



Spring Semester course

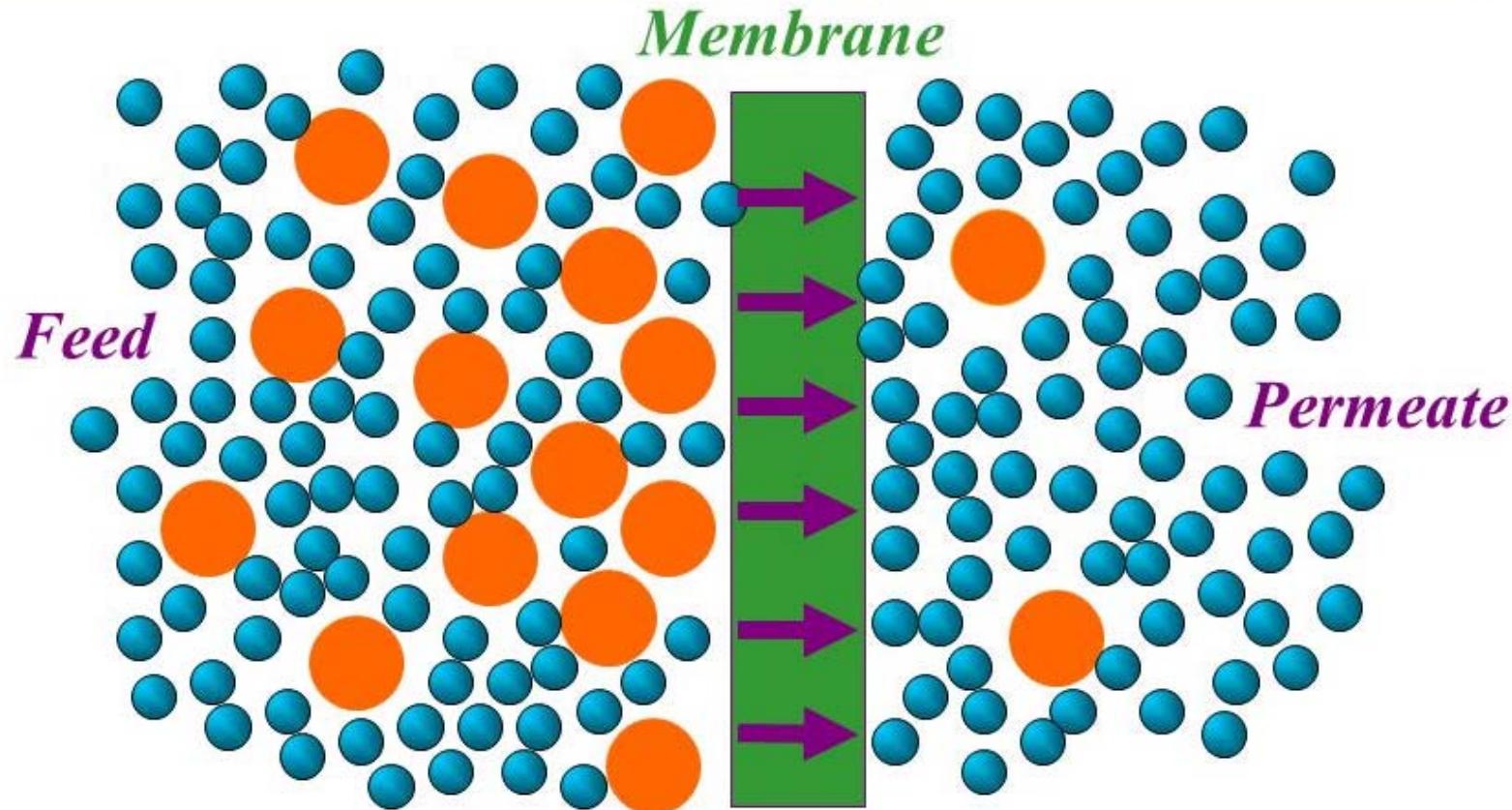
CH31010: Mass Transfer II

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L5: Membrane Separation

Membrane Separation

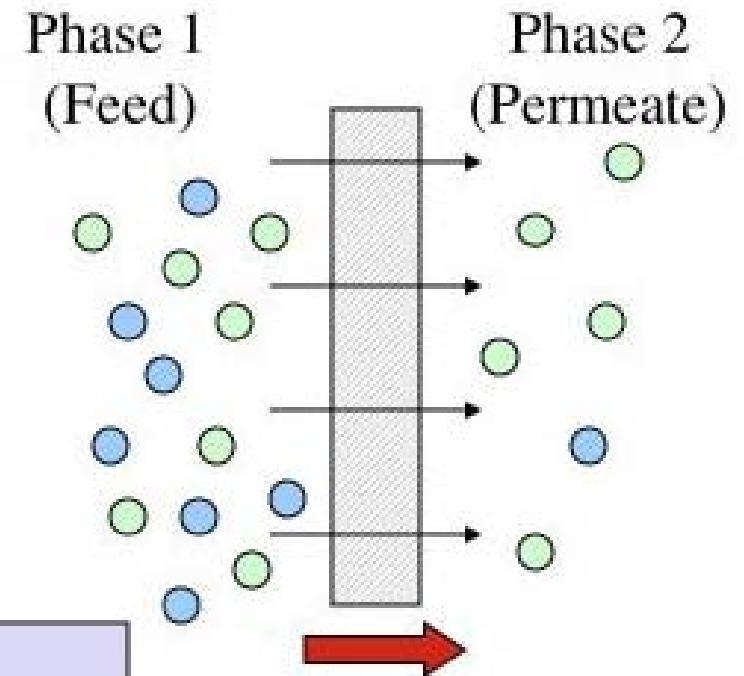
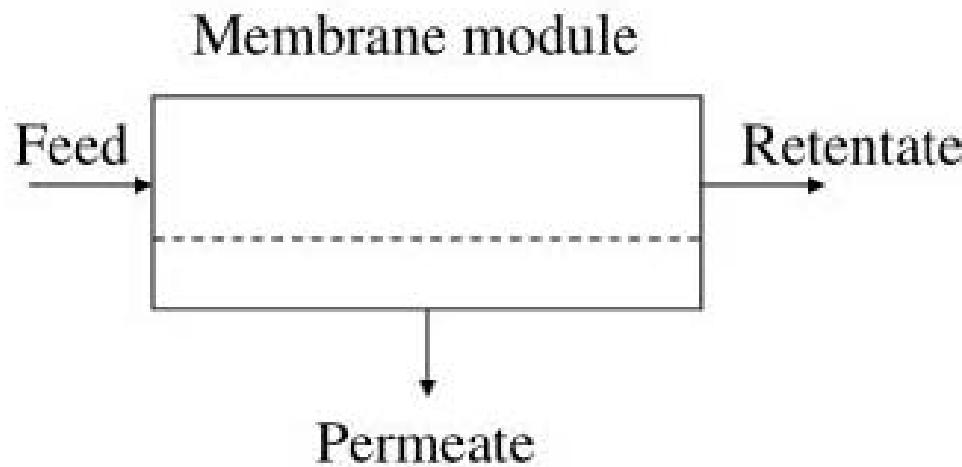


*Particle or
Solute Molecule*



Solvent

Principles of Membrane Separation



Membrane

- a physical barrier from semi-permeable material that allows some component to pass through while others are held back.

