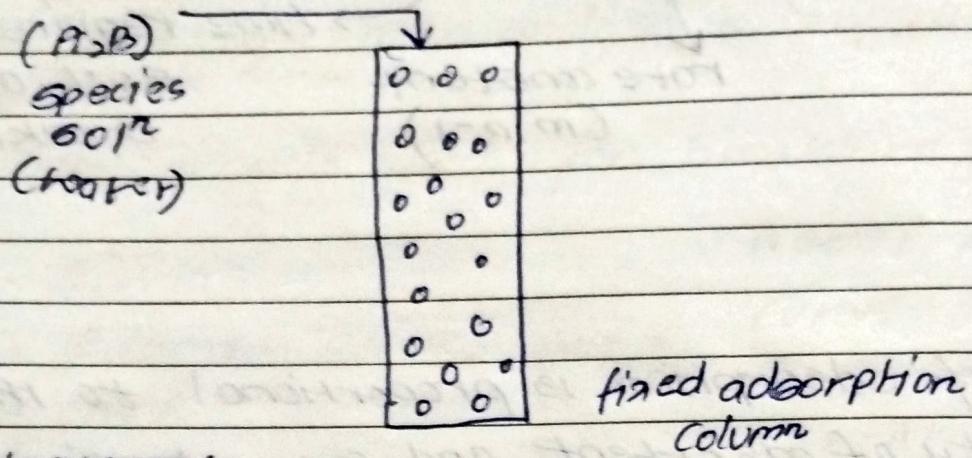
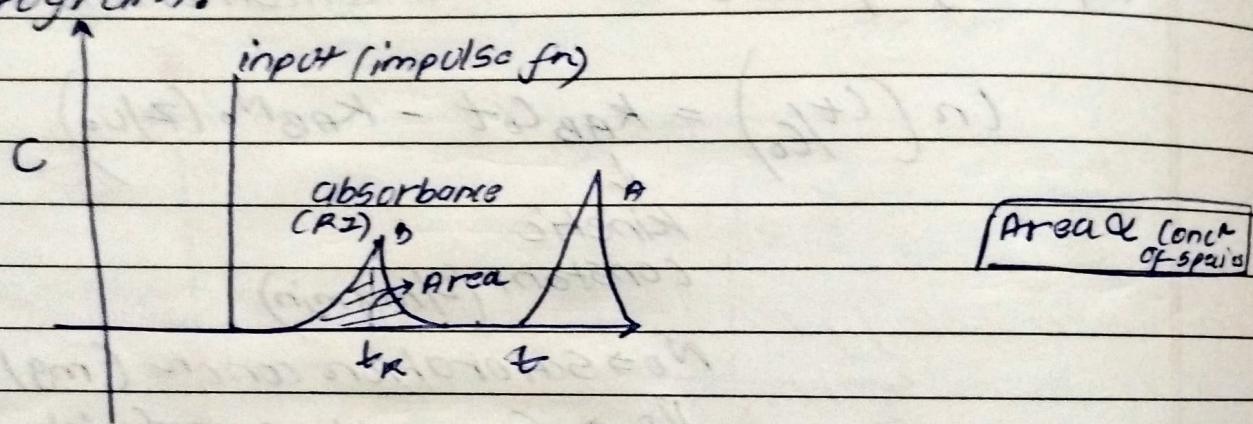


→ Chromatography:



Chromatogram:

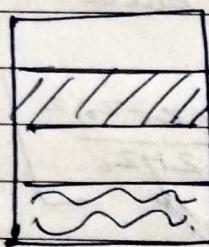
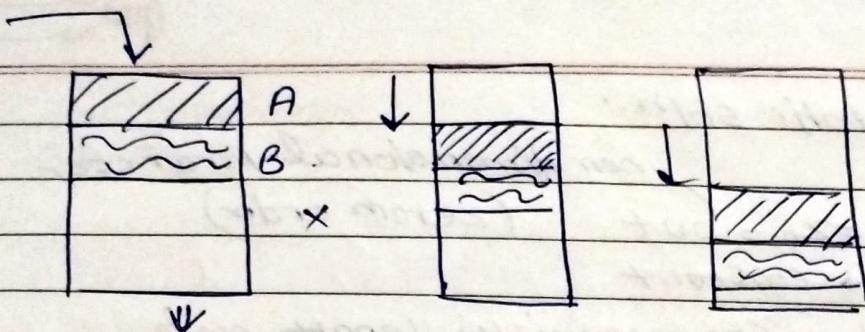


