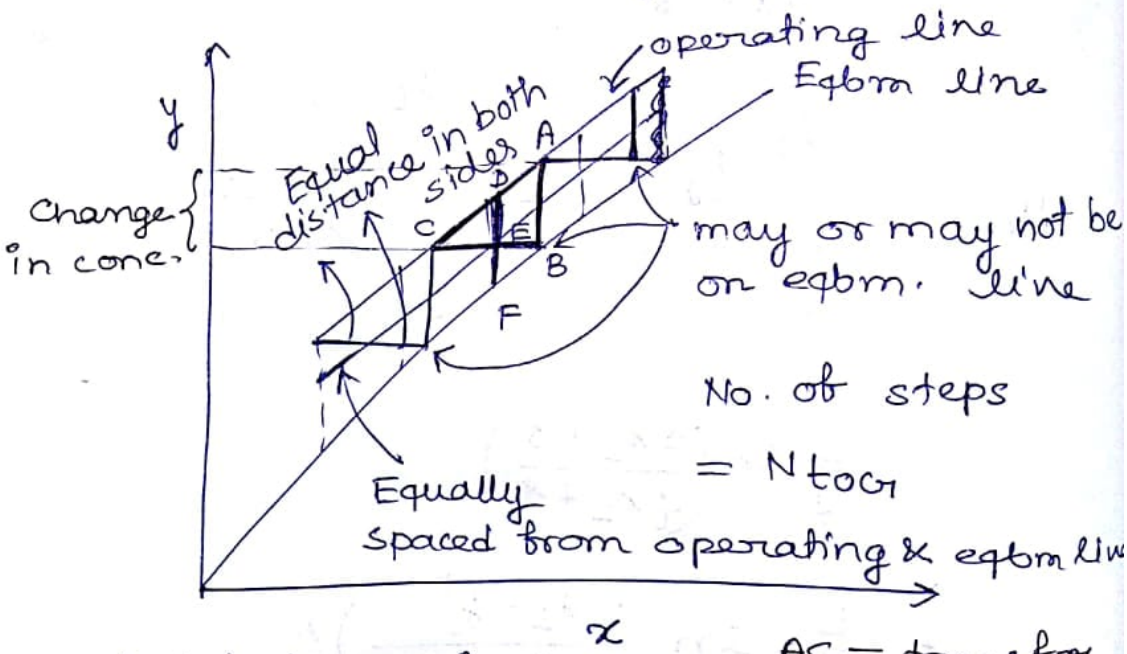
$$= \frac{y_1 - y_2}{(x_1 - x_2)\left(y_1 - y_2 - m(x_1 - x_2)\right)} = \frac{y_1 - y_2}{(y_1 - mx_1 - n) - (y_2 - mx_2 - n)}$$

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

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

12/10/17

$$N_{toG} = \frac{\text{total change in conc.}}{\text{average driving force}}$$



AB ≡ total change in concentration

AC ≡ transfer unit

DF ≡ overall driving force

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$$\frac{AB}{BC} = \frac{DE}{CE}$$

$$AB = \frac{BC}{CE} \cdot DE = 2DE$$

$$AB = 2DE = DF$$

Dilute System - Henry's Law

Eqbm. line: $y^* = mx$

$$y = \frac{L}{G}(x - x_2) + y_2 \quad : \text{operating line}$$

$$= \frac{L}{G}\left(\frac{y^*}{m} - x_2\right) + y_2$$

$$y = \cancel{\frac{L}{mG}}^{\,A}(y^* - mx_2) + y_2$$

$$\boxed{y^* = \frac{1}{A}(y - y_2) + mx_2}$$

$$y - y^* = \left(1 - \frac{1}{A}\right)y + \frac{y_2}{A} - mx_2$$

for dilute systems

$$N_{toG} = \int_{y_2}^{y_1} \frac{dy}{y - y^*}$$

$y_{BM} \simeq 1$

$1 - y \simeq 1$

$$= \int_{y_2}^{y_1} \frac{dy}{\left(1 - \frac{1}{A}\right)y + \frac{y_2}{A} - mx_2}$$

$$= -\frac{1}{\left(1 - \frac{1}{A}\right)}\left[\ln\left[\left(1 - \frac{1}{A}\right)y + \frac{y_2}{A} - mx_2\right]\right]_{y_2}^{y_1}$$

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$$= \frac{1}{1-\frac{1}{A}} \ln\left[\frac{\left(1-\frac{1}{A}\right)y_1 + \frac{y_2}{A} - mx_2}{\left(1-\frac{1}{A}\right)y_2 + \frac{y_1}{A} - mx_1}\right]$$

$$\cancel{= \frac{1}{1-\frac{1}{A}} \ln\left(\frac{y_2 - mx_2}{y_1 - mx_1}\right)}$$

$$= \frac{1}{1-\frac{1}{A}} \ln\left[\frac{(y_1 - mx_2) - \frac{1}{A}(y_1 - mx_2) + \frac{1}{A}(y_2 - mx_2)}{y_2 - mx_2}\right]$$

For absorption

$$\boxed{N_{tOG} = \frac{1}{1-\frac{1}{A}} \ln\left[\frac{y_1 - mx_2}{y_2 - mx_2}\left(1-\frac{1}{A}\right) + \frac{1}{A}\right]}$$

only difference from Kremser Eqn

For stripper

$$\boxed{N_{tOG} = \frac{1}{1-\frac{1}{S}} \ln\left[\frac{x_2 - y_1/m}{x_1 - y_1/m}\left(1-\frac{1}{S}\right) + \frac{1}{S}\right]}$$

$$\boxed{N_{tOG} = \frac{1}{1-A} \ln\left[\frac{x_2 - y_1/m}{x_1 - y_1/m}(1-A) + A\right]}$$

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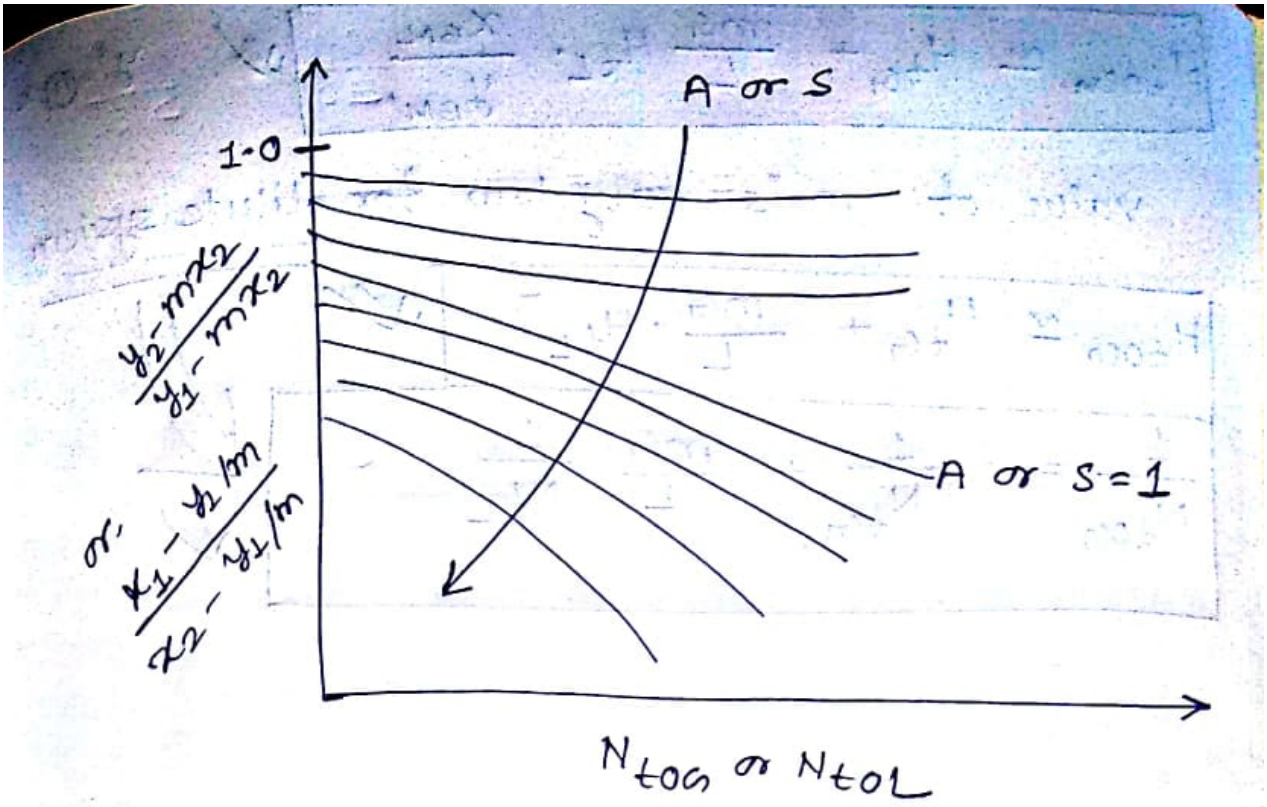

In general $A_{optimum} \in (1.25, 2.0)$

$$Z = H_{tL} \times N_{tL} = H_{tG} \times N_{tG} = H_{toG} \times N_{toG}$$

$$H_{toG} = \frac{G'}{K_y a \, y^*_{BM}} = \frac{G'}{y^*_{BM}} \left(\frac{1}{k_y a} + \frac{m}{k_x a} \right)$$

slope of eqbm. line in the operating range

$$= \frac{G'}{k_y a \, y_{BM}} \cdot \frac{y_{BM}}{y^*_{BM}} + \frac{mG'}{L'} \cdot \frac{L'}{k_x a \, x_{BM}} \cdot \frac{x_{BM}}{y^*_{BM}}$$

$$= H_{tG} \cdot \frac{y_{BM}}{y^*_{BM}} + \frac{mG}{L} H_{tL} \frac{x_{BM}}{y^*_{BM}}$$

For dilute system

$$y - y_i \simeq y - y^*$$

→ most of the resistance is offered by gas phase

Scanned by CamScanner

$$\boxed{H_{tOG} \simeq H_{tG} + \frac{mG}{L} H_{tL} \cdot \frac{x_{BM}}{y_{BM}^*}}$$

$y^* = mx$

value of m is very low for dilute system

$$\boxed{H_{tOG} \simeq H_{tG} + \frac{mG}{L} \cdot H_{tL}}$$

$$\boxed{\frac{1}{N_{tOG}} = \frac{1}{N_{tG}} + \frac{mG}{L} \frac{1}{N_{tL}}}$$

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$$\boxed{H_{tOG} \simeq H_{tG} + \frac{mG}{L} H_{tL} \cdot \frac{x_{BM}}{y_{BM}^*}}$$

$y^* = mx$

value of m is very low for dilute system

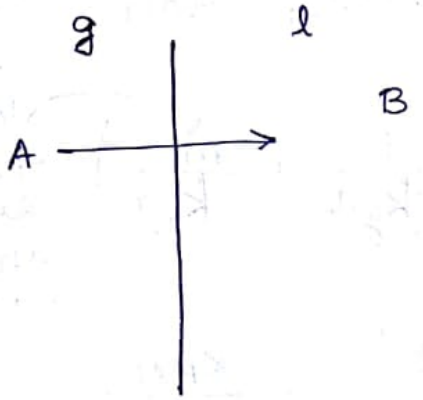
$$\boxed{H_{tOG} \simeq H_{tG} + \frac{mG}{L} \cdot H_{tL}}$$

$$\boxed{\frac{1}{N_{tOG}} = \frac{1}{N_{tG}} + \frac{mG}{L} \frac{1}{N_{tL}}}$$

16/10/17

Absorption with Chemical Reaction

- When there are multiple processes taking place, usually the slowest step is rate determining



$A + zB \longrightarrow P$

- Depending on nature of reaction, either absorption or reaction will be dominating the entire process
- Contactors are used to increase mass transfer rate to maximum.
- Even after that, mass transfer rate can be increased if reaction takes place.

Heterogeneous Reaction Vol. 2 by Sharma

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Absorption with chemical reaction

- → **Regime 1** : Very slow reaction
- → **Regime 2** : Slow reaction
- → **Regime 3** : Fast reaction
- → **Regime 4** : Instantaneous reaction

- B is in large excess ⇒ $C_B \simeq C_{B_0} = \text{const.}$

$$A + ZB \xrightarrow{k_2} P$$

$$r_A = l\, k_2 C_A C_B$$

, $l \equiv$ volume fraction of liquid $= \dfrac{\text{volume of liquid}}{\text{Total volume}}$

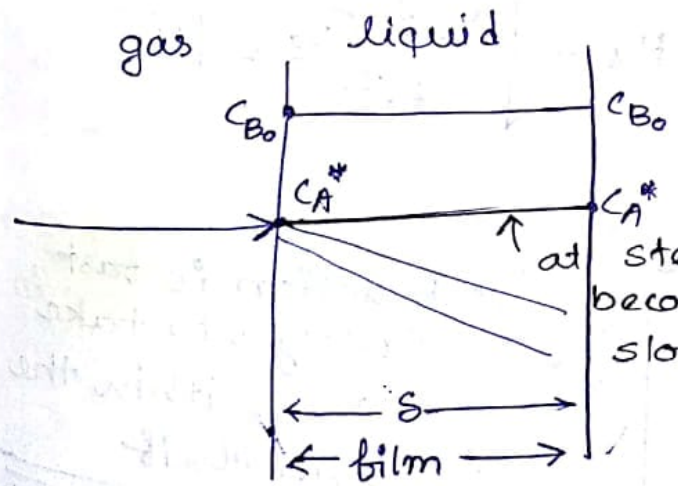
$$r_A = l(\cancel{k_2 C_{B_0}})\, C_A \quad \nearrow k_1$$

$$r_A = l\, k_1 C_A$$

Regime 1 :

$$R_A = l\, k_2 C_{B_0} C_A^*$$

, R_A = rate of $\dfrac{\text{absorption}}{\text{Mass Transfer}}$



↑ at steady state, liquid conc. becomes const $\simeq C_A^*$ due to slow reaction rate

Condition: $k_L a C_A^* \gg l\, k_2 C_{B_0} C_A^*$

$$\boxed{k_L a \gg l\, k_2 C_{B_0}} \checkmark$$

- No enhancement in rate of absorption is possible

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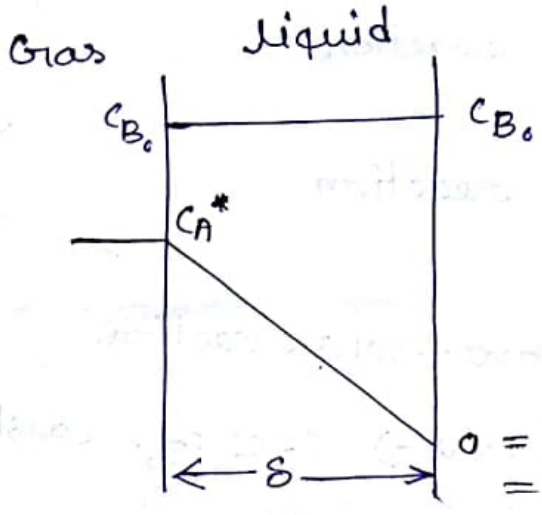
Regime 2

- $R_A = k_L a C_A^*$



No enhancement

Condition: $\boxed{k_L a \ll k_2 C_{B_0}}$

- Reaction is not fast enough to take place within the film. But reaction occurs beyond the film.

condition for above situation:

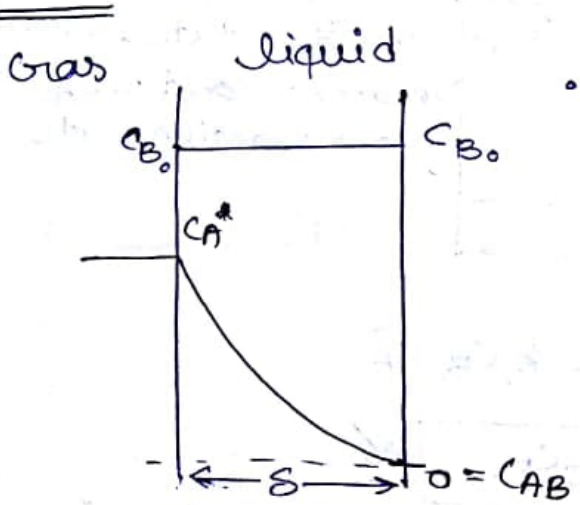
$$\sqrt{M} < 1$$

$$M = \frac{D_A k_2 C_{B_0}}{k_L^2}$$

$$\frac{\sqrt{D_A k_2 C_{B_0}}}{k_L} < 1$$

Hatta number, $Ha = \sqrt{\frac{D_A k_2 C_{B_0}}{k_L^2}} = \sqrt{M}$

Regime 3



- Reaction is fast enough to take place within the film itself

- $\boxed{R_A = k_L a C_A^* \frac{\sqrt{M}}{\tanh\sqrt{M}}}$

- $\sqrt{M} \gg 3$

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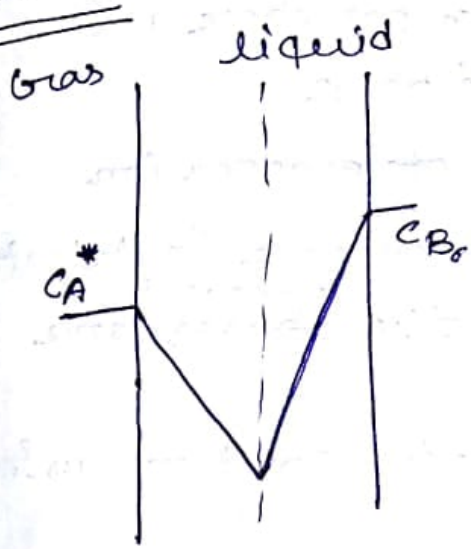
- Mass transfer rate is enhanced over pure mass transfer.

$$\boxed{\phi = \frac{\sqrt{M}}{\tanh \sqrt{M}} = \text{enhancement rate}}$$

Regime 4



- There is no co-existance of species A and B in the liquid phase (both film & bulk)
- Reaction is instantaneous

- $R_A = k_L a C_A^* \left(1 + \cancel{\frac{D_B C_{B_0}}{Z D_A C_A^*}}\right) \rightarrow q$

$$\boxed{R_A = k_L a C_A^* (1+q)}$$

- $\boxed{\sqrt{M} \gg (1+q)}$
- $\boxed{\phi = 1+q}$

* Phase transfer catalyst facilitates, transfer of reactant from aquesous phase to organic phase

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Distillation

23/10/17

- All the components are present in both the phases (gas and liquid) [distinguishing charectoristic from evaporation]
- Depending on their volatility (B.P) components are concentrated in either of the phases.
- More volatile component in gas phase and less volatile component in liquid phase
- No mass transfer in case of evaporation
- Equimolar counter diffusion takes place if latent heat of vaporisation of both the ~~phases~~ components are equal
- In evaporation there is no transport of mass from one phase to other.