Microfiltration

Ultrafiltration

Reverse Osmosis

Molecular sieving

Gas separation

Membrane contactors

Pervaporation

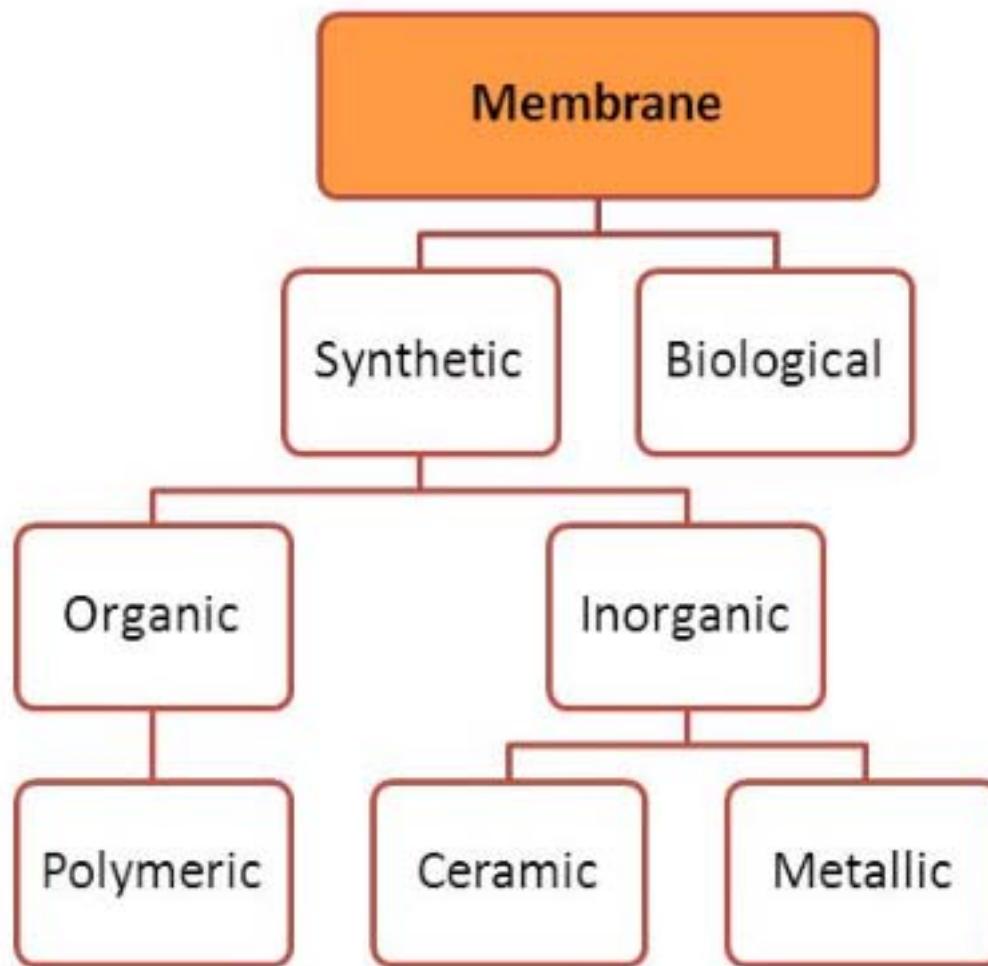
Flux
Selectivity

	Cut-offs of different liquid filtration techniques						
Micrometer logarithmic scaled	0,001	0,01	0,1	1	10	100	1000
Angstroms logarithmic scaled	1	10	100	1000	10^4	10^5	10^6
Size ratio of substances to be separated			Viruses	Bacteria	Yeast	Sand	
	Solved salts				Pollen		
		Pyrogens			Human hair		
	Sugar				Red blood cells		
	Atomic radius		Albumin (66 kD)				
Separating process	Reverse osmosis	Ultra filtration				Particle filtration	
				Micro filtration			
	Nano filtration						

Types of membrane filtration of liquid streams

Membrane process	Separation mechanism	Feed	Driving force	Rejected species	Permeated species	Applications
Microfiltration	Sieving	Liquid/gas containing suspended particulates	Pressure difference $\Delta P < 2$ bar	0.1 μm to 20 μm	The suspending medium, liquid/gas	Separation of cells, sterilization of liquid/gas streams, separation of emulsified oil from water, clarification of liquids/beverages in food industries.
Ultrafiltration	Sieving	Liquid	Pressure difference $\Delta P = 2$ to 3.5 bar	Relatively large molecules (1-100 nm)	Solvent, low MW solute	Separation of biomolecules, proteins, emulsions, dispersed droplets, macromolecules, auto-paints from solutions.
Reverse osmosis	Solution-diffusion	Salt solutions, sea water	$\Delta P = 10$ to 100 bar or more	Low MW solutes, hydrated ions	Solvent (generally water)	Desalination of sea water, brackish water, treatment of wastewater.
Dialysis	Sieving, solution-diffusion	Solutions	Concentration difference	Larger molecules (5–50 Å) MW 50 to 10^4 dalton	Microsolute, solvent	Haemodialysis, recovery of selected solutes
Pervaporation	Solution-diffusion	Liquid mixtures	Activity difference	Molecules that have higher affinities for the membrane are preferentially sorbed on the feed side of the membrane and then diffuse through it. The molecules get desorbed on the permeate side under vacuum (for pervaporation) or under the effect of pressure difference causing enrichment.	Production of absolute alcohol, dehydration of solvents, removal of trace organics from water.	
Gas separation	Sorption-diffusion	Gas mixtures	Difference of fugacity, or Δp			Separation of air (O_2/N_2), CO_2 from methane, organic vapours from air or a carrier gas, H_2 from other light gases