- Solution - mobile phase
- Bed - stationary phase
- Sample injection in pulse

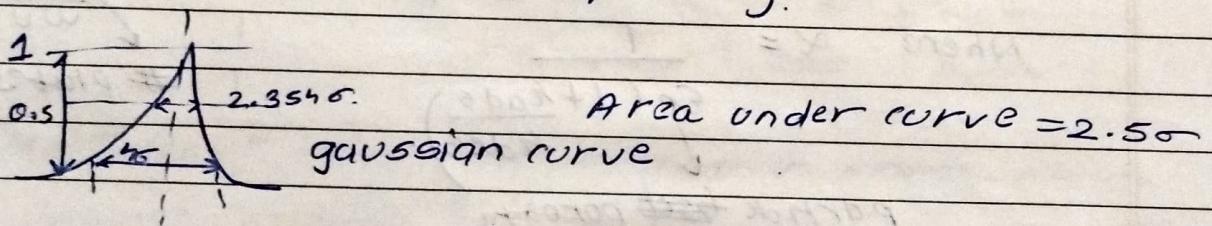
$$q_A = \frac{H_A C_A}{1 + H_A C_A + H_B C_B}$$

$$q_B = \frac{H_B C_B}{1 + H_A C_A + H_B C_B}$$

Selectivity: $\frac{H_A/C_A}{H_B/C_B} \left\{ \frac{H_A/H_B}{q_A/q_B} \right\} \left\{ q_A/q_B \right\}$



- Residence time (helps in identification of species)
- Peak area/ height (helps in determining concn of species).



- Species balance:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} = \frac{1-\epsilon}{\epsilon} \frac{\partial \bar{q}}{\partial t}$$

$$\bar{q} = \frac{1}{R} \int_0^R q dr \quad (\text{cross sectional average})$$

Diffusion (intra & inter particle)

$$\frac{4}{3} \pi R_p^3 \frac{\partial \bar{q}}{\partial t} = 4 \pi R_p^2 k [\bar{q}^* - \bar{c}]$$

mass transfer coefficient.

Pulse input

$$C(t) = \frac{m_0 \delta(z)}{Ae}$$

↓
Solute mass

Length of column (L) = $N \times H$



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→ Asymptotic soln

$$@ z=z_0 = w_0 t \quad (\text{zeroth order})$$

w → constant

$w_0 t \rightarrow$ characteristic length scale

$$C(z,t) = \frac{m_0 w}{A \sqrt{2 \pi H z_0}} \exp \left[-\frac{(z-z_0)^2}{2 H z_0} \right]$$

Gaussian fn.

$$w = \frac{1}{1 + \frac{1-\epsilon}{\epsilon} \alpha}$$

$$\sigma = \sqrt{\frac{H}{w u}}$$

where

$$\text{Where } \alpha = \frac{1}{\epsilon p (1 + \frac{k_{ads}}{k_{des}})}$$

$$\overline{F} = \frac{N H}{w u}$$

plates

particle bed porosity.

$$\rightarrow H \equiv 2 \left(\frac{D}{u} + \frac{w(1-w) R_p u}{3 \alpha k_{tot}} \right)$$

$k_{tot} \rightarrow$ total mass transfer coefficient

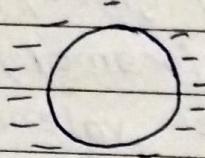
$$k_{tot} = \frac{1}{k_c} + \frac{R_p}{S E P D_p} + \frac{3}{R_p k_{ads} S E P} \left(\frac{k_{ads}}{1+k_{ads}} \right)^2$$

Resolving power:

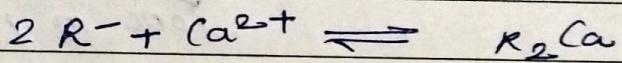
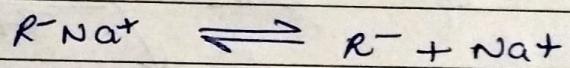
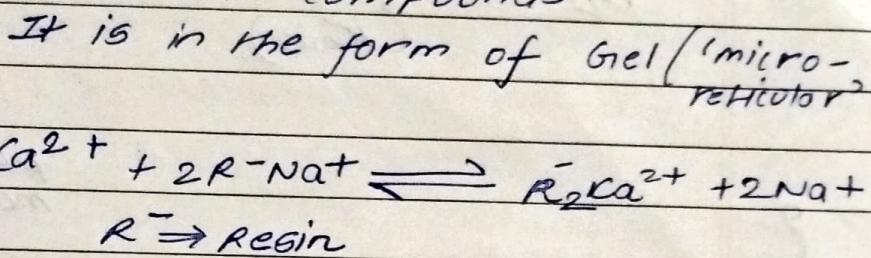
$$R_{ij} = \frac{s_{ij} \sqrt{N}}{w_i + w_j}$$

$$\text{where } s_{ij} = \frac{z' |w_i - w_j|}{w_i + w_j}$$

→ Ion exchange: equilibria



Polymeric resins made up of aromatic compounds.



$$\frac{k_1 - k_2}{k_3}$$

Mg²⁺/Ca²⁺ salts are present in water which increase water's hardness.