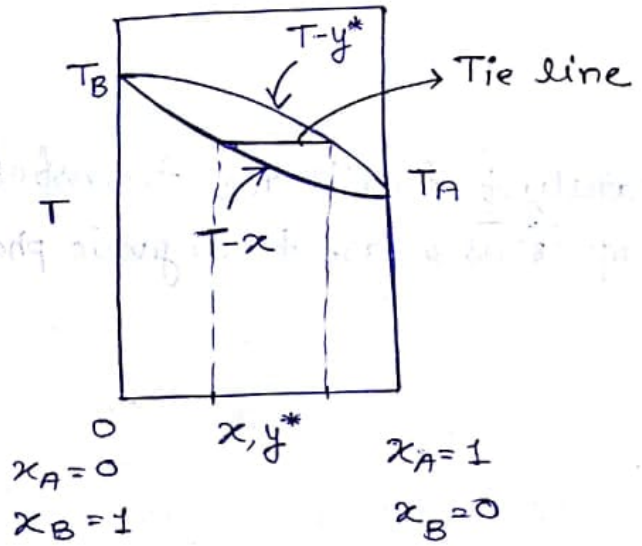
Vapor - liquid Equilibria (VLE)

A + B

$F = C - P + 2$

$2 - 2 + 2$

Const. Pressure : T - x, y diagram :



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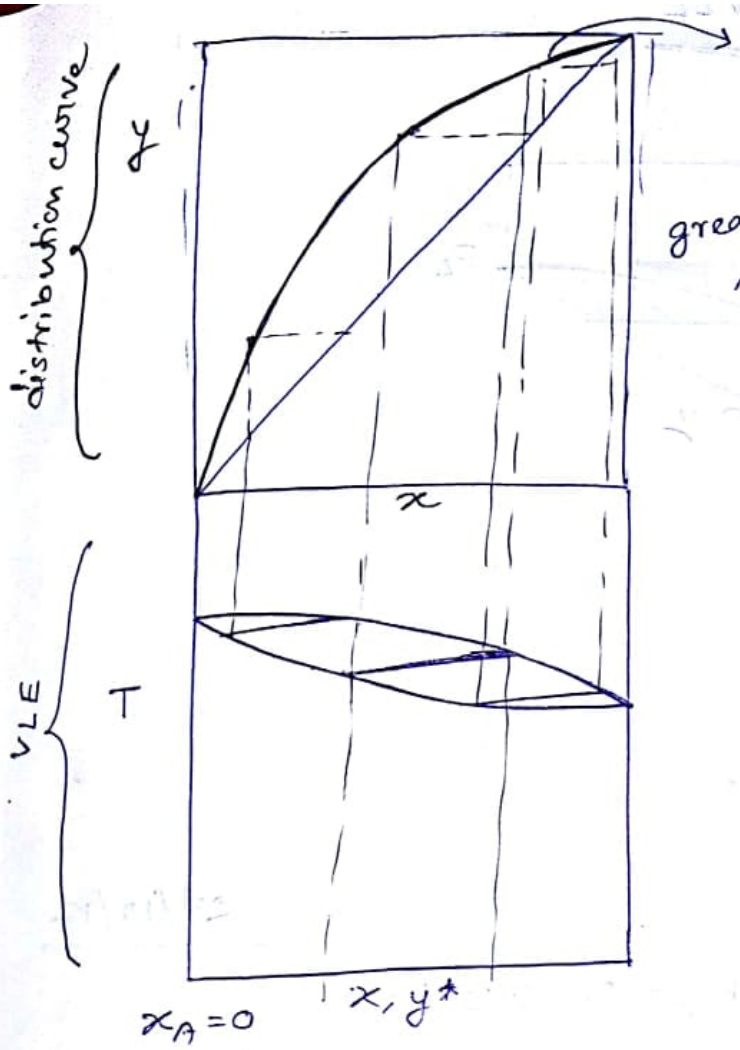
C = P + 2
2 = 2 + 2



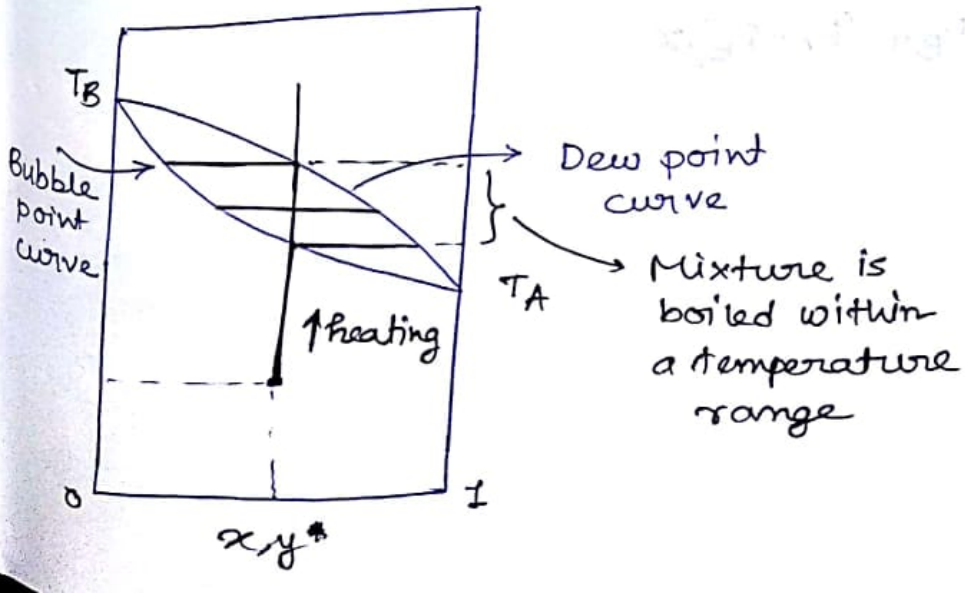
Further away the distribution diagram from the diagonal, greater is the feasibility of the distillation process. Feasibility is determined by relative volatility

Reative volatility (α_{AB})

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

$$\boxed{\alpha_{AB} = \frac{y^*/(1-y^*)}{x/(1-x)} = \frac{y^*(1-x)}{x(1-y^*)}}$$

$\alpha_{AB} > 1$ for distillation to occur.



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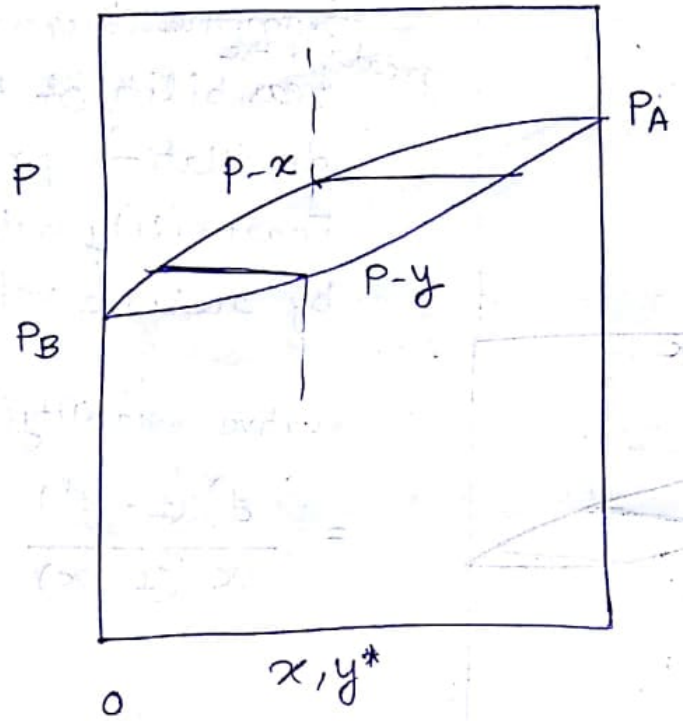
Const T p-xy VLE



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Ideal solution: Obeys Rault's Law

$$p_A^* = P_A x$$

$$p_B^* = P_B (1-x)$$

$$p_t = p_A^* + p_B^* = P_A x + P_B (1-x)$$

$$= P_B + (P_A - P_B) x$$

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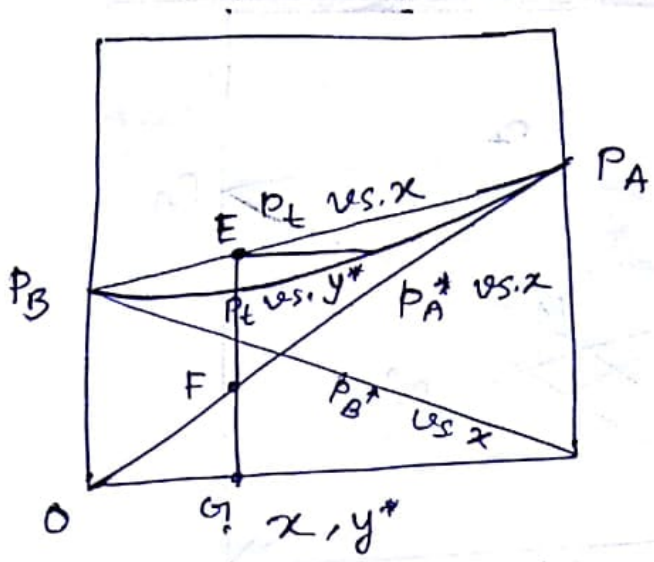

$$y^* = \frac{P_A^*}{P_t} = \frac{FG}{EG}$$

$$y^* = \frac{P_A^*}{P_t} = \frac{P_A x}{P_t}$$

$$1 - y^* = \frac{P_B^*}{P_t} = \frac{P_A(1-x)}{P_t}$$

$$\frac{y^*}{1-y^*} = \frac{P_A x}{P_B(1-x)}$$

$$\frac{y^*/(1-y^*)}{x/(1-x)} = \frac{P_A}{P_B}$$

$$\alpha_{AB} = \frac{P_A}{P_B} \qquad y^* = \frac{\alpha x}{1+(\alpha-1)x}$$

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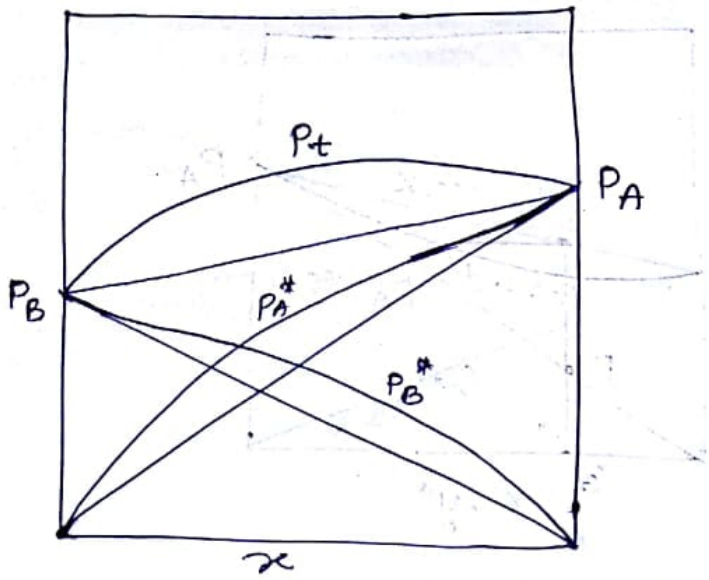
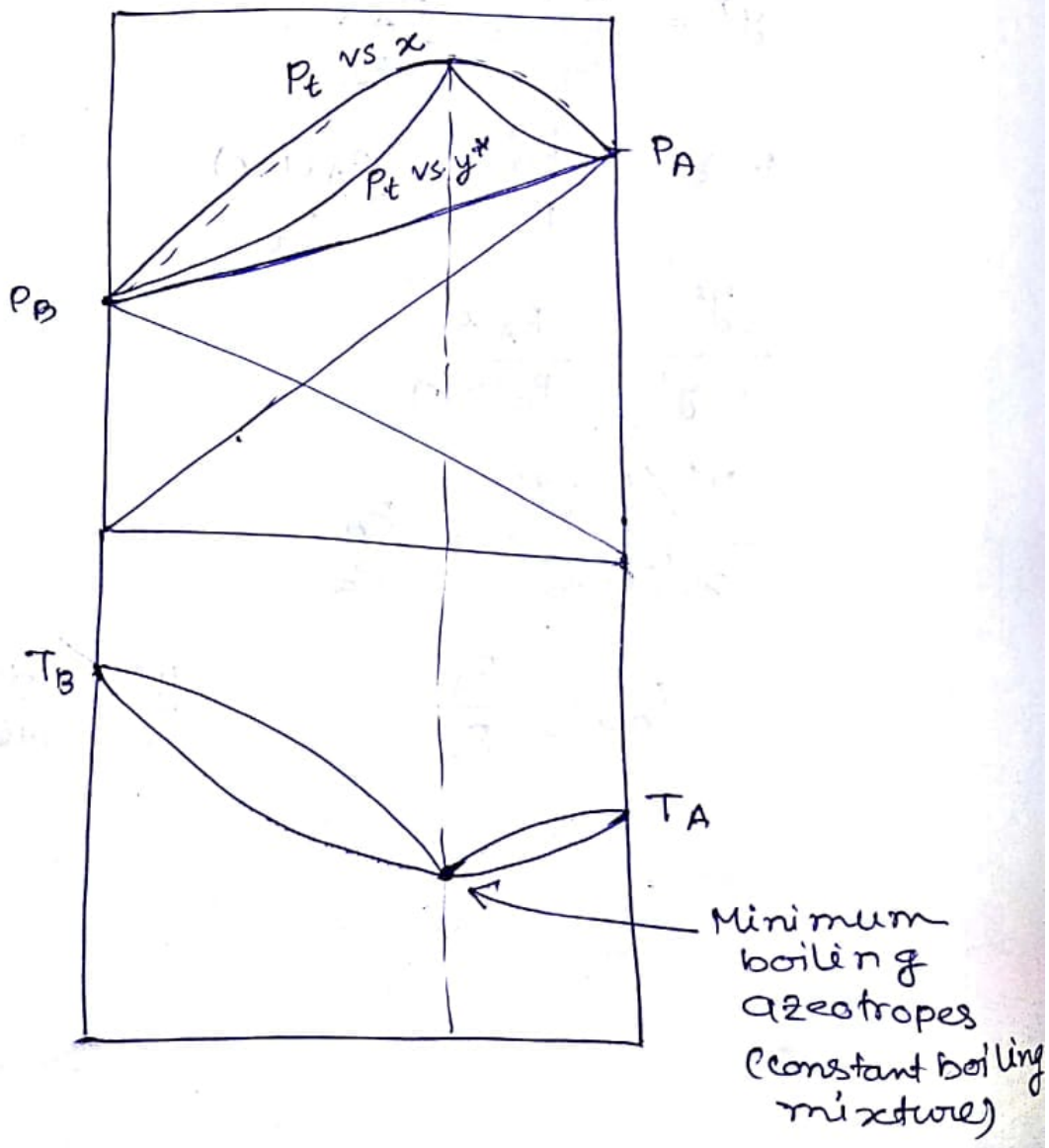


fig : +ve deviation from ideality



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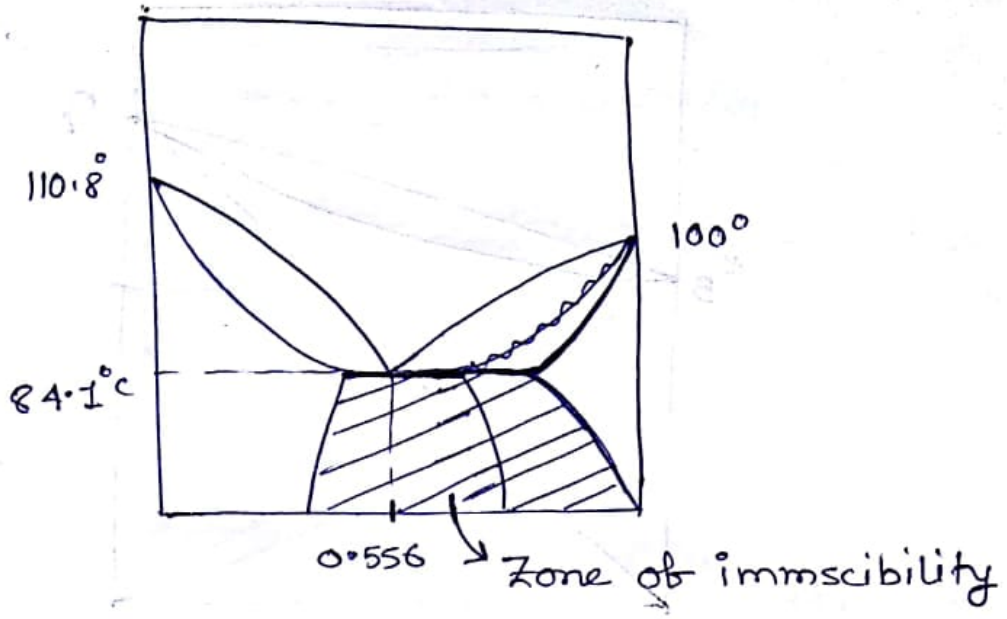


fig: Extreme deviation from ideality (Heteroazeotropes)