Membrane material



Membrane materials

Polymer (organic) >>> Inorganic

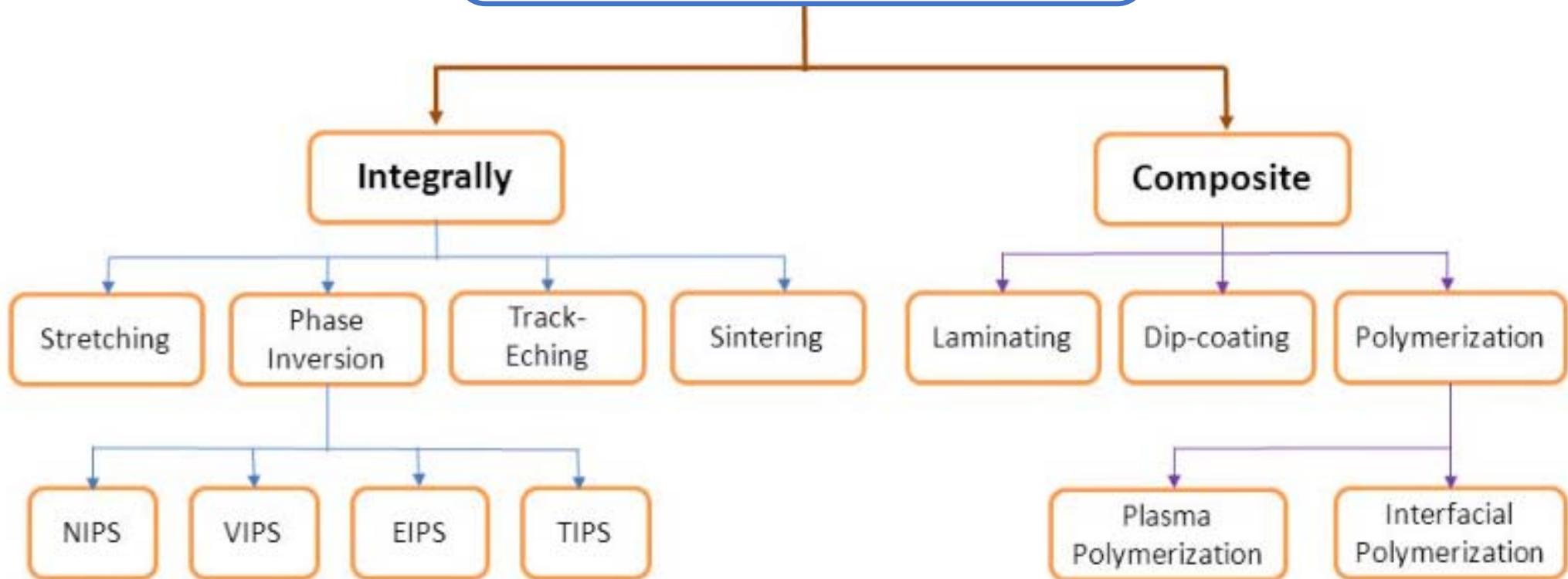
- (i) many different types of polymeric material are commercially available,
- (ii) a large variety of different selective barriers, i.e., porous, nonporous, charged and affinity, can be prepared by versatile methods,
- (iii) production of large membrane area with consistent quality is possible in technical scale at reasonable cost based on reliable manufacturing processes, and
- (iv) various membrane shapes (flat sheet, hollow-fiber, capillary, tubular, capsule;) and formats including membrane modules with high packing density can be produced

A very well defined regular pore structure is difficult to be achieved, and the mechanical strength, the thermal stability and the chemical resistance (e.g., at extreme pH values or in organic solvents) are rather low for many organic polymers.