∴ Ion exchange can be used to convert hard water to soft water

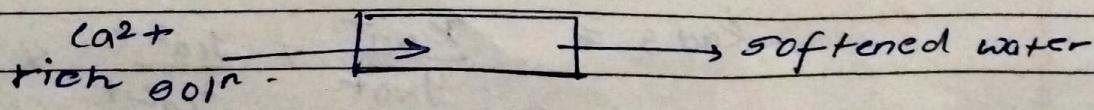
Also,

- Used for treating boiler feed water to avoid scaling.
- Used to deionise water.

$$\text{Ionic eqm constant (K)} = \frac{k_{Ca^{2+}}}{k_{Na^+}}$$

(for all ions) \leftrightarrow Ce → ionic concn in soln

(for all ions) \leftrightarrow Qe → ionic concn in adsorbent (resin).



$$Q_e \approx f(Ce)$$

Separation factor

$$S_{A,B} = \frac{y_A / y_B}{x_A / x_B}$$

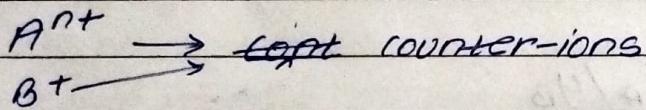
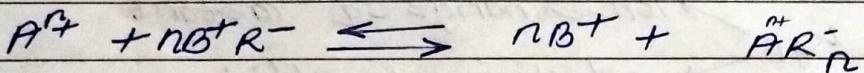
Exn:

$$k_f = k_f q_A^n +$$

$$k_b = k_b (q_B)^n$$

→ self-study:

→ Ion exchange equilibria:



$R \rightarrow$ ion exchange resin

$$K_{AB} = \frac{q_A q_R^n \times (C_B^+)^n}{(q_B R)^n \times (C_A^+)} \downarrow$$

ion exchange equilibrium constant

$C \rightarrow$ total concn of solution

$\phi \rightarrow$ total concn of resin phase

$y_i \rightarrow$ equivalent fraction of counterion (i) in resin phase

$\gamma_i \rightarrow$ equivalent fraction of counterion (i) in solution (mobile phase)

$z_i \rightarrow$ charge / valence of ion.

$$\frac{C \gamma_i}{z_i} = c_i$$

$$\frac{\phi y_i}{z_i} = q_i$$

c_i & q_i are in equivalents

$$K_{AB} = \frac{\phi y_A}{\phi (q_B)^n} \times \frac{C_B^n \times \phi}{C_A^n}$$

$$K_{AB} = \frac{y_A}{x_A} \times \left(\frac{x_B}{y_B} \right)^n \times \left(\frac{c}{\phi} \right)^{n-1}$$

$$K_{AB} = \frac{y_A}{x_A} \left(\frac{1-x_A}{1-y_A} \right)^n \left(\frac{c}{\phi} \right)^{n-1}$$

$x_A + x_B = 1$
 $y_A + y_B = 1$] for two counter-ion system.

K_{AB} → ion-exchange eq^m constant
 ↓ → selectivity co-efficient.

$$\alpha_{AB} = \frac{y_A/x_B}{x_A/y_B}$$

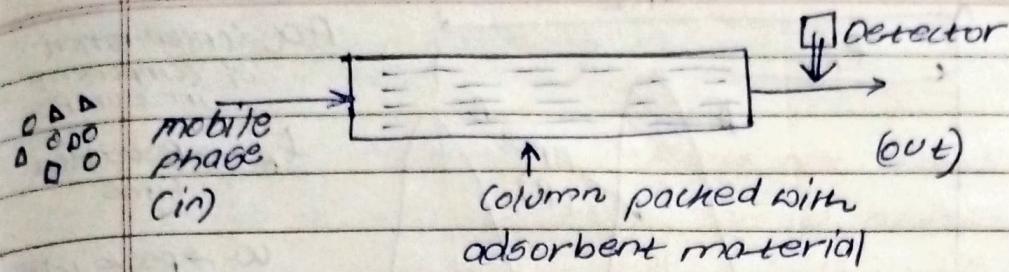
separation factor for the exchange of ions B in the resin by ions A present in the solution.