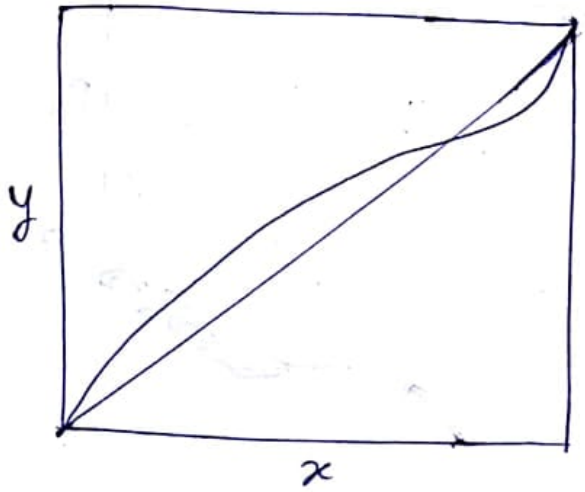
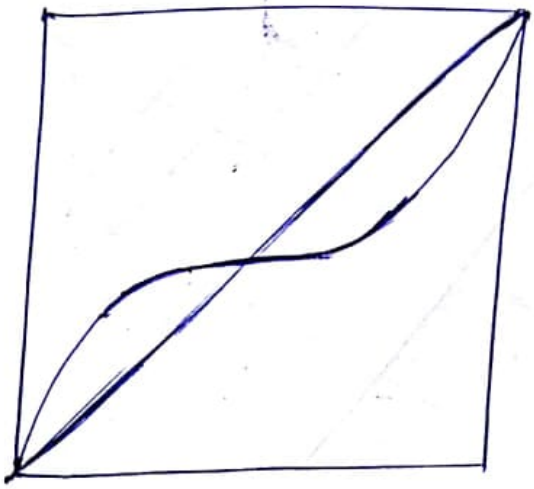


fig: for normal azeotropes

Dean & Stark Apparatus



Toluene + water
110.8°c 110°c
↓
84.1°C
44.4 mole% Toluene

fig: for heteroazeotropes

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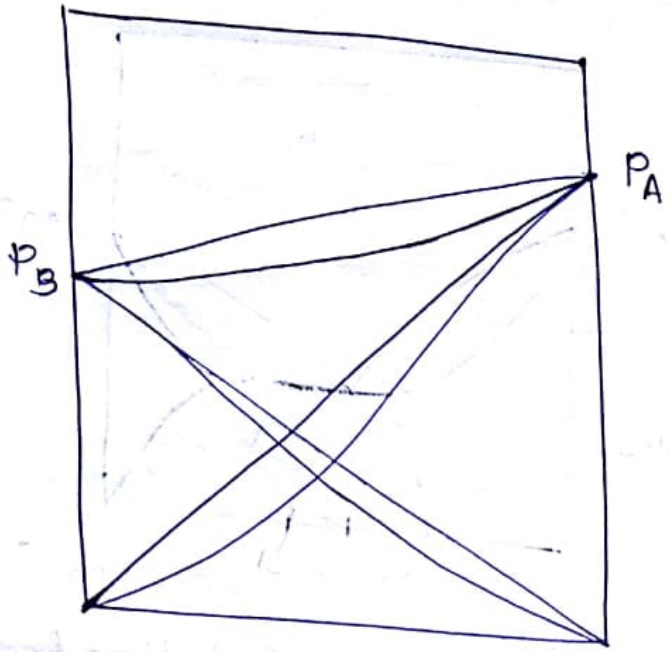
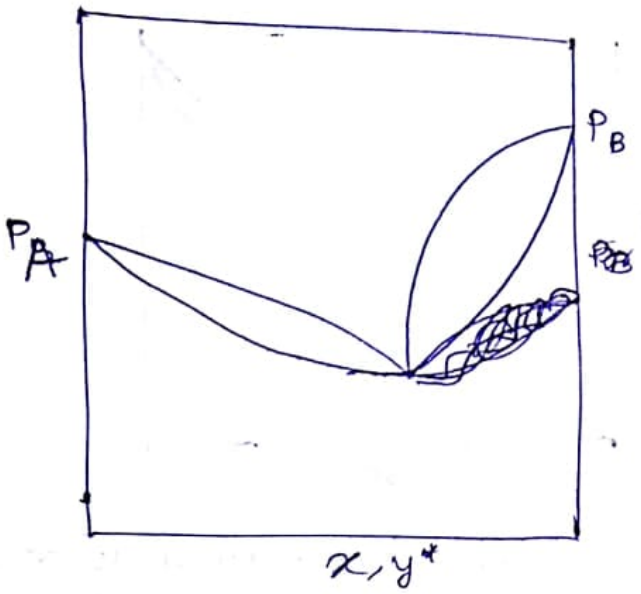
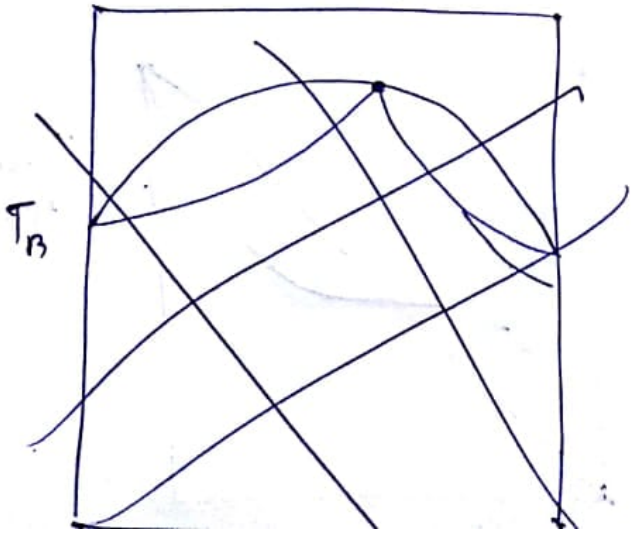


fig: Negative Deviation





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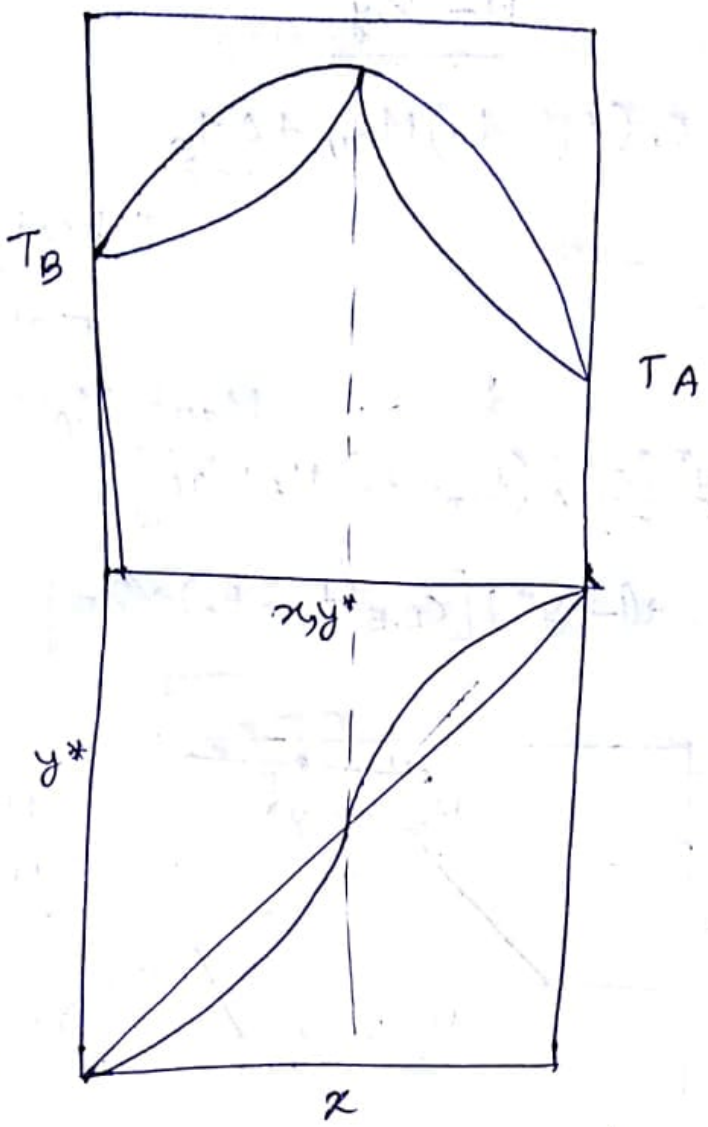

fig: Maximum boiling azeotrope

eg.
1) H_2O – HCl

100°c 85°c

↓

110°c

11.1 mole% HCl

2) Chloroform – ~~acetone~~ acetic acid

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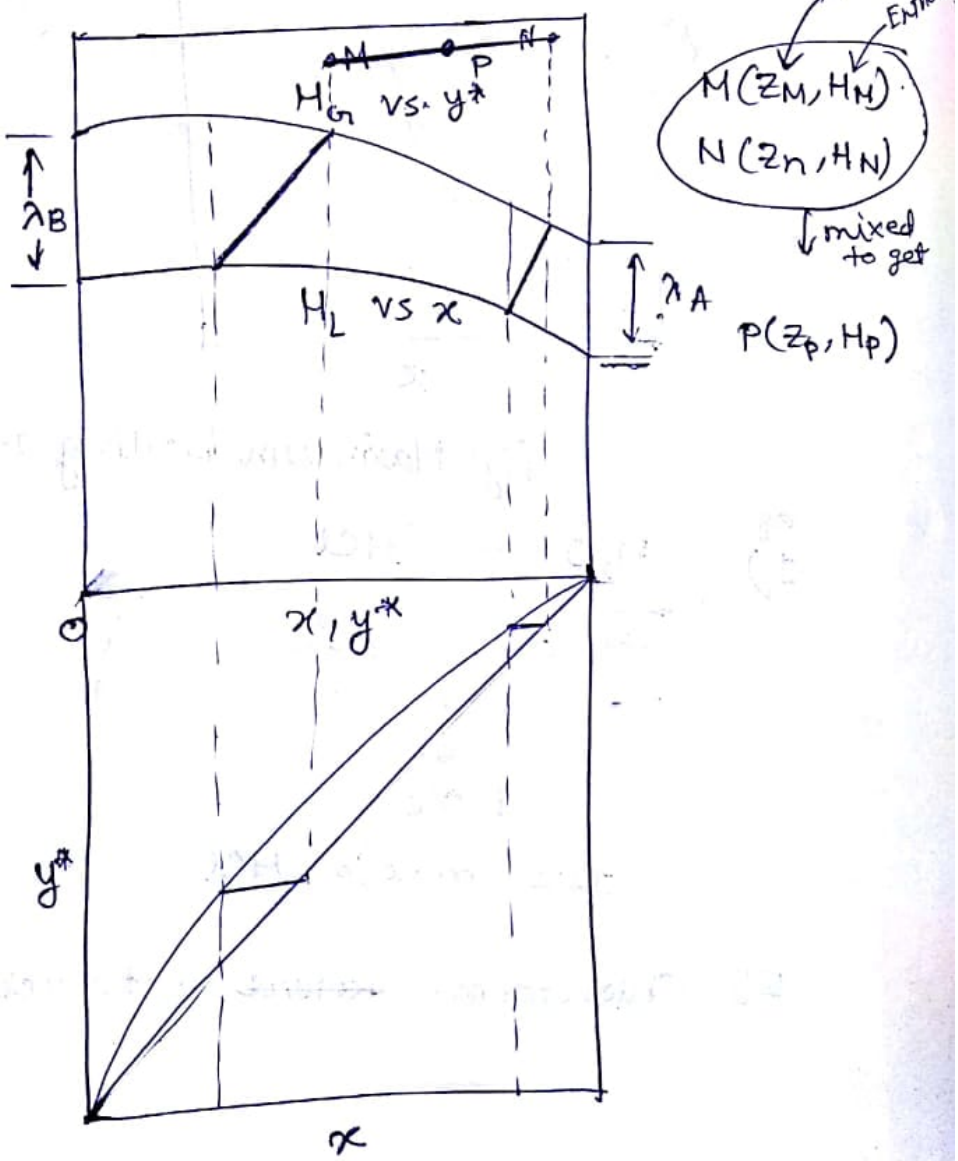
H – x, y

$$H_L = C_L (t_L - t_0) M_{av.} + \Delta H_S$$

ΔH_S → heat of solⁿ or heat of mixing

$$M_{av} = M_A x + M_B (1-x)$$

$$H_G = y^* \left[C_{L,A} (t_G - t_0) M_A + \lambda_A \right] + (1 - y^*) \left[C_{L,B} (t_G - t_0) + \lambda_B \right]$$



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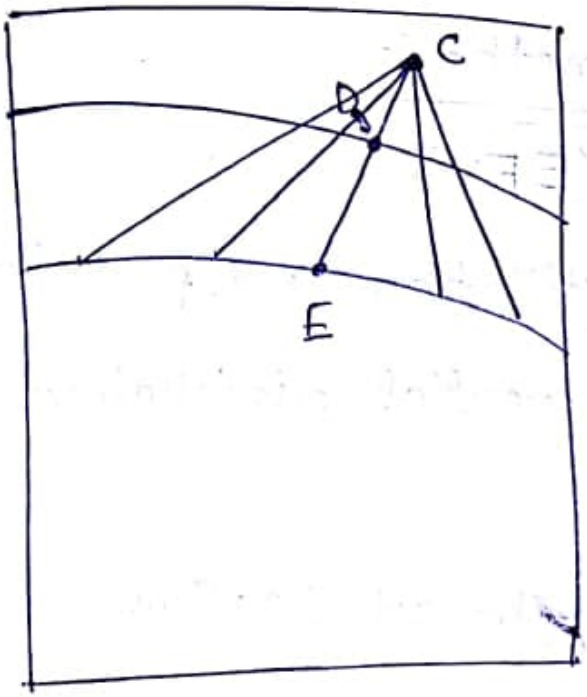

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- Simple distillation method
  - → Single stage
  - → less rectification/purification

- Complex method
  - → multiple stage
  - → Reflux stream
  - → Continuous distillation
  - → Better purification

- Simple distillation methods

1) Flash distillation (EFV)

or

Equilibrium flash distillation or vaporization

2) Simple batch or differential distillation

3) Steam Distillation

- EFV used for crude characterisation
  ↓curve
  Volume distilled vs. Temperature (analogus to ASTM distillation of petroleum products)

- Differential distillation is carried out in such a manner that liquid & vapor formed are maintained at equilibrium

- Steam distillation is used for pharmaceutical & fragrances.

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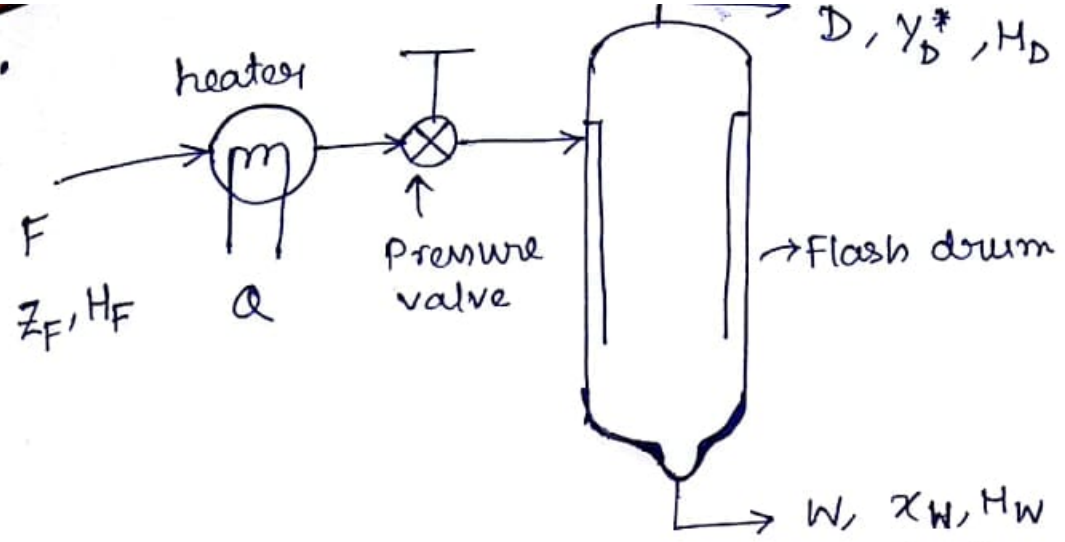


Feed enters the flash drum tangentially.

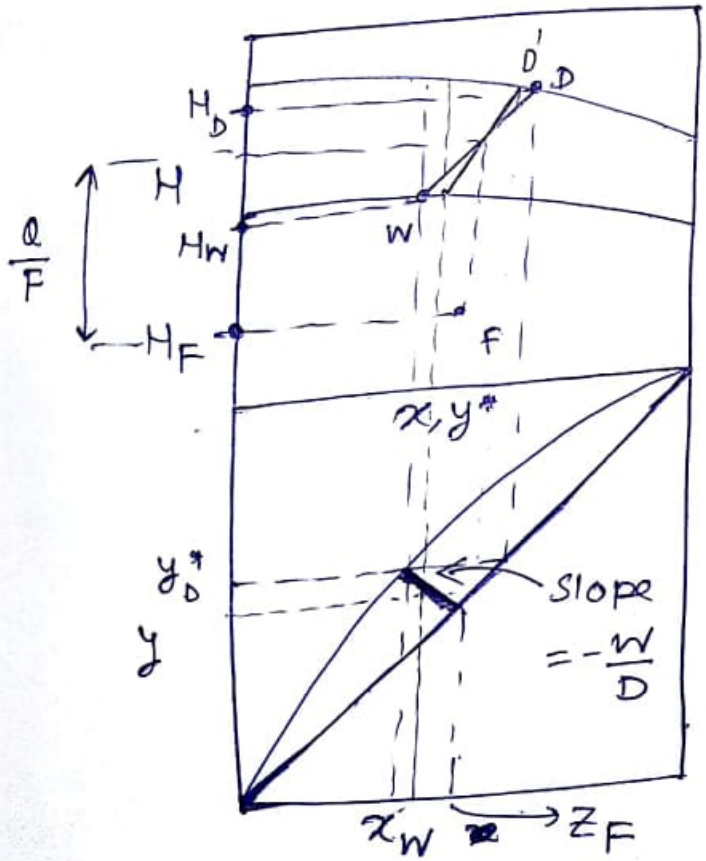
1) $F = D + W$ -- overall material balance

2) $FZ_F = Dy_D^* + Wx_W$ -- component balance

3) $Q + FH_F = DH_D + WH_W$ ---- Energy balance (Enthalpy)

from 1, 2, 3

$$-\frac{W}{D} = \frac{y_D^* - Z_F}{x_W - Z_F} = \frac{H_D - (H_F + Q/F)}{H_W - (H_F + Q/F)}$$



— Non eqbm.