Polymeric membrane materials

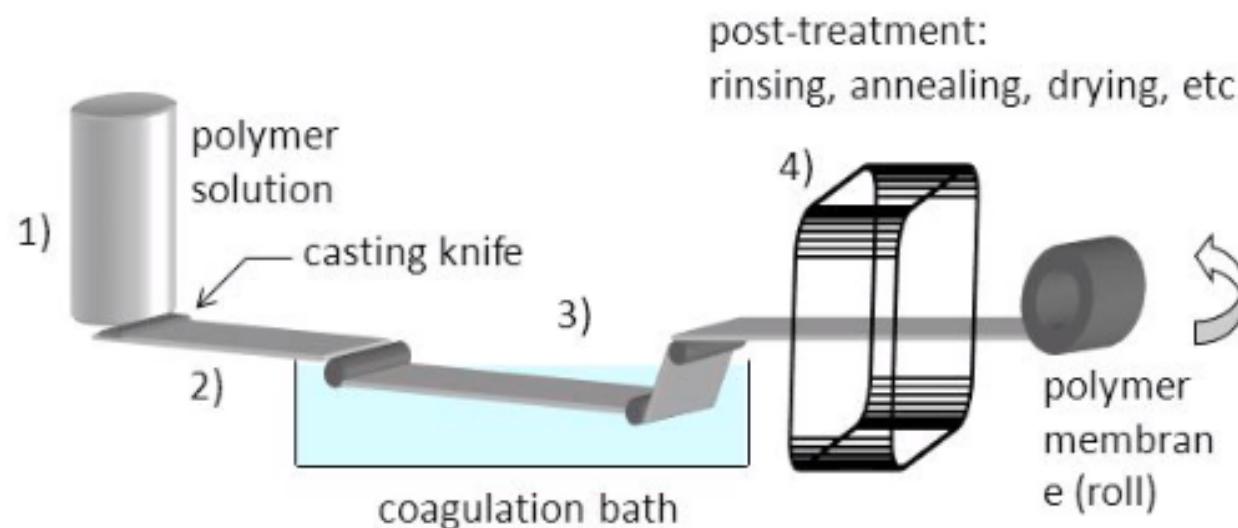
<i>Polymer</i>	<i>Type</i>	<i>Representative repeat unit/formula</i>	<i>T_g, °C</i>	<i>M.P., °C</i>
Cellulose triacetate	Crystalline			300
Polyisoprene (natural rubber)	Rubbery	$\left[\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2 \right]_n$	-70	
Aromatic polyamide	Crystalline			275
Polycarbonate	Glassy		150	
Polyimide	Glassy			310–365
Polystyrene	Glassy		74–110	
Polysulphone	Glassy		190	
Polytetrafluoro-ethylene (Teflon)	Crystalline	$-\text{CF}_2\text{--CF}_2-$		327
Perfluorosulphonic acid ionomer, Nafion		$\left[(\text{CF}_2\text{--CF}_2)_m \text{--CF}(\text{O})\text{CF}_2 \right]_n$ $(\text{CF}_2\text{--C}(\text{O}\text{--O}_p)\text{--CF}_2\text{--CF}_2\text{--SO}_3\text{H})$		

Membrane preparation



Phase inversion

Schematic depiction of the continuous manufacturing process of polymeric membranes



Factors:

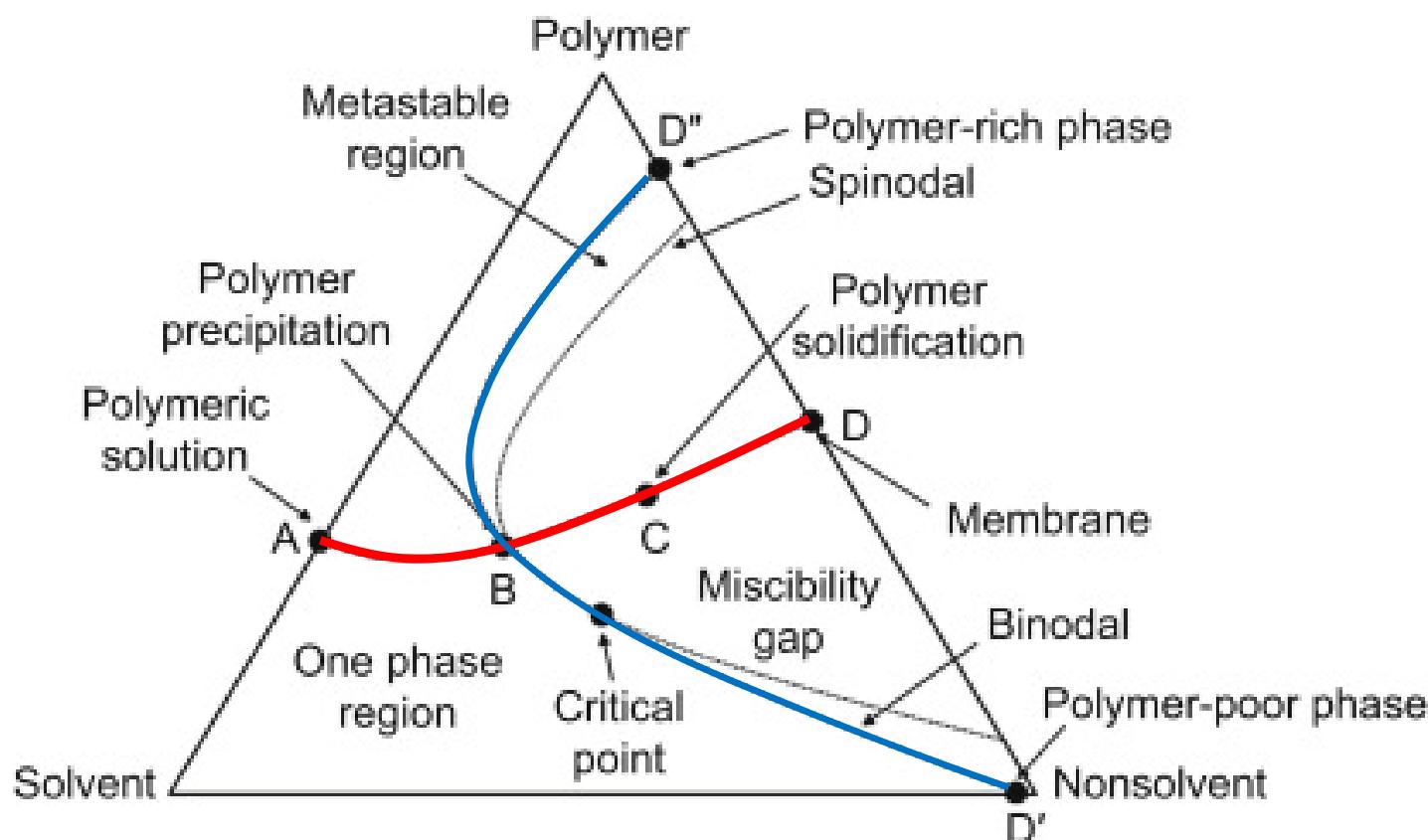
- (i) Thermodynamic aspects.
- (ii) The rate of precipitation in the liquid film; the mass-transfer (non-solvent in-flow, and solvent out-flow) can have tremendous influence: Instantaneous liquid-liquid demixing, which will result in a porous membrane, delayed onset of liquid-liquid demixing, which can result in a membrane with nonporous barrier skin layer