Definition:

Ion-exchange is a separation process in which a solid containing mobile ~~ions~~, replaceable ions is contacted with a solution of an ionisable species, where the mobile ions of the solid are exchanged by ions of similar charge in the solution.

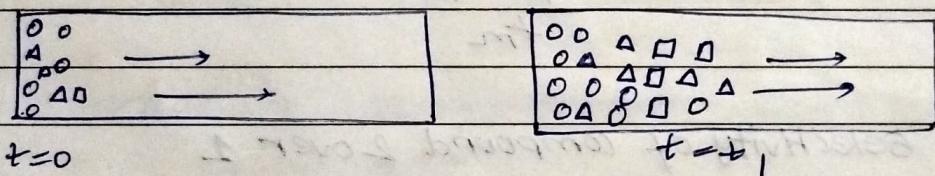
→ chromatography:

- Separation technique used for analytical purpose.
 The technique is based on difference in affinities of the compounds in a mixture towards a suitable adsorbent

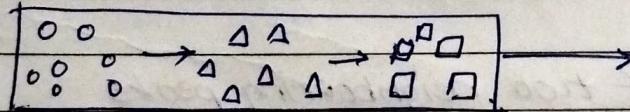


A component in the mobile phase is retarded less or more wrt others depending upon its affinity to the adsorbent. As a result the components get separated along the column.

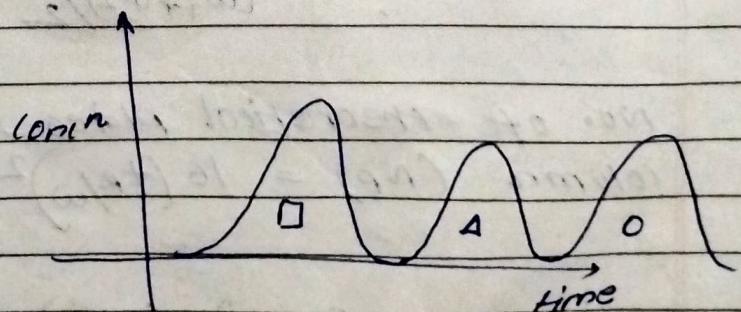
A detector detects the concentrations of components in outlet mobile phase as a fn time. The concentration of a component appears as distinct peaks on a plot called the chromatogram.



$t = t_2$



chromatogram



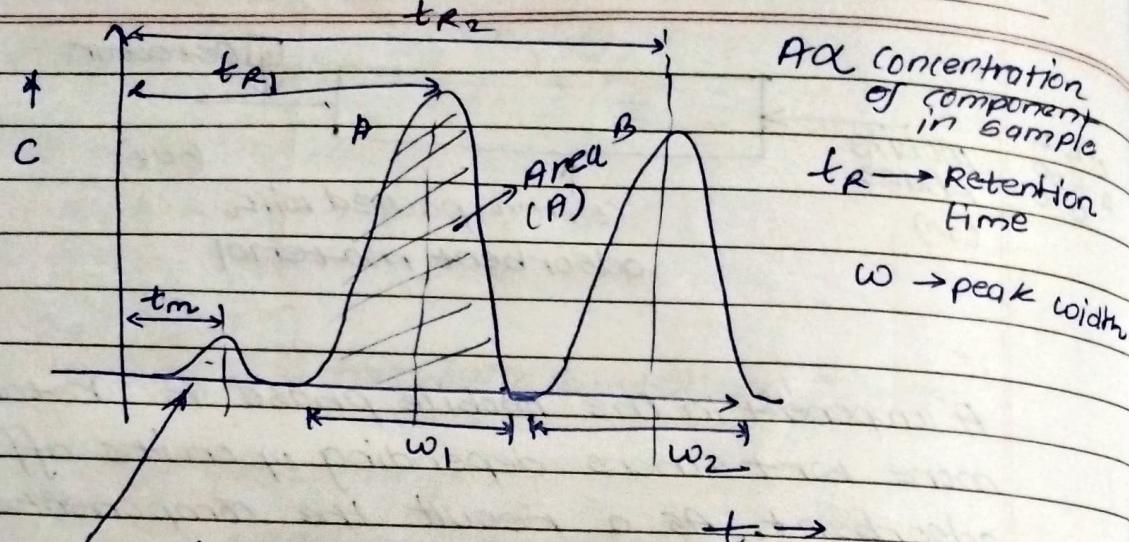
$$k' \text{ (capacity factor)} = \frac{\text{total amount of solute in stationary phase}}{\text{total amount of solute in mobile phase}}$$

The peaks we get are usually normally distributed gaussian conc/bell shaped.