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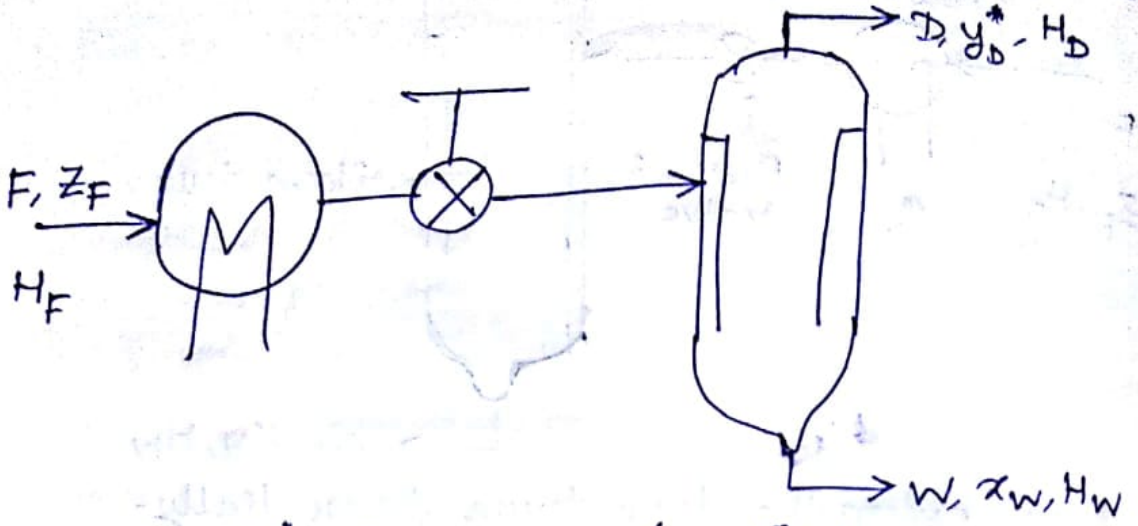
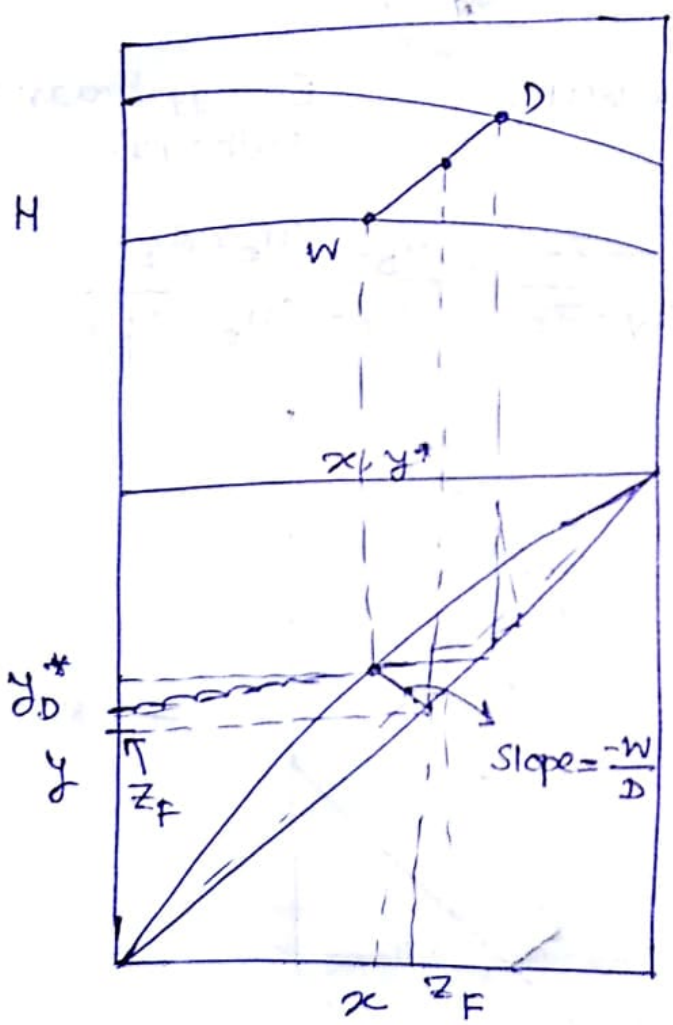


$$-\frac{W}{D} = \frac{y_D^* - z_F}{x_W - z_F} = \frac{H_D - (H_F + Q/F)}{H_W - (H_F + Q/F)}$$



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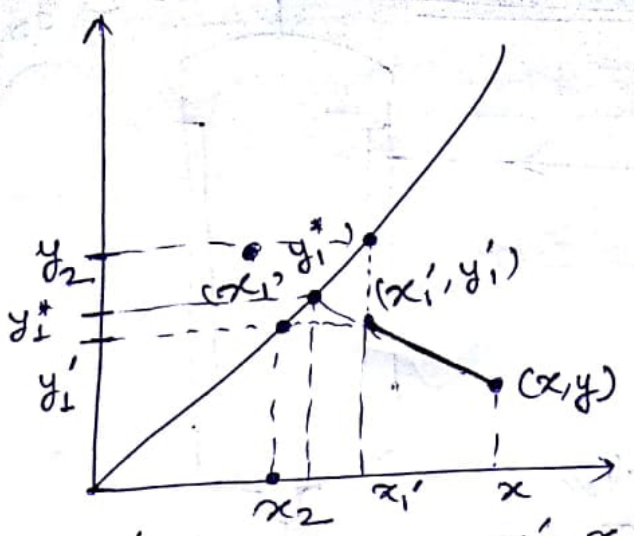
Interphase M.T



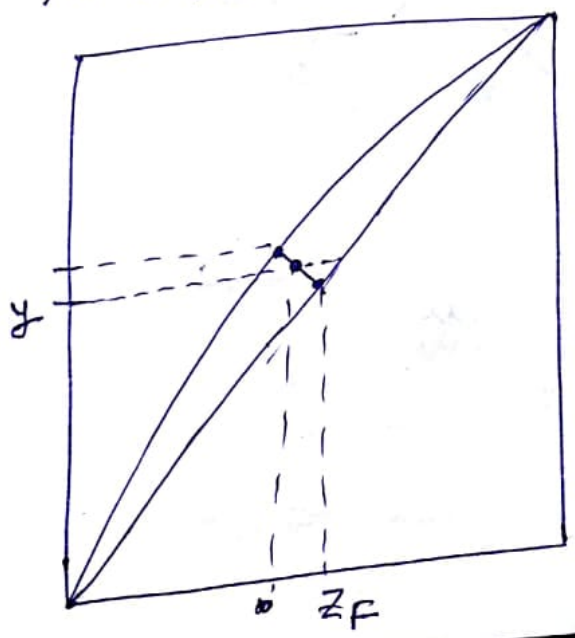
$$E_G = \frac{y_1' - y}{y_1^* - y} \qquad E_L = \frac{x_1' - x}{x_1 - x}$$ Point efficiency

Murphree efficiency $$E_{MG} = \frac{y_1' - y}{y_2'' - y} \qquad E_{ML} = \frac{x_1' - x}{x_2 - x}$$

$$E_G = \frac{y - Z_F}{y_D^* - Z_F} = 0.6$$

$$y - Z_F = 0.6 y_D^* - 0.6 Z_F$$

$$y = 0.6 y_D^* + 0.4 Z_F$$



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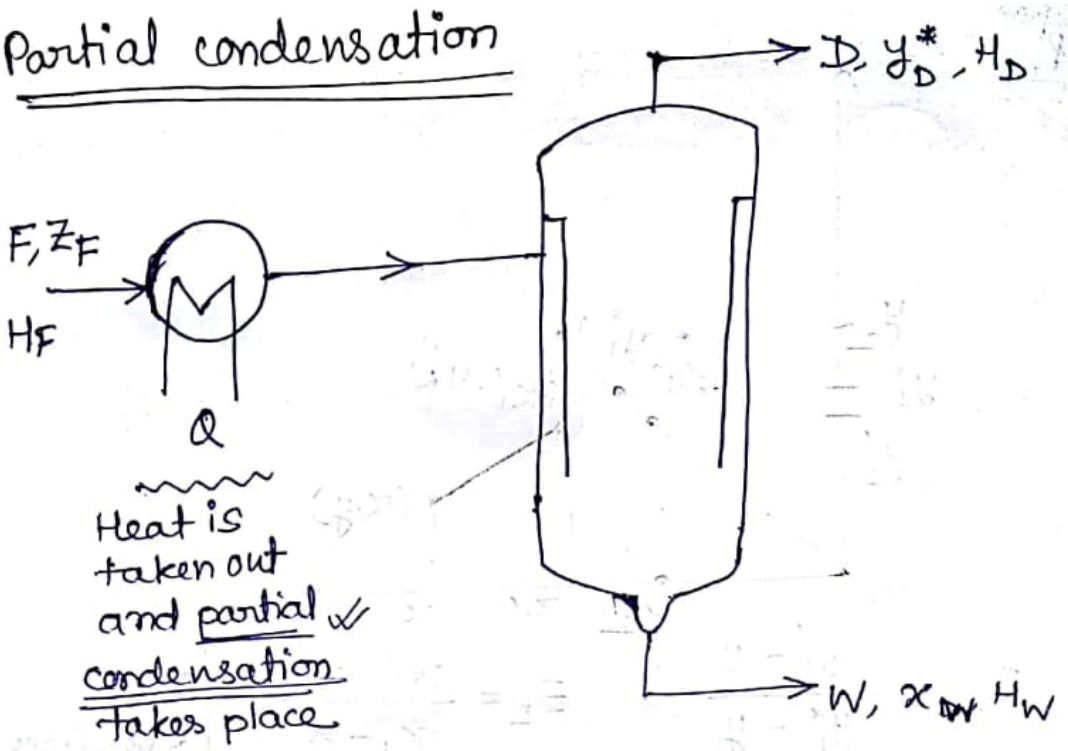
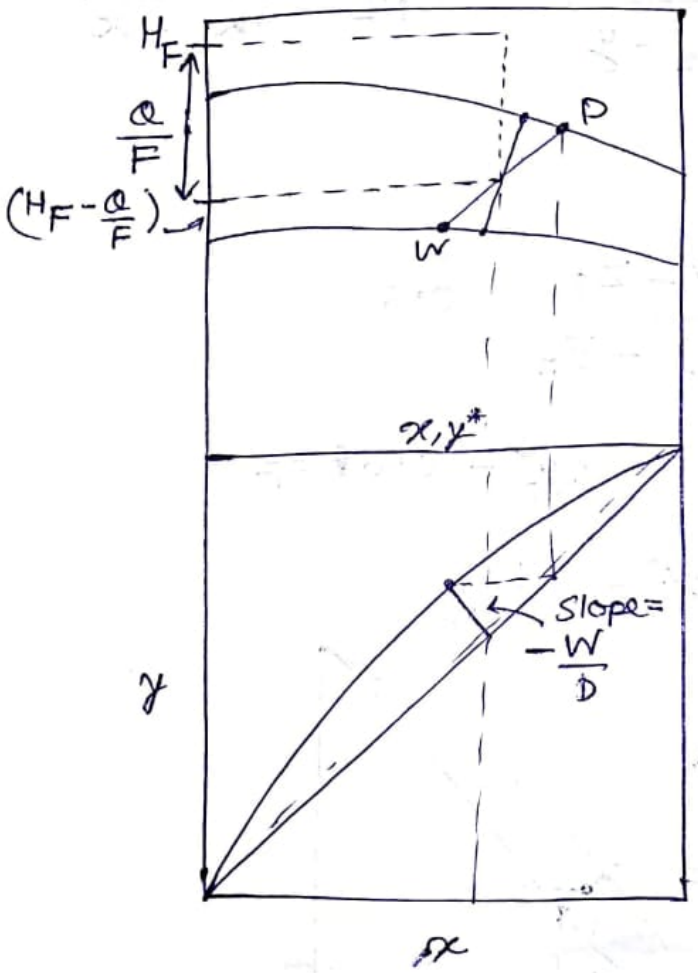
Partial condensation





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Multicomponent System – Ideal solutions

components: A, B, C, . . . , N

$$p_j^* = P_j x_j$$

$$\Rightarrow \frac{p_j^*}{p_t} = \frac{P_j}{P_t} x_j = m_j x_j$$

$$\Rightarrow y_i^* = m_j x_j \quad \Rightarrow \quad m_j = \frac{y_j^*}{x_j}$$

For multicomponent mixture

$$y_{i,D}^* = m_j x_{j,W} \quad \text{--- (I)}$$

$$+ \frac{W}{D} = \frac{y_{i,D}^* - z_{j,F}}{z_{j,F} - x_{j,W}} \quad \text{--- (II)}$$

Replacing $x_{j,W} = \dfrac{y_{i,D}^*}{m_j}$

$$\frac{W}{D} = \frac{y_{i,D}^* - z_{j,F}}{z_{j,F} - \dfrac{y_{i,D}^*}{m_j}}$$

$$\Rightarrow y_{j,D}^* \left[\frac{W}{D m_j} - 1\right] = -z_{j,F}\left(1 + \frac{W}{D}\right)$$

$$\Rightarrow y_{j,D}^* = \frac{z_{j,F}(1 + W/D)}{1 + W/D \; x_{j,W}}$$

$$\boxed{\sum y_{i,D}^* = 1.0}$$ ✓ check for correctness of obtained solution.

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Partial condensation of multi component mixtu

$$x_{j,W} = \frac{z_{j,F}(1 + W/D)}{m_j + W/D}$$

$$\sum x_{j,W} = 1.0$$

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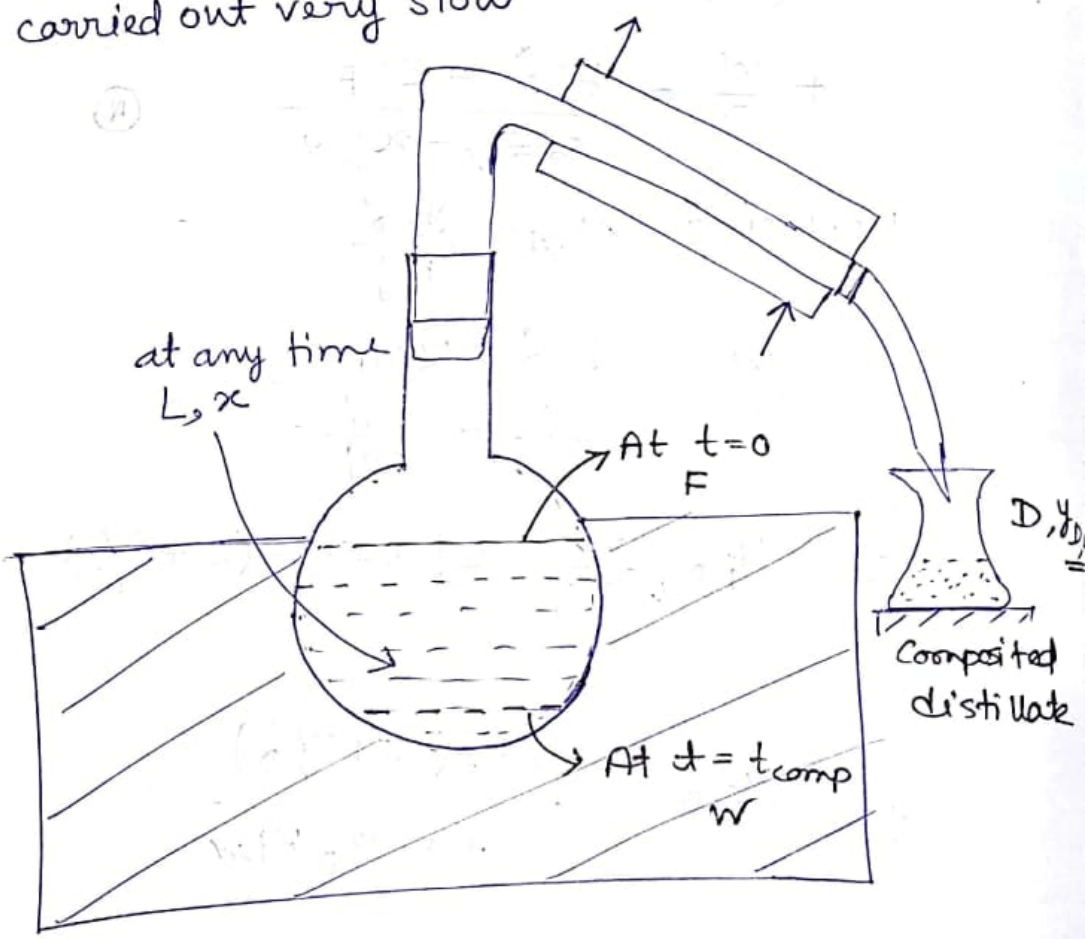
Differential Ditillation

- discomposited distillate vs. composited distillate
- carried out very slow



- Combination of infinite no. of flash distillation with very small (fraction amount of liquid vaporised distillated) in each step.
- Differential material balance is required

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	Total moles	Moles of A
In	0	0
out	dD	$y^* dD$
Accumulation	dL	$d(Lx)$

In - out = accumulation

$$0 - dD = dL \quad \cdots (I)$$

$$0 - y^* dD = d(Lx) = L dx + x dL \quad \cdots (II)$$

from (I) & (II)

$$y^* dL = L dx + x dL$$

$$(y^* - x)\, dL = L dx$$

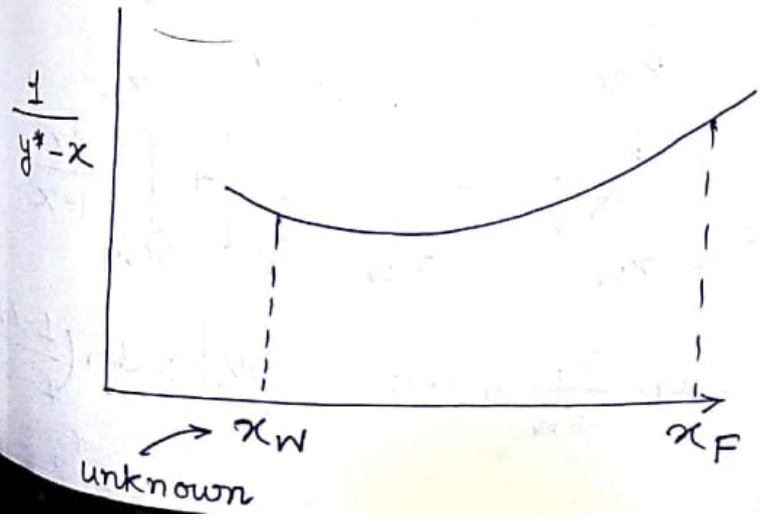
$$\int_F^W \frac{dL}{L} = \int_{x_F}^{x_W} \frac{dx}{y^* - x}$$

$$\boxed{\ln \frac{F}{W} = \int_{x_W}^{x_F} \frac{dx}{y^* - x}}$$

Rayleigh's Eq^n

composited distillate composition can be obtained from component balance of A

$$F x_F = D y_{D,av} + W x_W$$



x_W to be chosen, by trial & error

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$$\boxed{\ln\left(\frac{F}{D}\right) = \int_{y_F}^{y_D} \frac{dy}{y - x^*}}$$

For system with constant relative volatility, graphical sol^n is not required although ~~grea~~ sol^n by trial and error is to be obtained.

$$y^* = \frac{\alpha x}{1+(\alpha-1)x} \quad \text{where } \alpha = \text{const.}$$

$$\ln \frac{F}{W} = \int_{x_F}^{x_W} \frac{(1+(\alpha-1)x)\,dx}{\alpha x - x(1+(\alpha-1)x)}$$

$$\ln \frac{F}{W} = \int_{x_F}^{x_W} \frac{(1+(\alpha-1)x)\,dx}{-(\alpha-1)x^2 + (\alpha-1)x}$$

$$\boxed{\ln \frac{F}{W} = \int_{x_F}^{x_W} \frac{(1+(\alpha-1)x)\,dx}{x(\alpha-1)(1-x)}}$$

For α = const. i.e rel. volatility is const.

$$\ln \frac{F}{W} = \frac{1}{(\alpha-1)} \int_{x_W}^{x_F} \frac{dx}{x(1-x)} + \int_{x_W}^{x_F} \frac{dx}{(1-x)}$$

$$\ln \frac{F}{W} = \frac{1}{\alpha-1}\left[\int_{x_W}^{x_F} \frac{dx}{x} + \int_{x_W}^{x_F} \frac{dx}{1-x}\right] + \int_{x_W}^{x_F} \frac{dx}{1-x}$$

$$\ln \frac{F}{W} = \frac{1}{\alpha-1}\left[\ln \frac{x_F}{x_W} + \ln \frac{1-x_W}{1-x_F}\right] + \ln\left(\frac{1-x_W}{1-x_F}\right)$$