Types of phase inversion

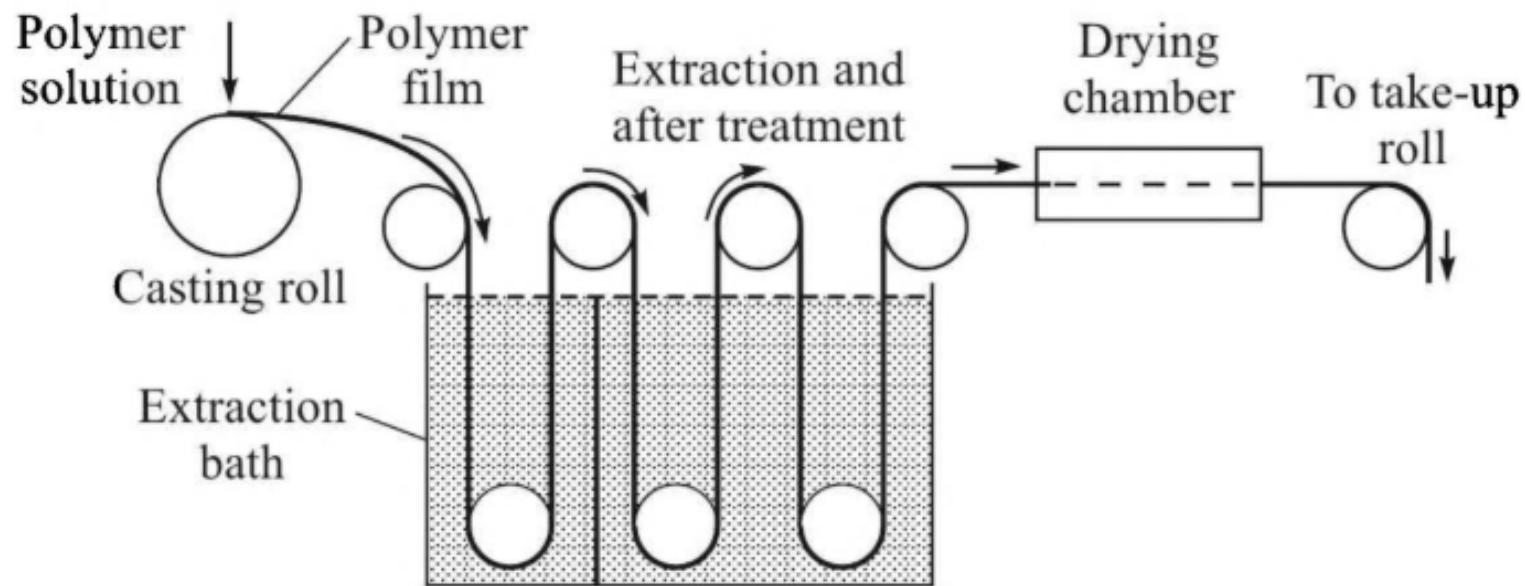
- ***Nonsolvent induced phase separation (NIPS)*** – the polymer solution is immersed in a nonsolvent coagulation bath (typically water); demixing and precipitation occur due to the exchange of solvent (from polymer solution) and nonsolvent (from coagulation bath), i.e., the solvent and nonsolvent must be miscible.
- ***Vapor induced phase separation (VIPS)*** – the polymer solution is exposed to an atmosphere containing a nonsolvent (typically water); absorption of nonsolvent causes demixing / precipitation.
- ***Evaporation induced phase separation (EIPS)*** – the polymer solution is made in a solvent or in a mixture of a volatile solvent and a less volatile nonsolvent, and solvent is allowed to evaporate, leading to precipitation or demixing / precipitation.
- ***Thermally induced phase separation (TIPS)*** – a system of polymer and solvent is used which has an upper critical solution temperature; the solution is cast or spun at high temperature, and cooling leads to demixing / precipitation