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The small peak is because of a non-retained substance, which was there before the sample was injected.

$$k' = \frac{t_R - t_m}{t_m}$$

Selectivity of compound 2 over 1

$$\alpha_{21} = \frac{t_{R2} - t_m}{t_{R1} - t_m}$$

Resolution of two neighbouring peaks

$$R' = \frac{t_{R2} - t_{R1}}{(w_1 + w_2)/2}$$

No. of theoretical plates in chromatographic column (N_p) = $16 (t_R/\omega)^2$

$$R' = \left(\frac{\alpha - 1}{2} \right) \left(\frac{k'}{1 + k'} \right) \sqrt{N_p}$$

$$k' = \frac{k'_1 + k'_2}{2}$$

→ Peak broadening & Tailing.

If the dispersion effects are small in the plug flow then a sharp peak can be obtained corresponding to the impulse/pulse injection of sample.

Dispersion effects make a broader peak and reduce its height. If peaks of various components broaden then adjacent peaks may partially overlap.

In many cases, the rear end of a peak is found to spread out forming a tail. This is called tailing.

→ Note calibration graphs can be used to determine conc'n of components in unknown samples.

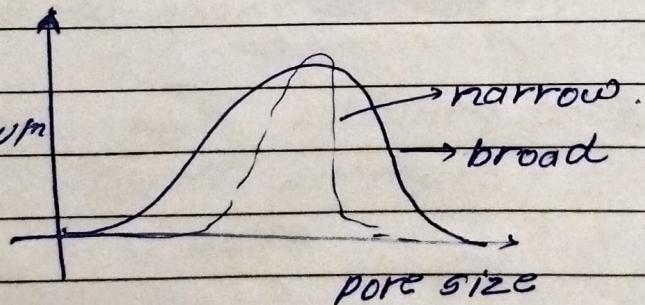
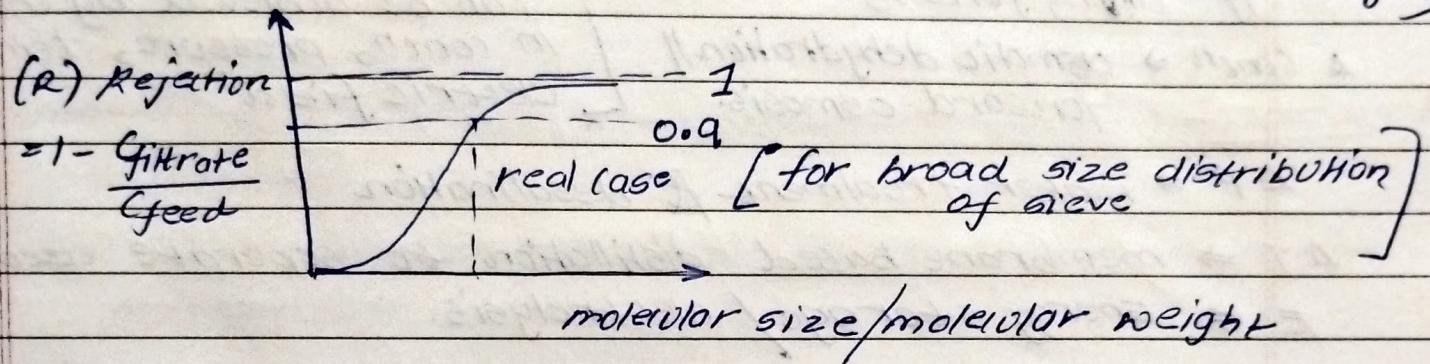
$$P_0 \Rightarrow$$

* numerical on chromatography & ion exchange equilibria from BKD

→ Membrane Separation:

Membranes in general work on the principle of sieving
 [Molecular sieves]

↳ Separation happens based on molecular size
 (molecular weight)



Molecular weight cut off (MWCO)

maximind® = MW at which $R = 0.9$

<u>Pore size / MW</u>	<u>Type of filtration.</u>	<u>Application</u>
10 μm - 0.1 μm	microfiltration	
0.1 μm - 2 kDa	ultra-filtration	
Permeability reduces reduces 2 kDa - 200 Da (or 2 kDa)	nanofiltration	dye separation
↓ 0.2 kDa	reverse osmosis.	separation of ions

→ Transport process through membranes.

membranes are porous medium.