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$$\cancel{\ln \frac{F}{W} = \frac{1}{\alpha-1} \ln \frac{x_F(1-x_W)}{}}$$

$$(\alpha-1)\ln\frac{F}{W} = \ln\frac{x_F}{x_W} + \ln\frac{1-x_W}{1-x_F} + (\alpha-1)\ln\frac{1-x_W}{1-x_F}$$

$$(\alpha-1)\ln\frac{F}{W} = \ln\frac{x_F}{x_W} + \alpha\ln\frac{1-x_W}{1-x_F}$$

$$\ln\left(\frac{F x_F}{W x_W}\right) = \alpha \ln \frac{F(1-x_F)}{W(1-x_W)}$$

$$\boxed{\log\left(\frac{F x_F}{W x_W}\right) = \alpha \log \frac{F(1-x_F)}{W(1-x_W)}}$$

System with const. rel. voltality

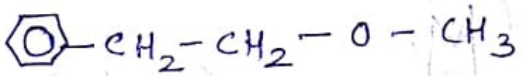
Steam Distillation

(A+B) → Not volatile compared to A

High boiling

A deteriates in quality at its boiling protein

Kewra water → 2-phenyl ethyl methyl ether



(A+B)
+C (steam)

$$P_t = P_A + P_C$$

Vapor pressure of components as the components are immiscible and exert pressure independent of the other components. The mixture will boil at lower temperature compared to the boiling point of pure A. Vapor mixture is condensed, which form two separate layers. Usually the bottom

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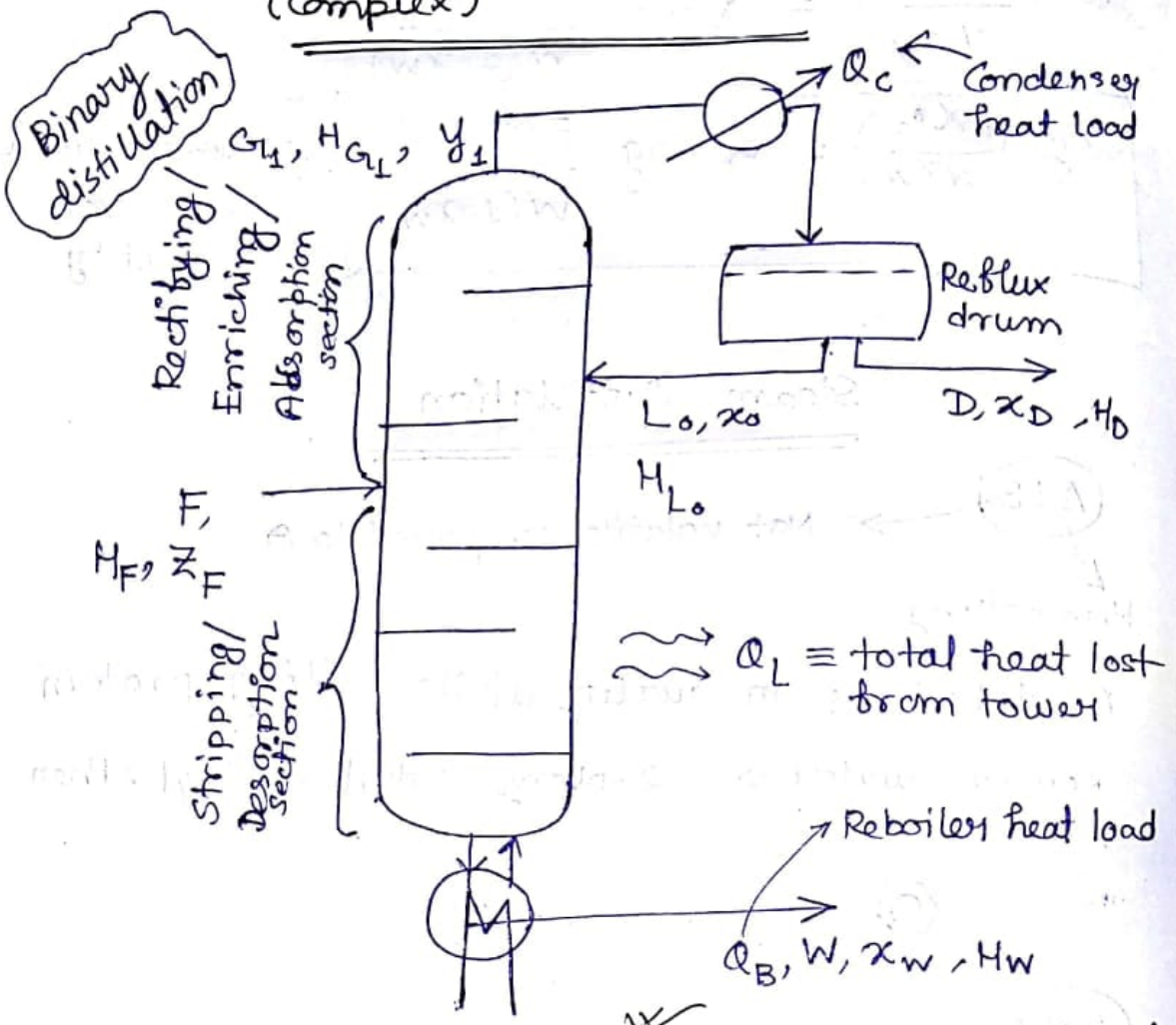
layer (extracted water) is refluxed back.

$$\frac{p_A}{P_t} = y_A \text{ in vapor} \qquad \frac{p_c}{P_t} = y_c \text{ in vapor}$$

Fractional Distillation (Complex)



i.e Total no. of trays = (obtained from stage wise construction − 1)

* Sometimes, partial condenser need to be considered as eqbm. stage but most often not.

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$$G_1 H_{G_1} = Q_c + D H_D + L_o H_{L_o} \quad \cdots (1)$$

$$Q_c = G_1 H_{G_1} - D H_D - L_o H_{L_o}$$

$$G_1 = L_o + D \quad \cdots (2) \qquad \underbrace{R = \frac{L_o}{D}}_{\text{Reflux ratio}} \quad \cdots (3)$$

$$= D(R+1)$$

$$Q_c = D(R+1) H_{G_1} - D H_D - R D H_{L_o}$$

$$\boxed{Q_c = D\left[(R+1) H_{G_1} - H_D - R H_{L_o}\right]}$$ Condenser heat load

$$F H_F + Q_B = Q_c + D H_D + W H_D + Q_L$$

$$\boxed{Q_B = Q_c + D H_D + W H_D + Q_L - F H_F}$$ Reboiler heat load

02/11/17

* Diameter is decided considering flooding in tower as well as the nature of liquid (foaming or non-foaming)

* Actual fluid velocity is a fraction of the flooding velocity. The fraction is determined by nature of flow (lower for foaming, higher for non-foaming)

* Packed towers are used for foaming liquids as gas is bubbled but not very high volume of foam is formed in a packed tower. As a result, very high ~~glass~~ gas flow rates can be employed.

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) Ponchon & Savarit Method → Detailed enthalpy composition as well as x vs y^* distribution data (eqbm.) data is required

) McCabe & Thiele Method

Only equilibrium data is required

1st method is applicable to all systems, where as 2nd method is applicable to *restricted systems (where molar latent heat of vaporisation of components are equal), although 2nd method can be employed to most of the systems with modifications.

McCabe Thiele Method is based on Principle of Equimolal overflow and vaporisation.

Unless above assumption is considered, i.e in 1st method the flow rates of liquid and gas change along the length of the tower. As a result, the operating line slope will change with tower length. In such cases, detailed enthalpy composition data is required.

• Assumptions

• Total condenser at
• Reflux liquid is bubble point (no subcooling)
• Gas is ~~at~~ saturated.
• i.e Liquid and Gas rates are equal.

Mole balance in envelop 1

(i) $G = L + D$ - - - - Total material balance

(ii) $G y_{n+1} = L x_n + D x_D$ - - - - Total component balance

$$y_{n+1} = \frac{L}{G} x_n + \frac{D}{G} x_D$$

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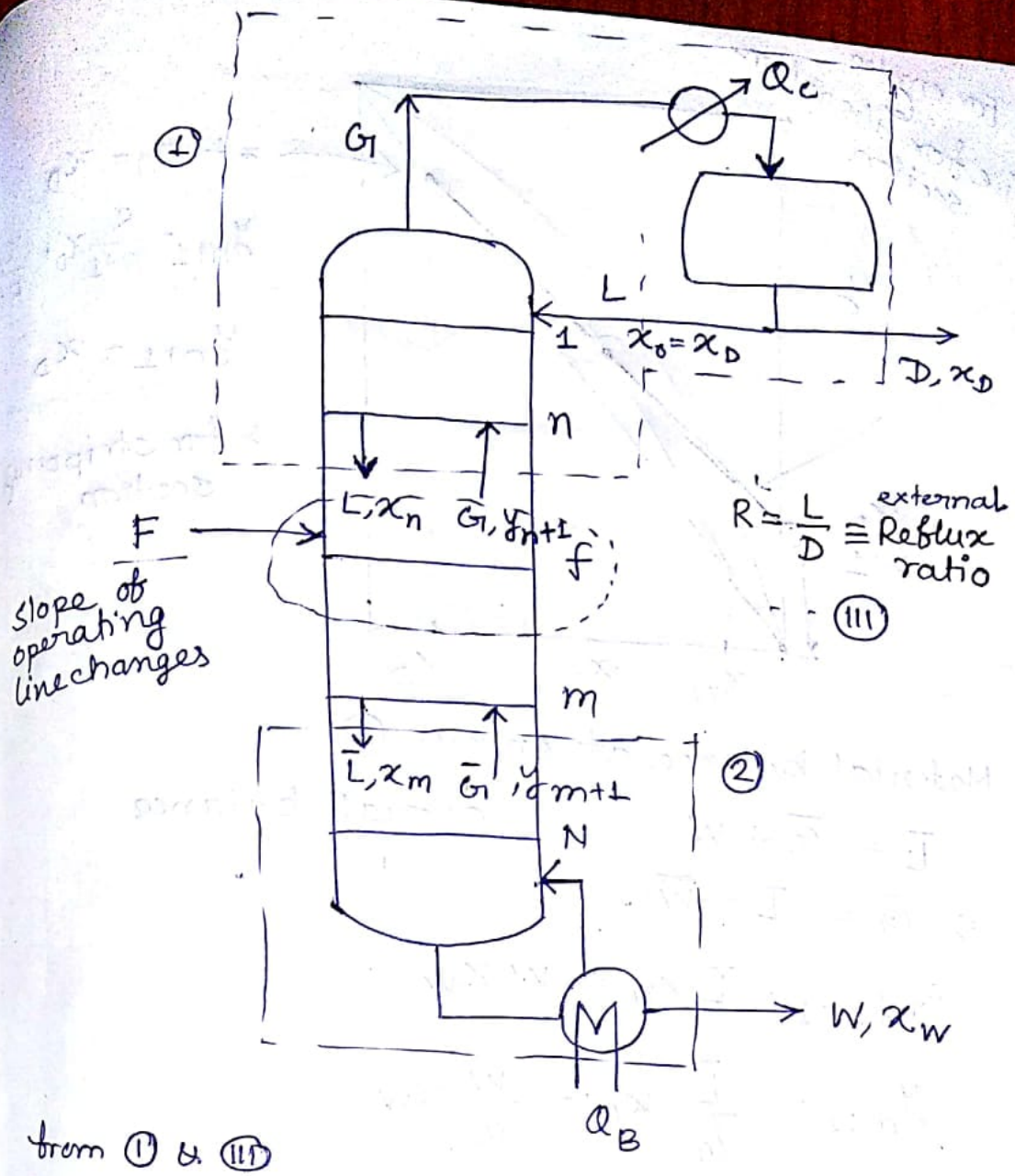

from I & III

$$G = RD + D = D(R+1)$$

similary from II & III

$$y_{n+1} = \frac{RD}{D(R+1)} x_n + \frac{D}{D(R+1)} x_D$$

$$\boxed{y_{n+1} = \underbrace{\left(\frac{R}{R+1}\right)}_{\text{slope}} x_n + \underbrace{\left(\frac{1}{R+1} x_D\right)}_{\text{intercept}}}$$

eq^n of operating line for ~~str~~ absorption section

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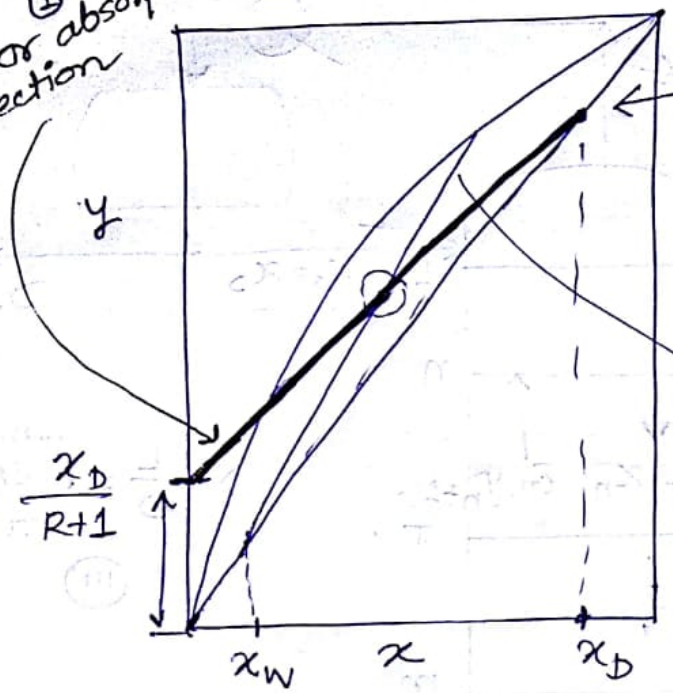
For envelop ① i.e for absorption section



at $x_n = x_D$

$y_{n+1} = \frac{R}{R+1} x_D + \frac{x_D}{R+1}$

$y_{n+1} = x_D$

for stripping section

Material balance at envelop ②

$\bar{L} = \bar{G} + W$ --- overall balance

$\Rightarrow \bar{G} = \bar{L} - W$

$\bar{G}\, y_{m+1} = \bar{L}\, x_m - W x_W$

$$y_{m+1} = \frac{\bar{L}}{\bar{G}} x_m - \frac{W}{\bar{G}} x_W$$

$$\boxed{y_{m+1} = \frac{\bar{L}}{\bar{L} - W} x_m - \frac{W}{\bar{L} - W} x_W}$$ for stripping section

at $x_m = x_W$, $y_{m+1} = x_W$

The operating lines intersect at the stage where feed is entering.

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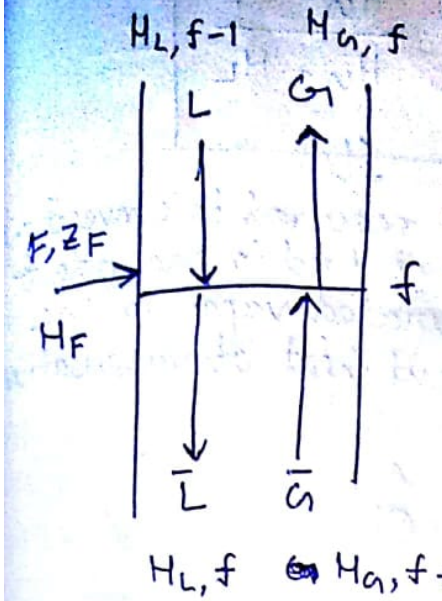

08/11/17

Overall material balance:

$$F + L + \bar{G} = \bar{L} + \bar{G}$$

$$\bar{G} - G = (\bar{L} - L) - F \quad \text{--- (I)}$$

Enthalpy balance:

$$F H_F + L H_{L,f-1} + \bar{G} H_{G,f+1} = \bar{L} H_{L,f} + G H_{G,f}$$

Assumption: Change in composition of the streams at the stage where feed is entering is not large. Thus we can conclude, $H_{L,f-1} = H_{L,f}$ and $H_{G,f} = H_{G,f+1}$

$$\Rightarrow F H_F + L H_L + \bar{G} H_G = \bar{L} H_L + G H_G$$

$$(\bar{G} - G) H_G = (\bar{L} - L) H_L - F H_F \quad \text{--- (II)}$$

Replacing $\bar{G} - G = (\bar{L} - L) + F$ from (I)

$$[(\bar{L} - L) - F] H_G = (\bar{L} - L) H_L - F H_F$$

$$(\bar{L} - L)(H_G - H_L) = F(H_G - H_F) \quad \text{--- (VI)}$$

$$\boxed{\frac{\bar{L} - L}{F} = \frac{H_G - H_F}{\underbrace{H_G - H_L}_{\text{Molar latent heat}}}} = q$$

H_G = specific enthalpy of saturated vapor

H_L = specific enthalpy of saturated liquid

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$\bar{L} - L = Fq$, $\boxed{q = \dfrac{H_G - H_F}{H_G - H_L}}$

$\Downarrow$

Heat required to convert one mole of feed to one mole of saturated vapor to the latent heat of vaporisation