flow through porous medium is described by

Darcy's law: $v \propto$ driving force

[change in chemical potential]

if driving force is

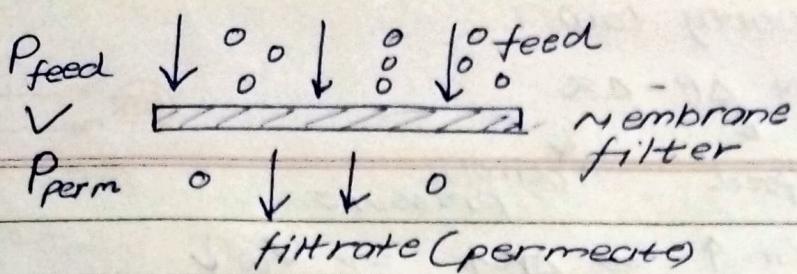
A concn \Rightarrow osmotic dehydration // forward osmosis.

can be achieved by change
in concn, pressure, temperature,
electric field

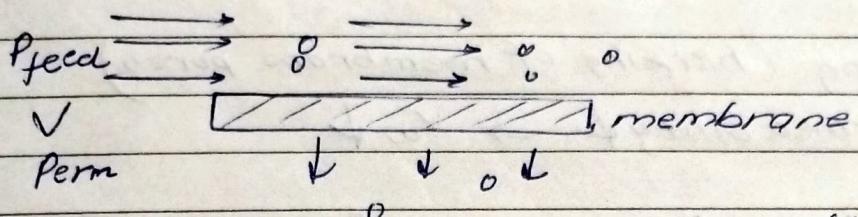
ΔP \Rightarrow water treatment & desalination

ΔT \Rightarrow membrane based distillation to separate azeotropes

E \Rightarrow Energy storage / electrolysis.

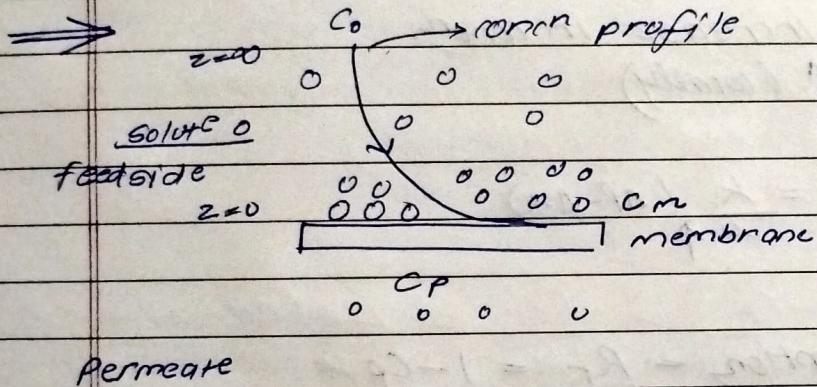


- feed flow is normal to membrane surface.



- cross flow occurring.

feed flow is parallel to membrane surface.



- the above phenomena is called as concentration polarization.

Consequences:

1. $C_m >$ solubility limit
then we will observe precipitation.

Precipitation will result in physical layer formation on membrane surface and will pose additional resistance to mass transfer.

2. for high solubility limit.

$$\text{osmotic pressure} = f(C_m) - f(C_p)$$

for salts $\propto = \alpha C$

$$\Delta P = \alpha (C_m - C_p)$$

from Darcy law

$$V_w \sim \Delta P - \Delta z$$

P_{feed} osmotic pressure

$$C_m \uparrow \Rightarrow \Delta z \uparrow \Rightarrow V_w \downarrow$$

Separation occurs as long as $\Delta P > \Delta z$ but rate will continue to decrease.

3. Fouling (blocking of membrane pores)

(k) permeability $\downarrow \Rightarrow V_w \downarrow$

$$\downarrow V_w = \frac{k}{\mu} (\Delta P - \Delta z) \quad [\text{Darcy eqn}]$$

4. Bcoz of increase in concn.
 $\mu \uparrow$ (locally)

$$\therefore \downarrow V_w = \frac{k}{\mu \uparrow} (\Delta P - \Delta z)$$

example: real retention = $R_r = 1 - \frac{C_p}{C_m}$

observed retention = $R_o = 1 - \frac{C_p}{C_0}$

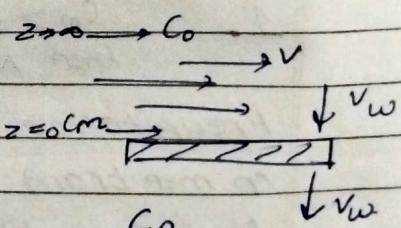
$$R_r \geq R_o \quad [\because C_m \geq C_0]$$

species balance:



$$V_w \ll V$$

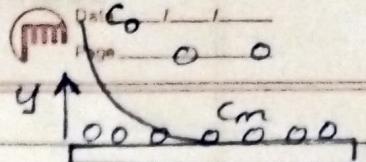
∴ flow in vertical direction won't be affected.