$\bar{G} - G = Fq - F$

$$\boxed{\bar{G} - G = F(q-1)} \quad \text{--- (V)}$$

For stripping section

$$\bar{G}y = \bar{L}x - Wx_W \quad \text{--- (I)}$$

For absorption section

$$Gy = Lx + Dx_D \quad \text{--- (II)}$$

Substracting (II) from (I)

$$(\bar{G} - G)y = (\bar{L} - L)x - (Dx_D + Wx_W)$$

For entire column

$$F = D + W \quad \text{--- (III)}$$

$$FZ_F = Dx_D + Wx_W \quad \text{--- (IV)}$$

$$\Rightarrow \quad y = \left(\frac{\bar{L} - L}{\bar{G} - G}\right)x - \frac{FZ_F}{\bar{G} - G}$$

$$\boxed{y = \frac{Fq}{F(q-1)}x - \frac{FZ_F}{F(q-1)}}$$

Locus of point of intersection of top and bottom section operating line

$$\boxed{y = \frac{qx}{q-1} - \frac{Z_F}{q-1}} \quad \text{--- (VII)}$$

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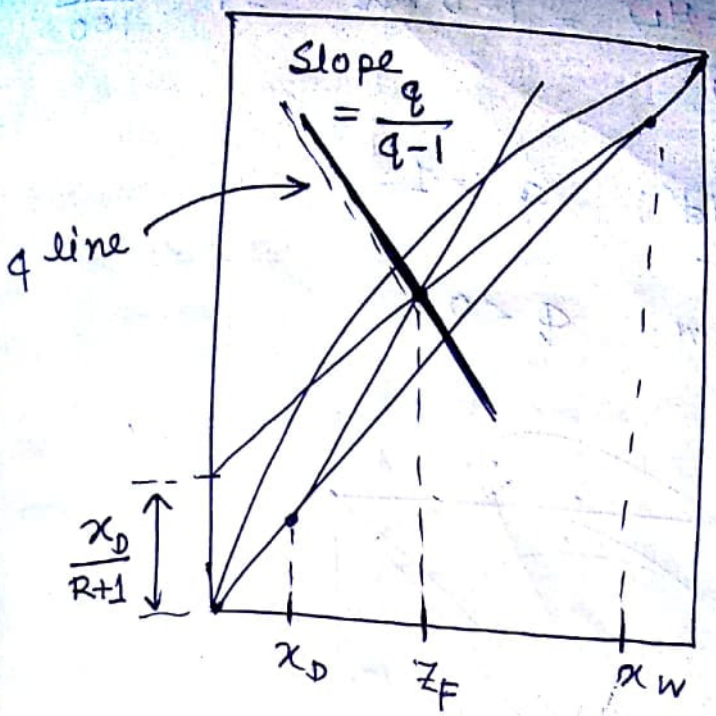
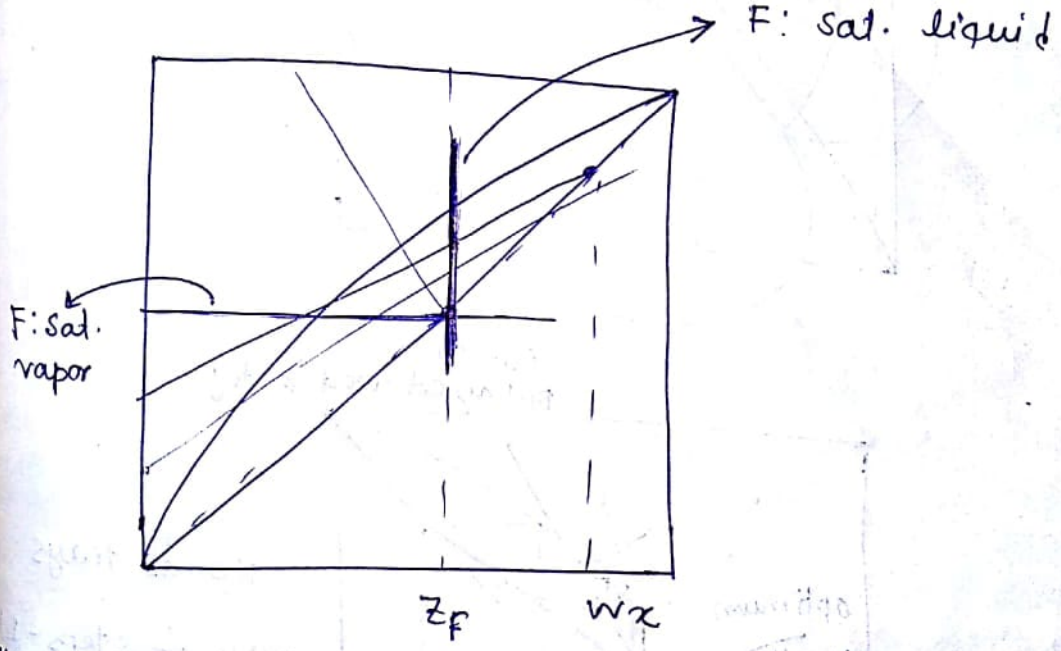


for $x = z_W$
from (VII)

$y = z_W$

i) Feed: Saturated liquid

$q = 1 \Rightarrow$ slope $= \infty$



ii) Feed: Saturated liquid, $q = 0 \Rightarrow$ slope $= 0$

iii) Feed: liquid + vapor, 'x'% vapor

$$q = \frac{H_G - \left(0.0x\, H_G + \frac{100-x}{100} H_L\right)}{H_G - H_L}$$

$$= \frac{(1-0.0x) H_G - (1-0.0x) H_L}{H_G - H_L}$$

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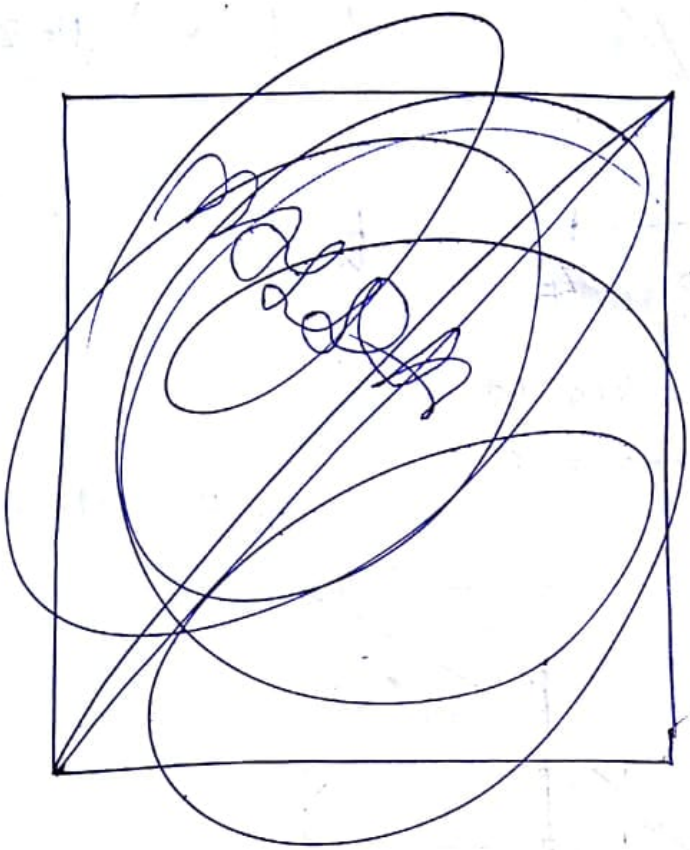
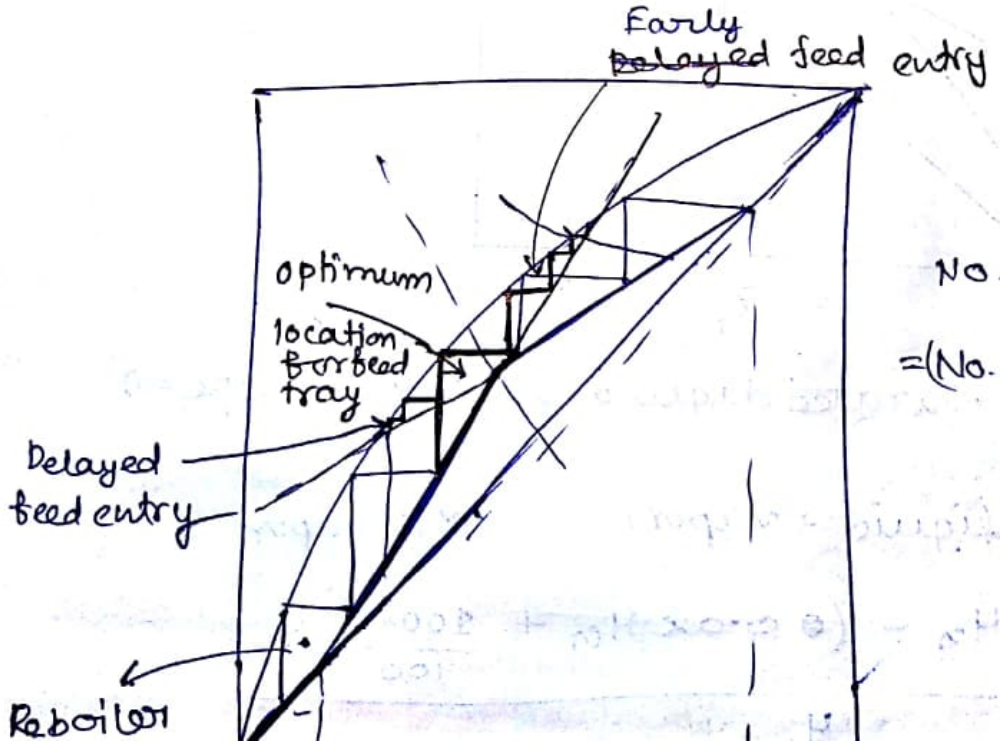
$$q = \frac{(1-0.0x)(H_G-H_L)}{(H_G-H_L)} = 1-0.0x = 1-\frac{x}{100}$$

iv) <u>Sub cooled liquid</u> : $q > 1$

v) Superheated vapor: $q < 0$





No. of trays

=(No. of steps-1)

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Note

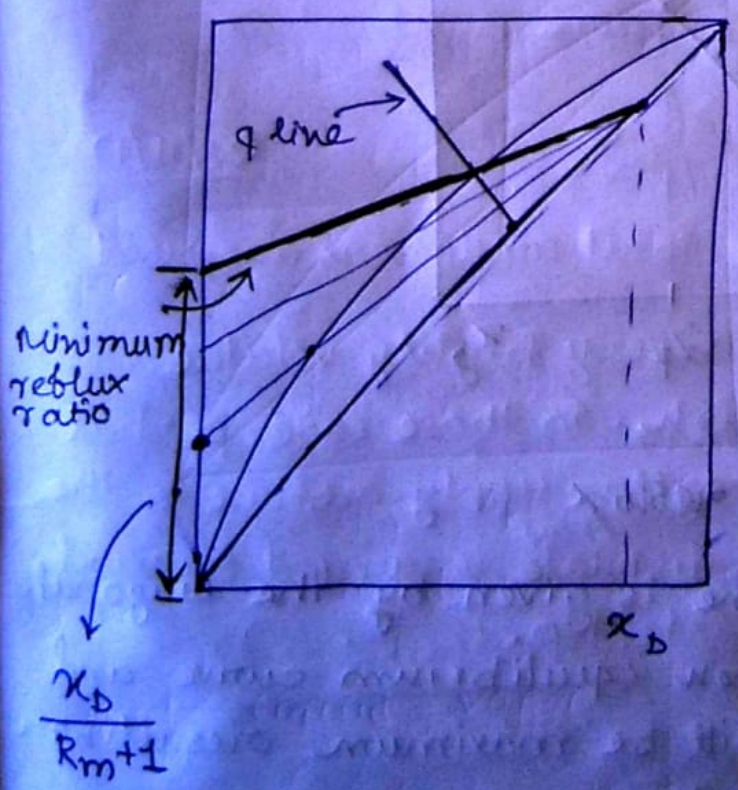
1) The tray corresponding to change in slope of operating line is feed tray (optimum location)

2) Delayed feed entry results in more no. of trays as the operating line approaches nearer to the equilibrium curve

- Optimum tray location is important for new tower design
- Delayed free entry is used in already functional tower to get desired product composition.

Reflux ratio

i) Minimum reflux ratio
ii) Optimum reflux ratio



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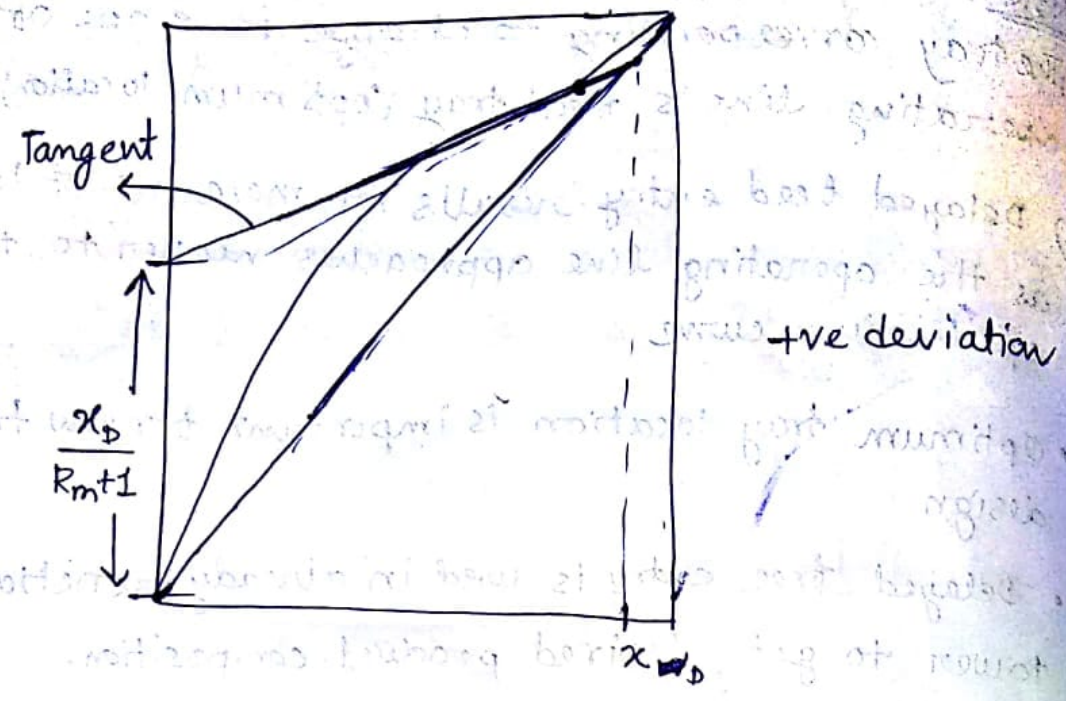

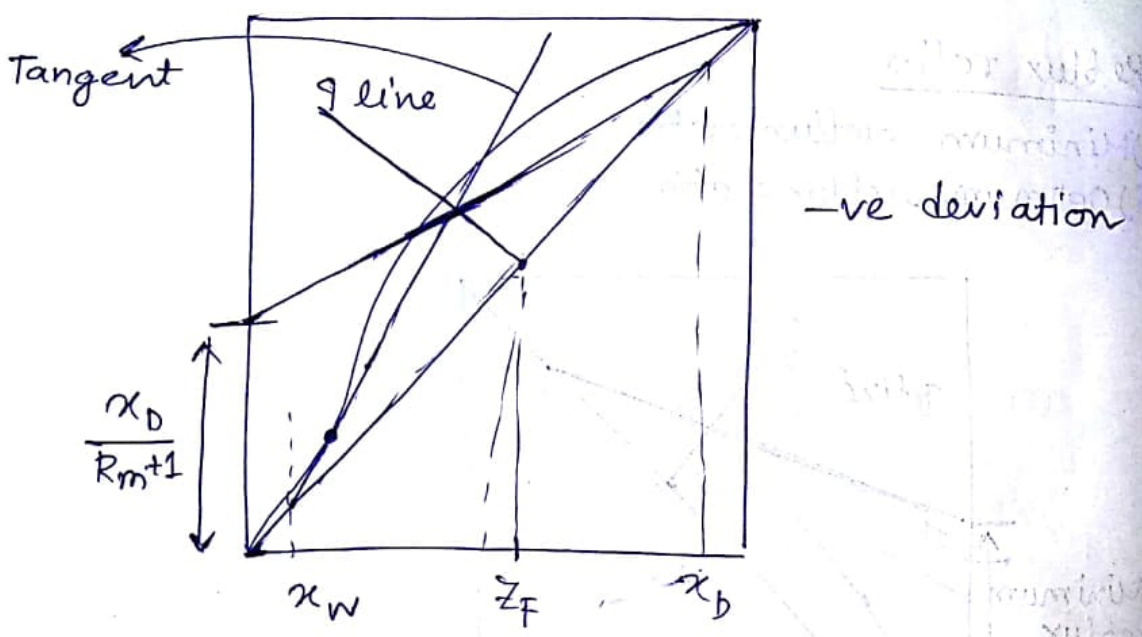

$R_m \to \infty \Rightarrow$ Total reflux

the operating line is given by the diagonal. i.e distance between equilibrium curve and operating line will be maximum resulting in minimum no. of trays

For minimum reflux ratio, no. of trays required is very high ($\to \infty$)

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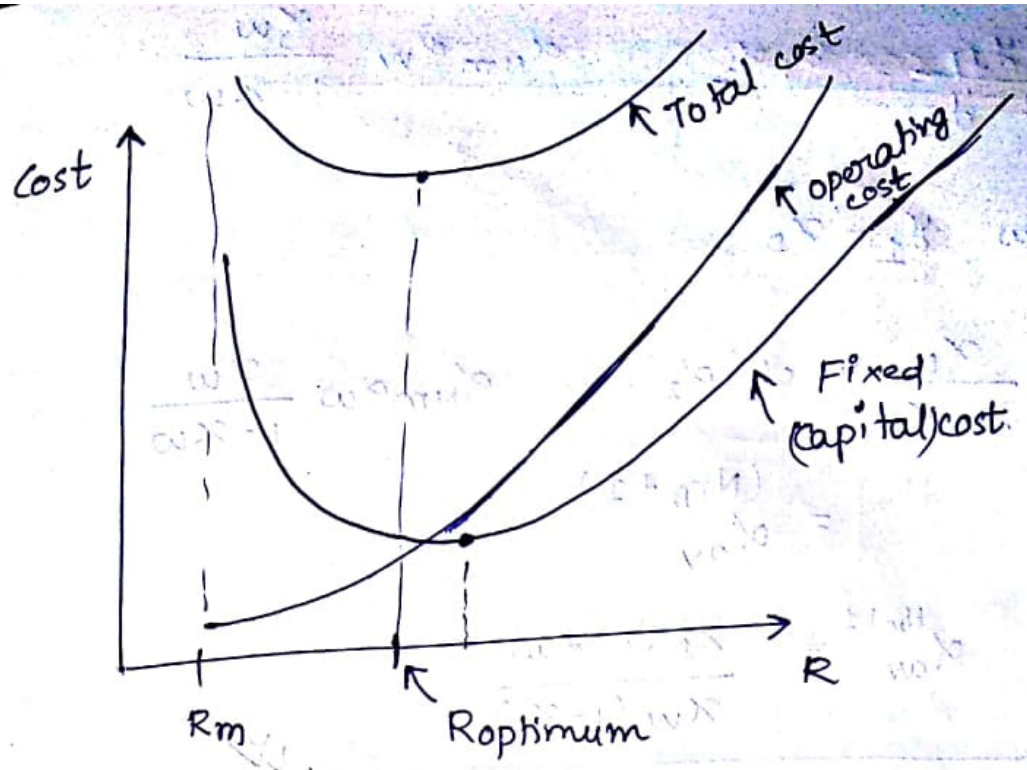
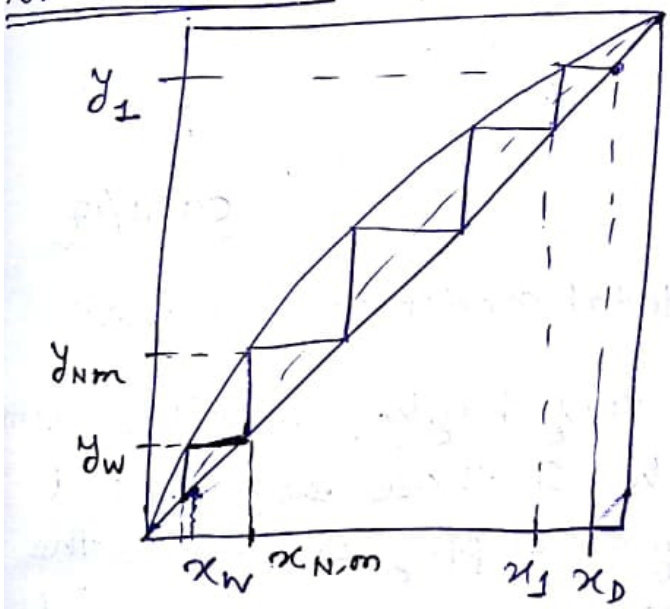