$$V_w = \frac{k}{\mu} (\Delta P)$$

solvent velocity (permeation rate/velocity)

$$V_w \times C \Rightarrow \text{solute flow}$$



flux balance:

$$\text{in-out} = 0 \quad \text{at } ss$$

$$V_w C - V_w C_p + D \frac{\partial C}{\partial y} = 0$$

$$V_w C + D \frac{\partial C}{\partial y} = V_w C_p$$

$$C_p \leftarrow C_m$$

$$D \frac{\partial C}{\partial y} = V_w (C_p - C)$$

$$\int_D \frac{\partial C}{C_p - C} dy = \int_{C_m}^S V_w dy$$

$\delta \Rightarrow$ thickness
of boundary
layer
 $\delta \neq f(x)$

$$-D \ln \left(\frac{C_p - C_0}{C_p - C_m} \right) = \delta V_w$$

$$\frac{C_p - C_0}{C_p - C_m} = e^{-\frac{\delta V_w}{D}}$$

$$C_p - C_0 = (C_p - C_m) e^{-\frac{\delta V_w}{D}}$$

$$C_p (1 - e^{-\frac{\delta V_w}{D}}) = C_0 + C_m e^{-\frac{\delta V_w}{D}}$$

$$C_p = \frac{C_0 + C_m e^{-\frac{\delta V_w}{D}}}{1 - e^{-\frac{\delta V_w}{D}}}$$

from film theory:

$$k = D/S$$

mass transfer coefficient

$$\therefore \ln \left(\frac{C_m - C_p}{C_0 - C_p} \right) = \frac{V_w S}{D} = \frac{V_w}{K} \quad \dots \quad (1)$$

from Darcy's law

$$D = \frac{k}{\mu} (\Delta P - \Delta \pi)$$

Driving force

$$D = L_p (\Delta P - \Delta \pi)$$

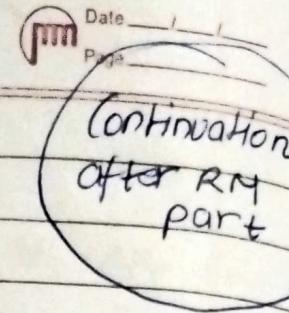
$\hookrightarrow m^2/Pas$

osmotic pressure is significant for low MW solutes

$$\tau \sim \frac{RT}{MW}$$

$$\tau \sim \frac{RT}{\underbrace{MW}_{\alpha}}$$

$$\therefore \Delta \tau \sim \alpha(c_m - c_p)$$



$$\therefore v_w = L_p (\Delta P - \alpha(c_m - c_p)) \quad \text{--- (2)}$$

↓ known ↓ known
membrane Property

unknown // c_m, c_p, v_w

$$R_r = 1 - c_p/c_m \quad \text{--- (3)}$$

↓ real retention

Sgn 1, 2, 3 & 3 unknowns.

$$\ln \left(\frac{c_m - c_p}{c_0 - c_p} \right) = \frac{v_w}{K} = \frac{L_p (\Delta P - \alpha(c_m - c_p))}{K}$$

$$(1 - R_r) c_p = c_p/c_m$$

$$c_m = c_p / 1 - R_r$$

$$\frac{c_p / 1 - R_r - c_p}{c_0 - c_p} = \exp \left[\frac{L_p (\Delta P - \alpha \left(\frac{c_p - c_p}{1 - R_r} \right))}{K} \right]$$

Implicit eqn $\Rightarrow \frac{R_r c_p}{(c_0 - c_p)(1 - R_r)} = \exp \left[\frac{L_p (\Delta P - \alpha R_r c_p)}{K} \right]$

Sherwood no. relation

$$Sh = 1.86 \left(\frac{Re Sc}{d_e} \right)^{1/3} \quad \text{laminar flow}$$

$$= 0.023 Re^{0.8} Sc^{1/3} \quad \text{turbulent flow}$$

for hollow fibre,

$$Sh = 1.6 \left(\frac{Re Sc d_e}{d_f} \right)^{1/3} \quad \text{laminar}$$

Turbulent is same

$$V_W = L_P \left[\Delta P - \frac{\alpha R_r C_0 e^{V_W/K}}{R_r + (1-R_r)e^{V_W/K}} \right]$$