Usually,

$R_{optimum} \in (1.2 \text{ to } 1.8) \times R_m$

<u>For total Reflux</u>



$$\frac{y_W}{1-y_W} = \alpha_W \frac{x_W}{1-x_W}$$

$$\frac{x_{Nm}}{1-x_{Nm}} = \alpha_W \frac{x_W}{1-x_W}$$

$$\frac{y_{Nm}}{1-y_{Nm}} = \alpha_{Nm} \frac{x_{Nm}}{1-x_{Nm}} = \alpha_{Nm}\alpha_W \frac{x_W}{1-x_W}$$

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$$\frac{y_1}{1-y_1} = \alpha_1 \alpha_2 \cdots \alpha_{Nm} \alpha_w \frac{x_w}{1-x_w}$$

Now $y_1 = x_D$

$$\frac{x_D}{1-x_D} = \alpha_1 \cdot \alpha_2 \cdots \alpha_{Nm} \alpha_w \frac{x_w}{1-x_w}$$

$$= \alpha_{av}^{(Nm+1)}$$

or $$\alpha_{av}^{Nm+1} = \frac{x_D(1-x_w)}{x_w(1-x_D)}$$

$$\boxed{N_m + 1 = \frac{\log\left(\frac{x_D(1-x_w)}{x_w(1-x_D)}\right)}{\log \alpha_{av}}}$$ Fenske's Eqn

~~minimum~~ no. of stages

09/11/17

- In ideal situation, total condensers are used
- If top product is very highly volatile, condenser load will be very high. In those case, partial condenser is used only to supply reflux to the tower, rest of the distillate is carried forward as vapor to the next step.
- partial condenser
  - → Equilibrium partial condenser ($y_D \neq x_0$)
  - → Differential condenser (not feasible)
  - → Rapid condenser (There is no change in composition of distillate & reflux stream, $y_D = x_0$

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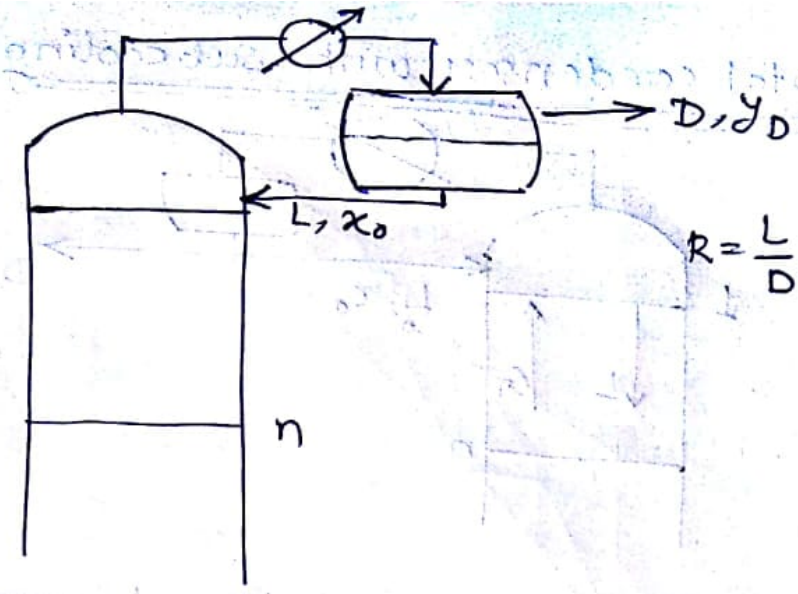
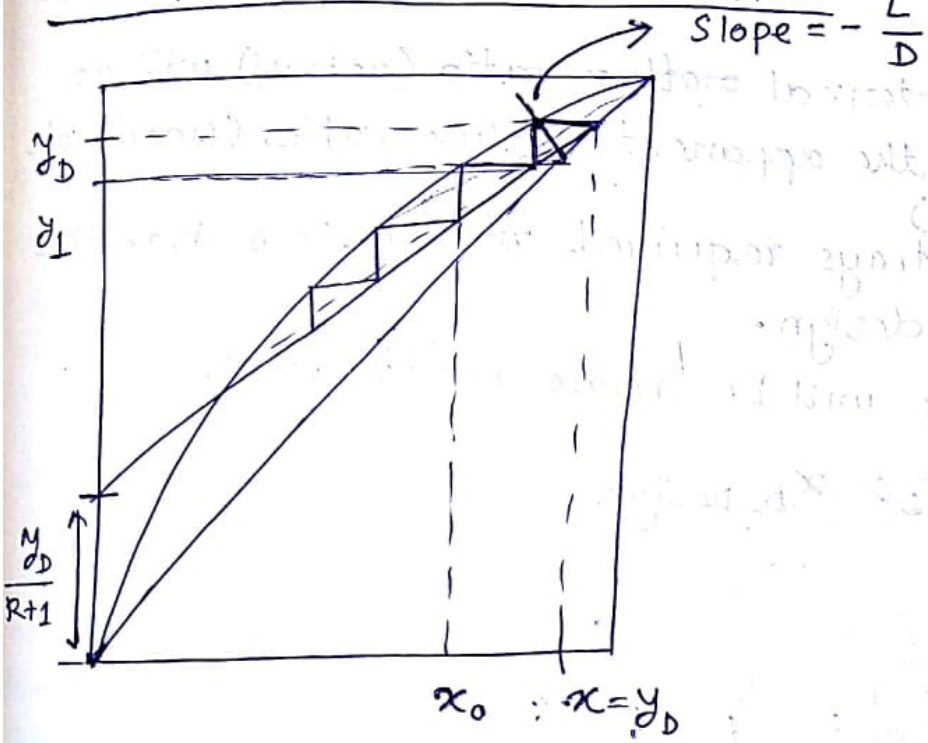


For Equilibrium Partial condenser



Total no. of trays

= (Total no of steps − 2)

1 + 1

Equilibrium partial condenser Reboiler

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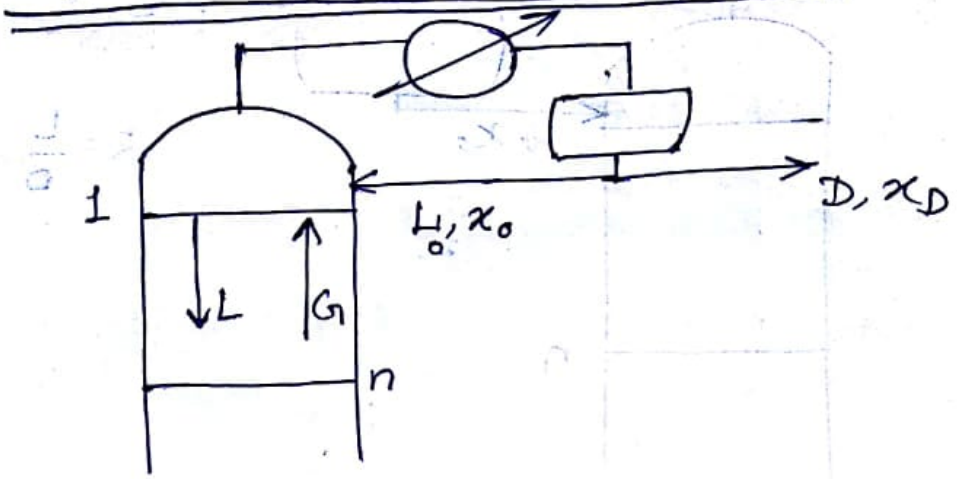
Total condenser with subcooling (cold Reflux)



- Results in condensation of vapor at the top tray
- So, the internal reflux ratio (actual) will go up than the apparent reflux ratio. (Liquid rate increases)
- No. of trays required, will be less than the actual in design.
- So, there will be more purification

$\Rightarrow \quad x_D > x_{D,\,design}$

$$R = \frac{L_o}{D}$$

$$L = L_o + \frac{L_o C_{Lo} M_{av} (t_{BP,R} - t_R)}{\lambda_{av}}$$

$$L = RD + \frac{RD_o C_{Lo} M_{av} (t_{BP,R} - t_R)}{\lambda_{av}}$$

$$L = RD\left[1 + \frac{C_{Lo} M_{av} (t_{BP,R} - t_R)}{\lambda_{av}}\right]$$

$$R' = \frac{L}{D} = R\left[1 + C_{Lo} M_{av} (t_{BP,R} - t_R)\right]$$

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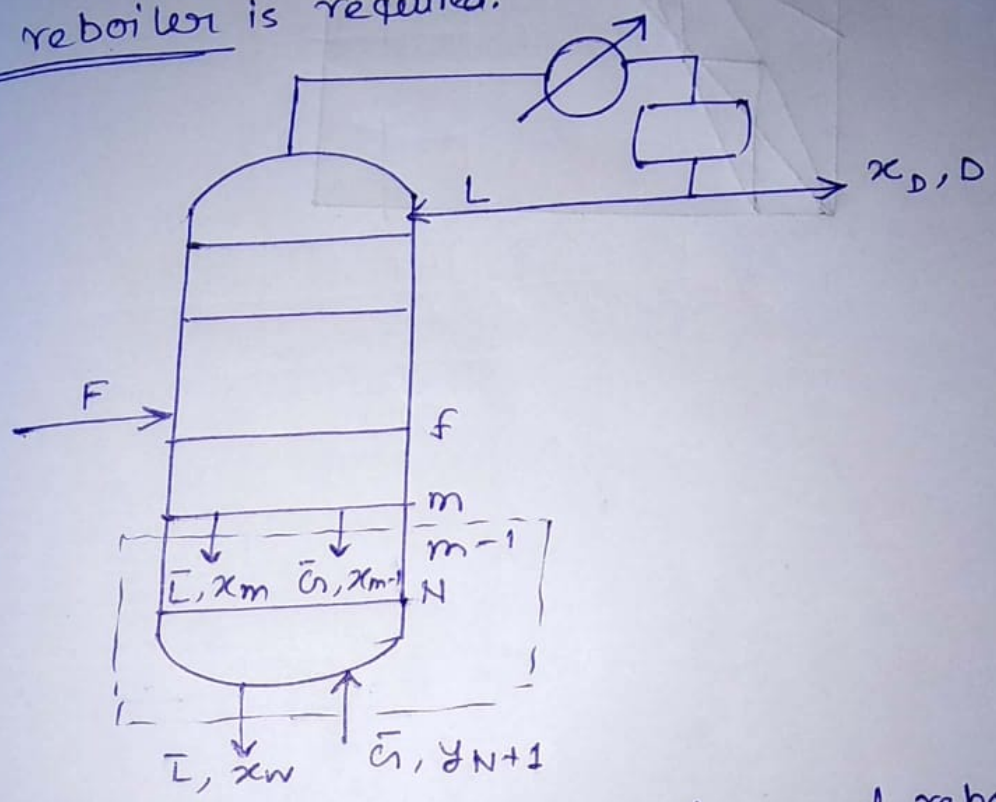
So, operating line:

$$y_{n+1} = \frac{R'}{R'+1} x_n + \frac{x_D}{R'+1} L$$

For aqueous sol^n (alcohol + water, ~~alcohol~~ acetic acid + water)

no. reboiler is required.



Because under product is water and reboiler is ~~using~~ producing steam, reboiler can be removed and instead utility steam stream can be fed

$$\bar{G}\, y_{m+1} + \bar{L}\, x_W = \bar{L}\, x_m + \bar{G}\, y_{N+1}$$

$$\frac{\bar{L}}{\bar{G}} = \frac{y_{m+1}}{x_m - x_W}$$

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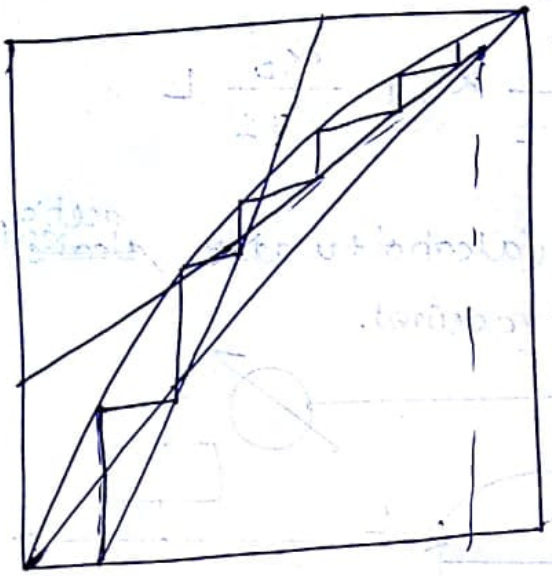

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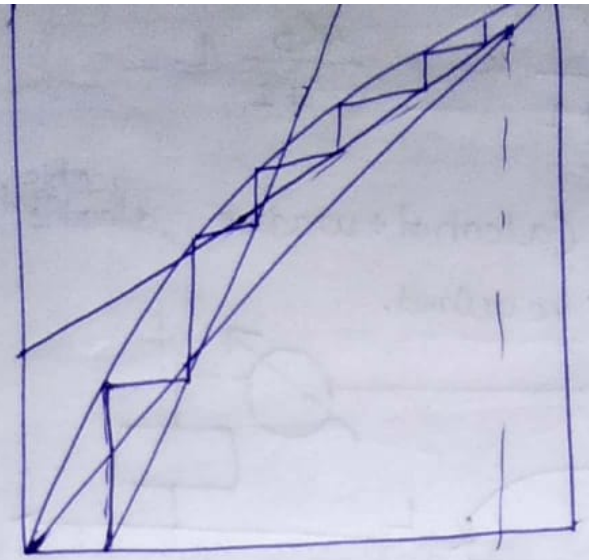

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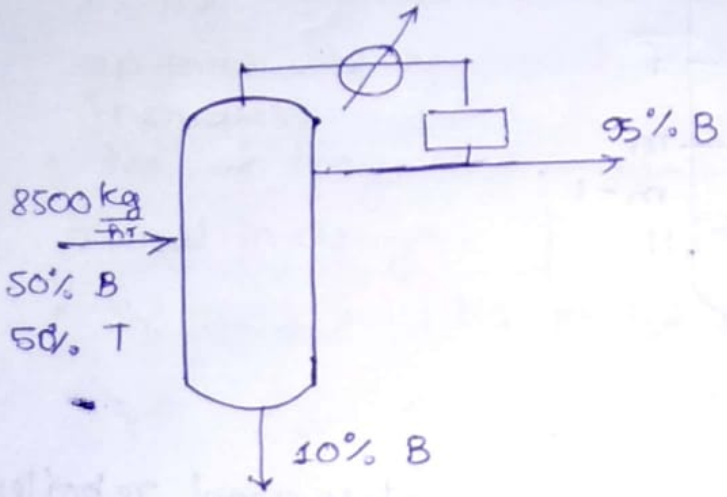

B = 78

T = 92

$(M_{av})_{Feed}$

= 39 + 46

= 85

No. of moles in feed

= 100 kmoles/hr.

Basis: 1 hr.

$50 = 0.95D + 0.1W$

$W + D = 100$

$W = 100 - D$

~~500~~ $50 = 0.95D + 0.1(100 - D)$

$50 = 0.95D + 10 - 0.1D$

$40 = 0.85D$

$D = \frac{40}{0.85} = 47.06$

$W = 52.94$

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~~D = 4263.53 kg/hr~~

$W = 52.94(0.478 + 0.9 \times 92)$

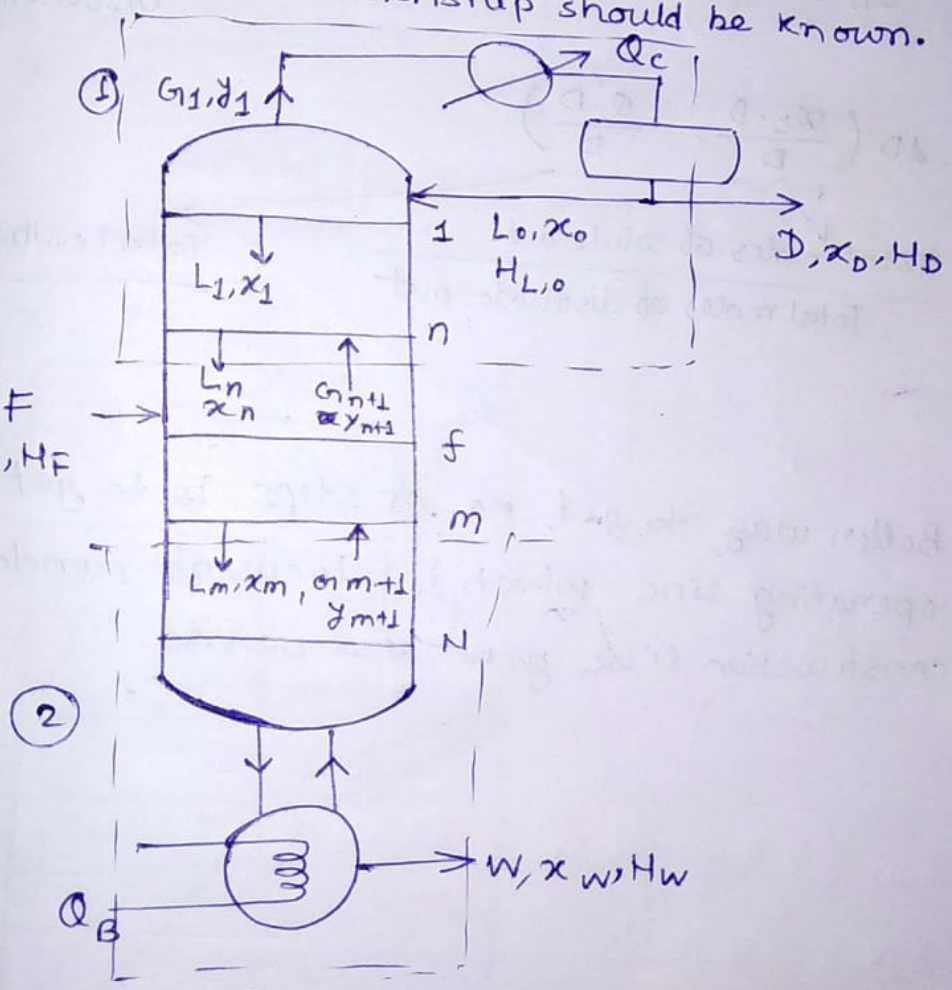
$= 4796.36$ kg/hr

$D = 3703.64$ kg/hr.