Simplified scenario:

1. NO polarisation,

$$C_m = C_0$$

$$e^{V_W/K} = 1$$

$$V_W = L_P \left[\Delta P - \frac{\alpha R_r C_0}{R_r + (1-R_r)e^{V_W/K}} \right]$$

$$V_W = L_P [\Delta P - \alpha R_r C_0]$$

2. Low polarisation, $C_m > C_0$

but not very high

$$e^{V_W/K} \approx 1 + \frac{V_W}{K}$$

$$V_W = L_P \left[\Delta P - \frac{\alpha R_r C_0 (1 + V_W/K)}{R_r + (1-R_r)(1 + V_W/K)} \right]$$

$$V_W = L_P \left[\Delta P - \frac{\alpha R_r C_0 (1 + V_W/K)}{+ (1-R_r)(1 + V_W/K)} \right]$$

quadratic eqn.

$$V_W \left[1 + (1-R_r) \left(\frac{1+V_W}{K} \right) \right] = L_P \Delta P \left[(1-R_r) \left(\frac{1+V_W}{K} \right) + 1 \right] - L_P \alpha R_r C_0 \left(\frac{1+V_W}{K} \right)$$

$$V_{W0} + V_{W2} + \frac{V_{W2}^2}{K} - R_r V_W - \frac{R_r V_W^2}{K} = L_P \Delta P + \frac{L_P \Delta P V_W}{K} - R_r L_P \Delta P - R_r \frac{L_P \Delta P}{K} \left(\frac{V_W}{K} + 1 \right) + L_P \Delta P$$

$$- L_P \alpha R_r C_0 - L_P \alpha R_r C_0 \frac{V_W}{K}$$

$$V_w^2 \left(\frac{1-R_r}{K} \right) + V_w \left(2 - R_r - \frac{L_p \Delta P}{K} + \frac{R_r L_p \Delta P}{K} + \frac{L_p \alpha R_r C_0}{K} \right) \\ - 2 L_p \Delta P + R_r L_p \Delta P + L_p \alpha R_r C_0 = 0$$

$$V_w^2 \left(\frac{1-R_r}{K} \right) + V_w \left(2 - R_r + \frac{L_p \Delta P}{K} \left(-1 + R_r + \frac{\alpha R_r C_0}{\Delta P K} \right) \right) \\ + L_p \left(-2 \Delta P + R_r \Delta P + \alpha R_r C_0 \right) = 0$$

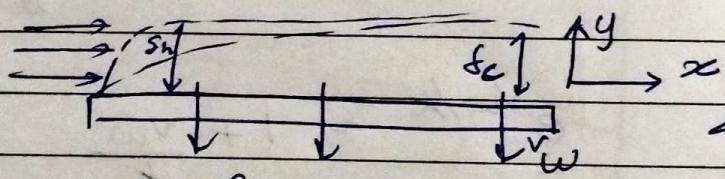
3. Low polarisation and perfectly rejecting membrane. $C_p \rightarrow 0$

$$R_r \rightarrow 1$$

$$V_w = L_p \left[\Delta P - \alpha C_0 \left(1 + \frac{V_w}{K} \right) \right]$$

~~approx~~

~~Dimensional~~



2-dimensional flow

$f_c \neq \text{constant}$

$$f = f(x)$$

∴ we use
2-dimensional
approach.

$$s_c = (f_c/f_h)^{1/3}$$

Species transport eqn

$$\frac{\partial c}{\partial x} + \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} + \cancel{D \frac{\partial^2 c}{\partial z^2}}$$

for fibre type arrangement

$$\frac{\partial c}{\partial z} + \frac{\partial c}{\partial r} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right)$$

$$V \sim -V_w$$



$$\frac{v \partial c}{\partial x} - v_w \frac{\partial c}{\partial y} = \rho \frac{\partial^2 c}{\partial y^2}$$

B.C. @ $y=0 \Rightarrow c = c_0$ (inlet)

$$@ y=0, v_w c + \rho \frac{\partial c}{\partial y} = v_w c_p$$

@ $y \rightarrow \delta_c, c \approx c_0 \Rightarrow \frac{\partial c}{\partial y} = 0$

$$v_w = L_P \left(\Delta P - \alpha (c_{l y=0} - c_p) \right)$$

$$R_f = 1 - \frac{c_p}{c_{l y=0}}$$

$$U \Rightarrow U_0 \left[1 - \left(\frac{2y}{d_e} \right)^2 \right] \Rightarrow \text{Poisson's eq.}^n.$$