15/11/17

Ponchon & Savarit's Method (for determination of no. of ideal trays)

- Detailed enthalpy composition (H-x-y) as well as (y-x) curve or relationship should be known.



for envelop 1

$G_{n+1} = L_n + D$ --- overall component balance

$\Rightarrow G_{n+1} - L_n = D$

$G_{n+1} y_{n+1} - L_n x_n = D x_D$ ... component balance

$G_{n+1} H_{G,n+1} = L_n H_{L,n} + D H_D + Q_c$ ... enthalpy balance

$G_{n+1} H_{G,n+1} - L_n H_{L,n} = D\left(H_D + \frac{Q_c}{D}\right) = D Q'$

Eleminating D,

$$\frac{L_n}{G_{n+1}} = \frac{x_D - y_{n+1}}{x_D - x_n} = \frac{Q' - H_{G,n+1}}{Q' - H_{L,n}}$$

The line passes through

$L_n(x_n, H_{L,n})$, $G_{n+1}(y_{n+1}, H_{G,n+1})$, $\Delta D(x_D, Q')$

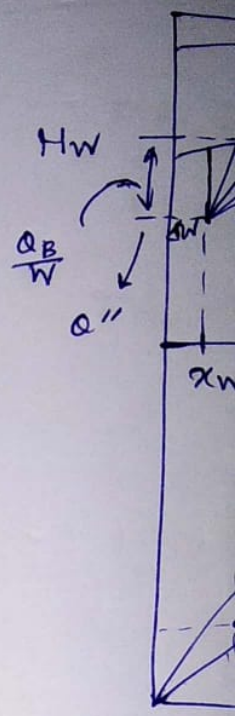
Difference point

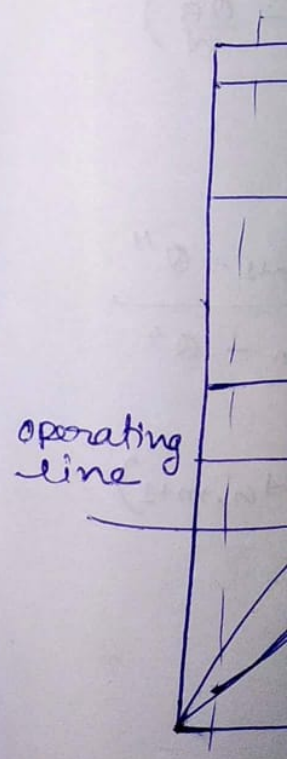
$$\Delta D\left(\frac{x_D \cdot D}{D}, \frac{Q' \cdot D}{D}\right)$$

$\frac{\text{Total moles of solute out}}{\text{Total moles of distillate out}}$

$\frac{\text{Total enthalpy of solute out}}{\text{" " of distillate out}}$

- Better way to get no. of steps is to get an operating line which is locus of random construction line generated points





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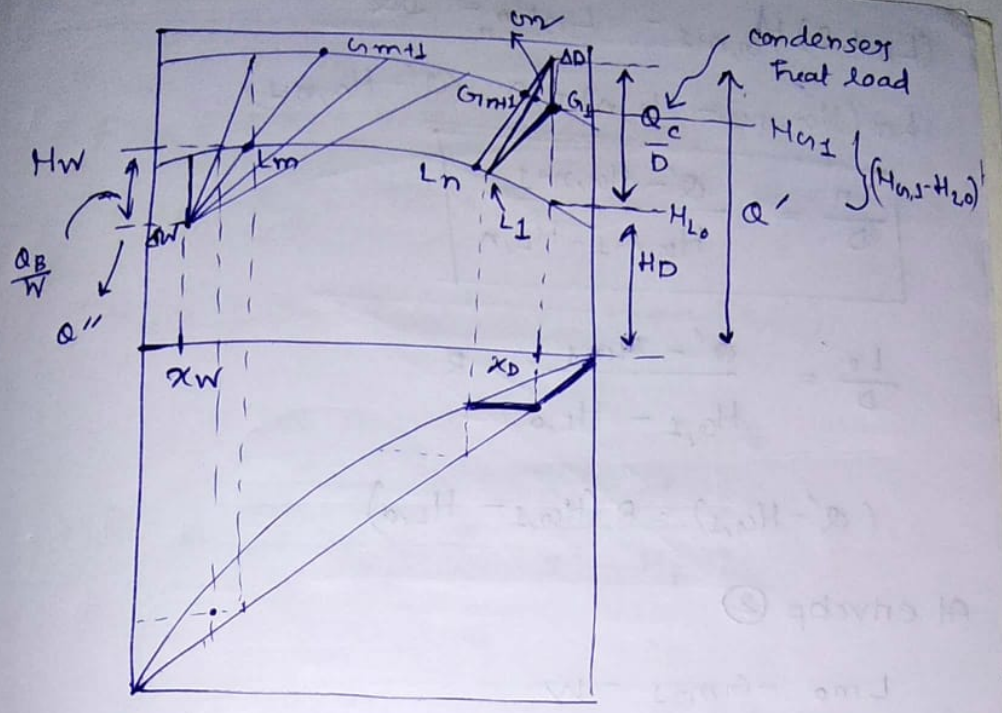
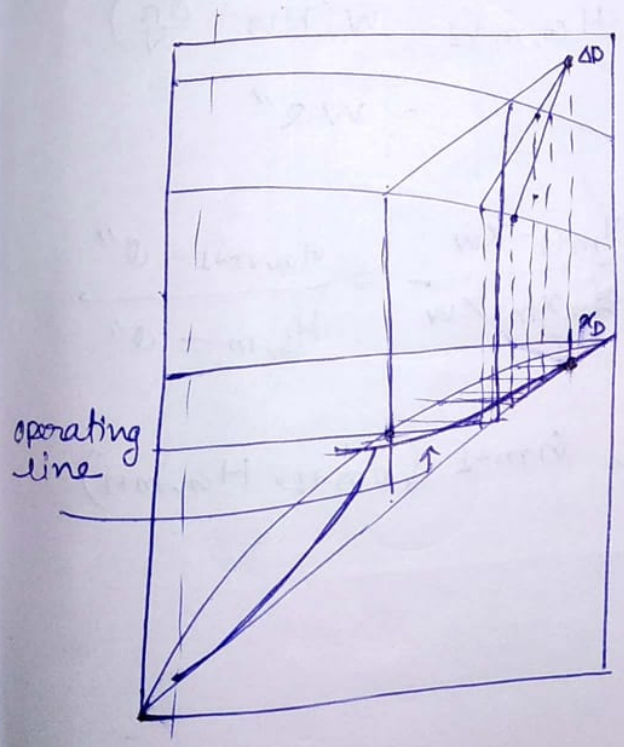

condenser
heat load
G_{m+1}
G_m
ΔD
G_{n+1}
G_1
Q_c
D
$H_{G_{n+1}}$
$(H_{G_{n+1}} - H_{L_0})'$
H_W
L_m
L_n
L_1
H_{L_0}
Q'
ΔW
$\frac{Q_B}{W}$
Q''
H_D
x_W
x_D


ΔD
x_D
operating line

$$(L_n + D) H_{G,n+1} - L_n H_{L,n} = DQ'$$

$$L_n (H_{G,n+1} - H_{L,n}) = D \; (Q' - H_{G,n+1})$$

$$\boxed{\frac{L_n}{D} = \frac{Q' - H_{G,n+1}}{H_{G,n+1} - H_{L,n}}}$$

$$\frac{L_0}{D} = \frac{Q' - H_{G,1}}{H_{G,1} - H_{L,0}} = R$$

$$(Q' - H_{G,1}) = R\,(H_{G,1} - H_{L,0})$$

At envelop ②

$$L_m - G_{m+1} = W$$

$$L_m x_m - G_{m+1} y_{m+1} = W x_W$$

$$H_{L,m} L_m + Q_B = G_{m+1} H_{G,m+1} + W H_W$$

$$\Rightarrow L_m H_{L,m} - G_{m+1} H_{G,m+1} = W\left(H_W - \frac{Q_B}{W}\right)$$

$$= W Q''$$

$$\frac{L_m}{G_{m+1}} = \frac{y_{m+1} - x_W}{x_m - x_W} = \frac{H_{G,m+1} - Q''}{H_{L,m} - Q''}$$

$L_m \; (x_m, H_{L,m})$, $G_{m+1} \; (y_{m+1}, H_{G,m+1})$

$\Delta W \; (x_W, Q'')$

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For whole tower

$$F = D + W$$

$$F z_F = D x_D + W x_W$$

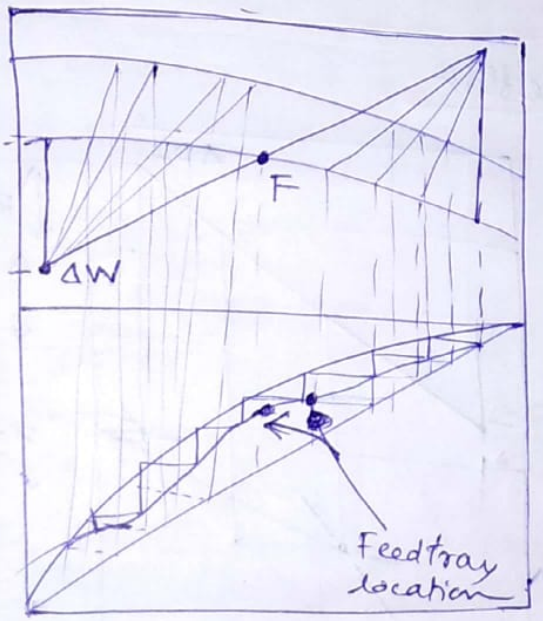
$$F H_F + Q_B = D H_D + Q_c + W H_W$$

Ignoring heat loss to the surrounding

$$F H_F = D(H_D + Q_c/D) + W(H_W - Q_B/W)$$

$$= DQ' + WQ''$$

$$\frac{D}{W} = \frac{z_F - x_W}{x_D - z_F} = \frac{H_F - Q''}{Q' - H_F}$$



considering feed to be liquid at bubble point

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Special Type of Distillation (Imp for GATE) 16/11/17

- used for separating, binary mixture having very low rel. volatility or azeotropic mixture.

- For normal distillation, if relative volatility is very small then
  - → tower should be longer
  - → huge sized reboiler & condenser are required leading to higher cost.

- **Azeotropic Distillation**

(A+B) Relative volatility is very low

+C ← Component C forms low boiling azeotrope either with A or with B.

↓

Component C is called entrainer

eg:- water + Acetic acid
(A) (B)
100°C 118·1°C
+
Butyl acetate
(C)
125°C

Buty Acetate + water form a low boiling azeotrope
90·2°C
72 mole% water

From top, azeotropic mixture is obtained. From bottom almost pure acetic acid is obtained. Water & Butyl Acetate form hetero azeotrope which separate in components on condensation.

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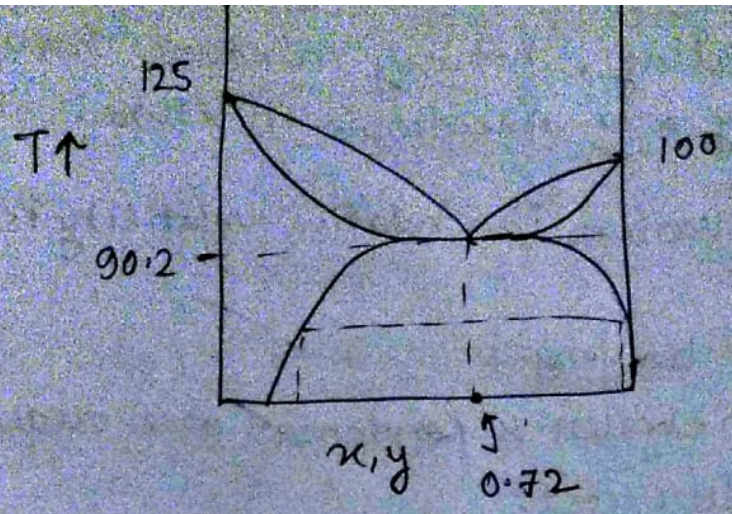

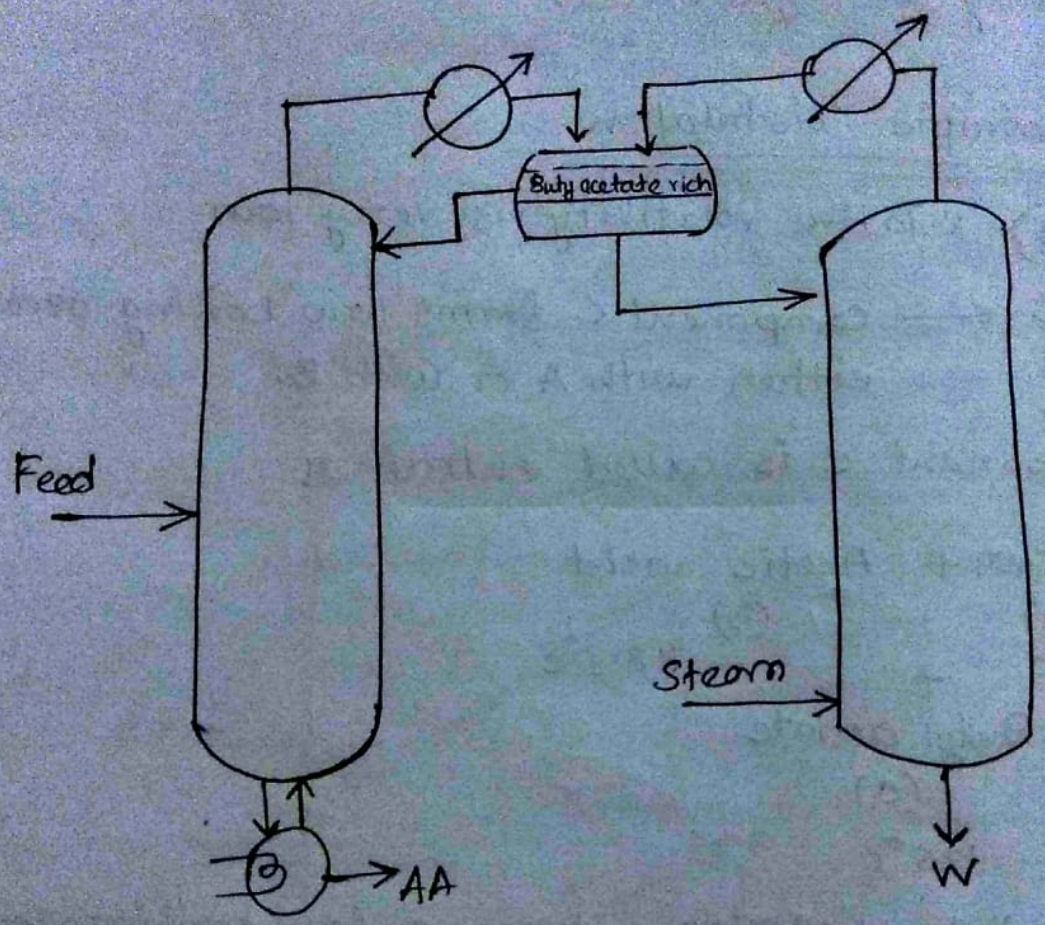

- Entrainer should be such that, it ~~should~~ forms heteroazeotrope with the minority component.
- Entrainer should have low latent heat of vaporisation.

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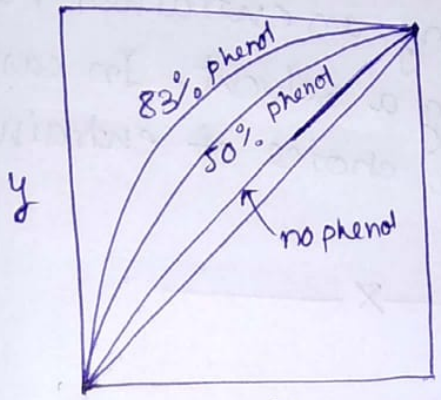
Extractive Distillation:

- Relative volatility of the components is very low.

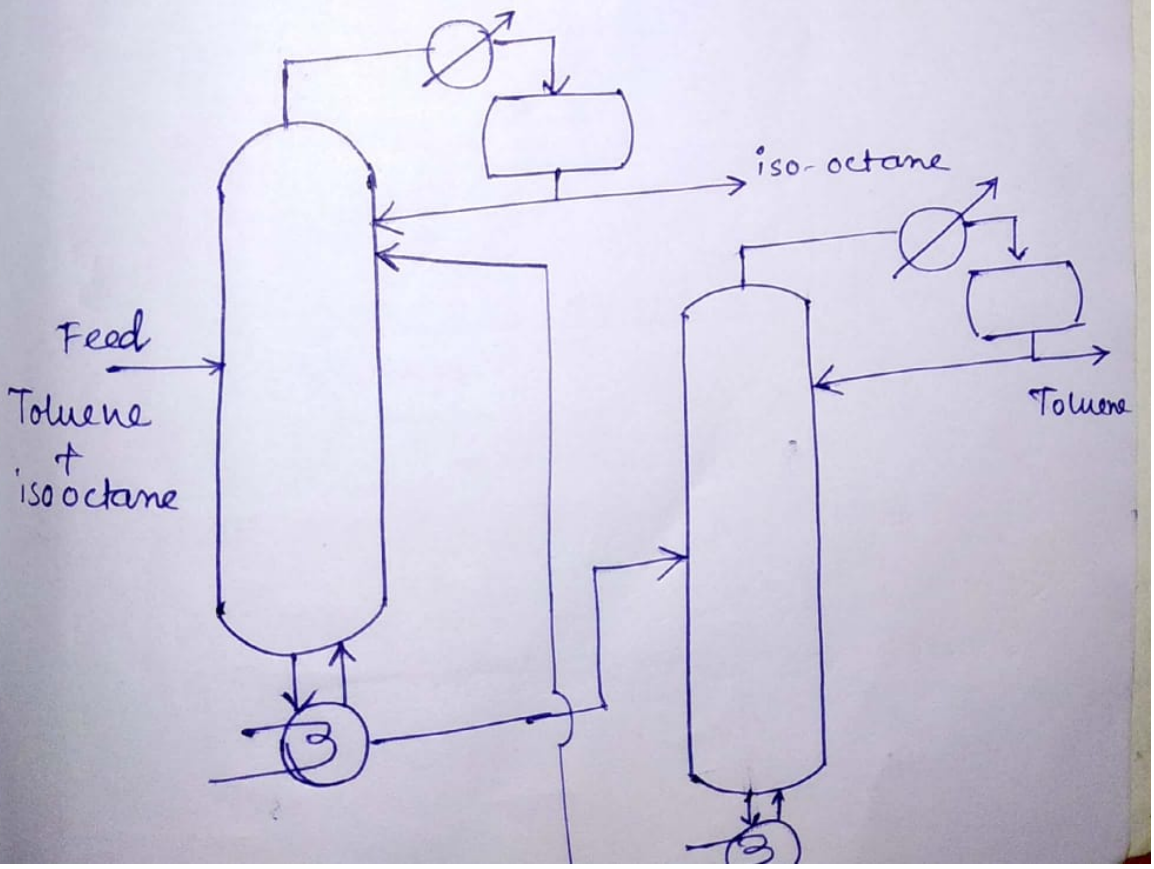
(A+B) + C

↳ solvent, changes the relative volatility of the components

Iso octane (A) 99.3°C + Toluene (B) 110.8°C + Phenol (C) 181.4°C



x, y → phenol free basis



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1) Selectivity: The solvent should be of high selectivity. It should be able to change the vapor liquid equilibria by great extent

2) Capacity: Solubility of component should be high. Solvents capacity to dissolve the component should be high

3) Volatility: should be low.

4) viscosity ↓, freezing point ↓, non-corrosive, non-toxic

For a system, finding an entrainer is difficult compared to selecting a solvent. In case of azeortopic distillation, choice of entrainer is limited

———x———

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