Thermodynamics of phase inversion

The method is described as *phase separation*: a one-phase solution containing the membrane polymer is transformed by a precipitation / solidification process into two separate phases (a polymer-rich solid and polymer-lean liquid phase)

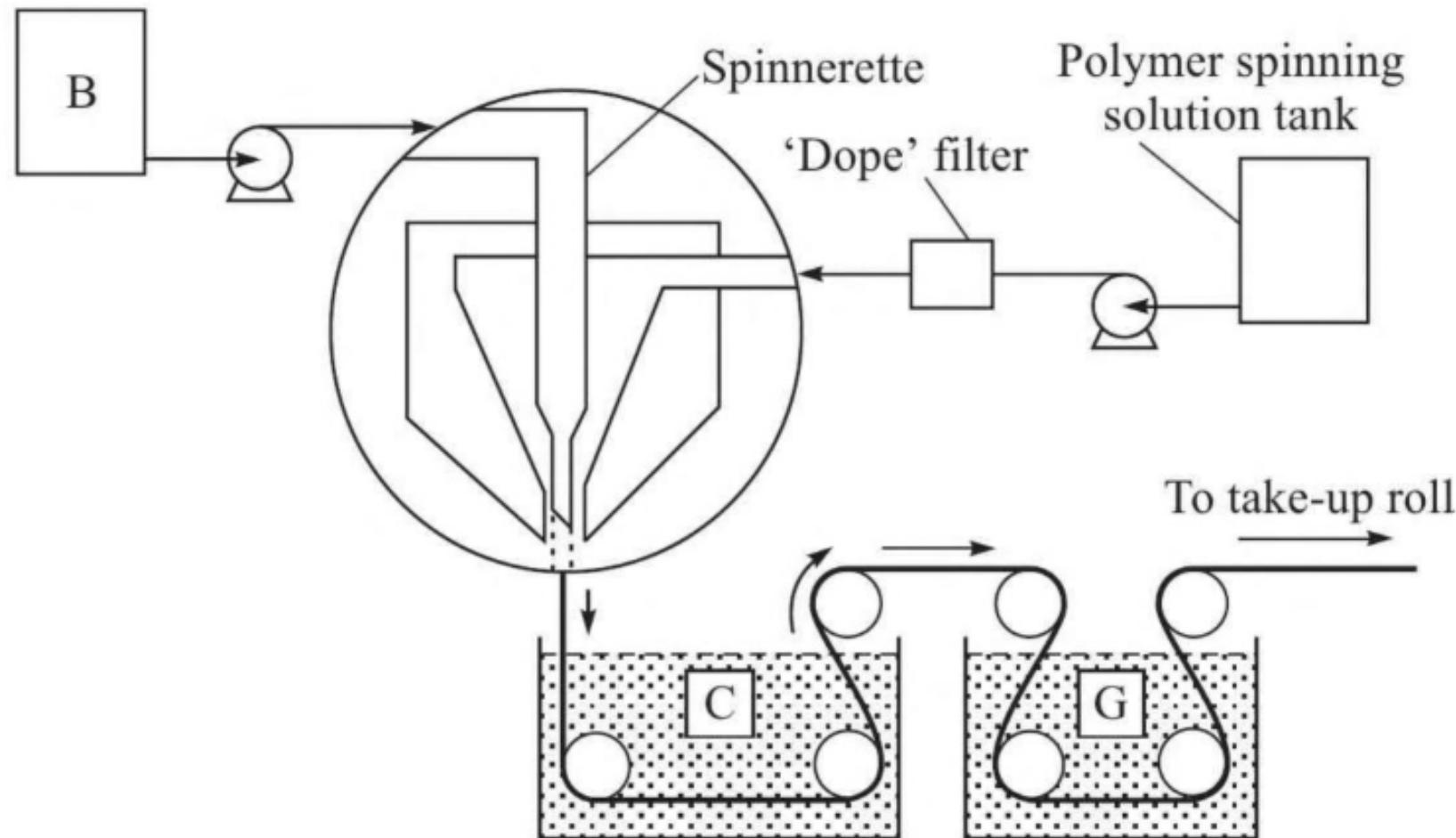


Fabrication of flat sheet membranes



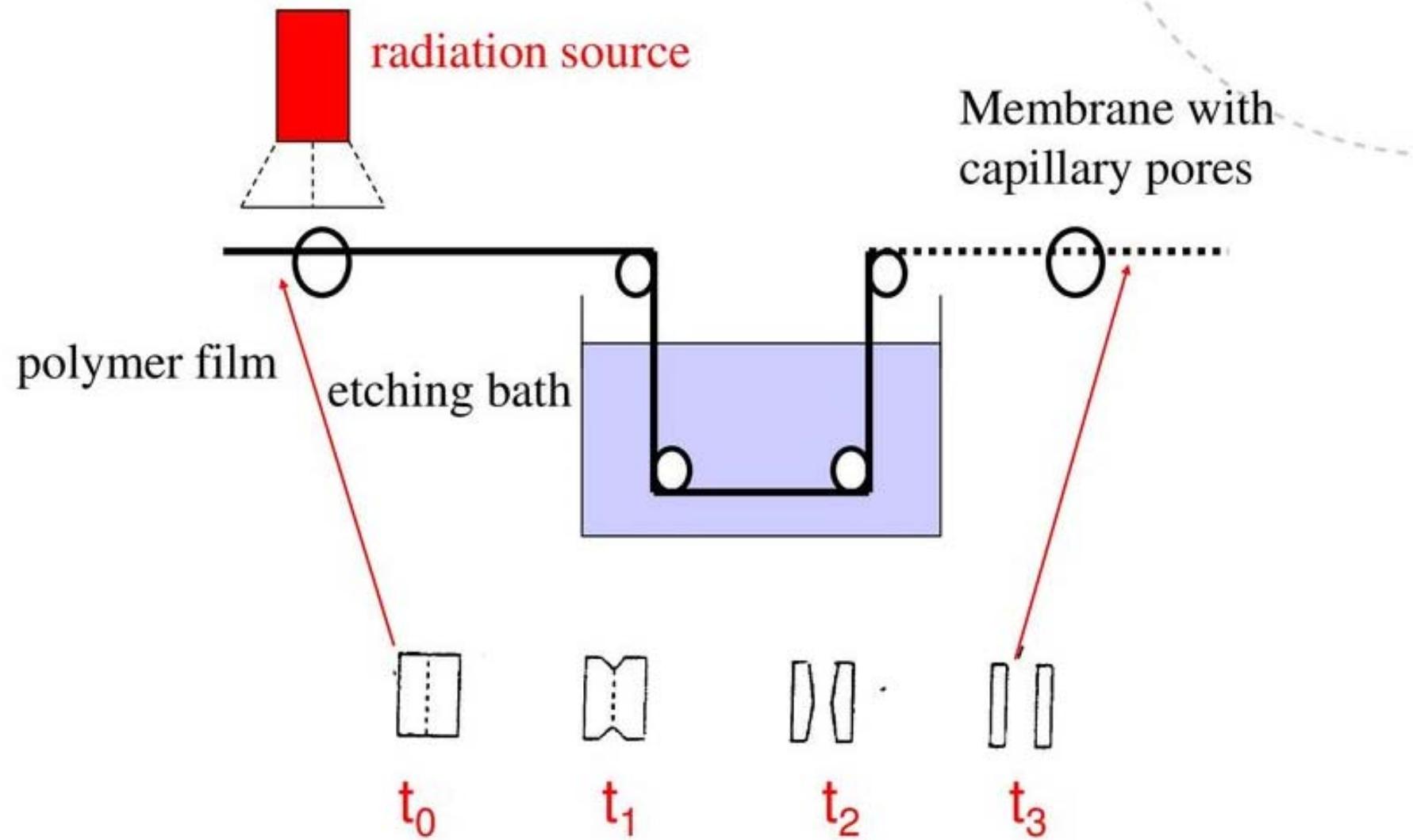
Schematic of a set-up for preparation of microporous membranes by the polymer precipitation technique.

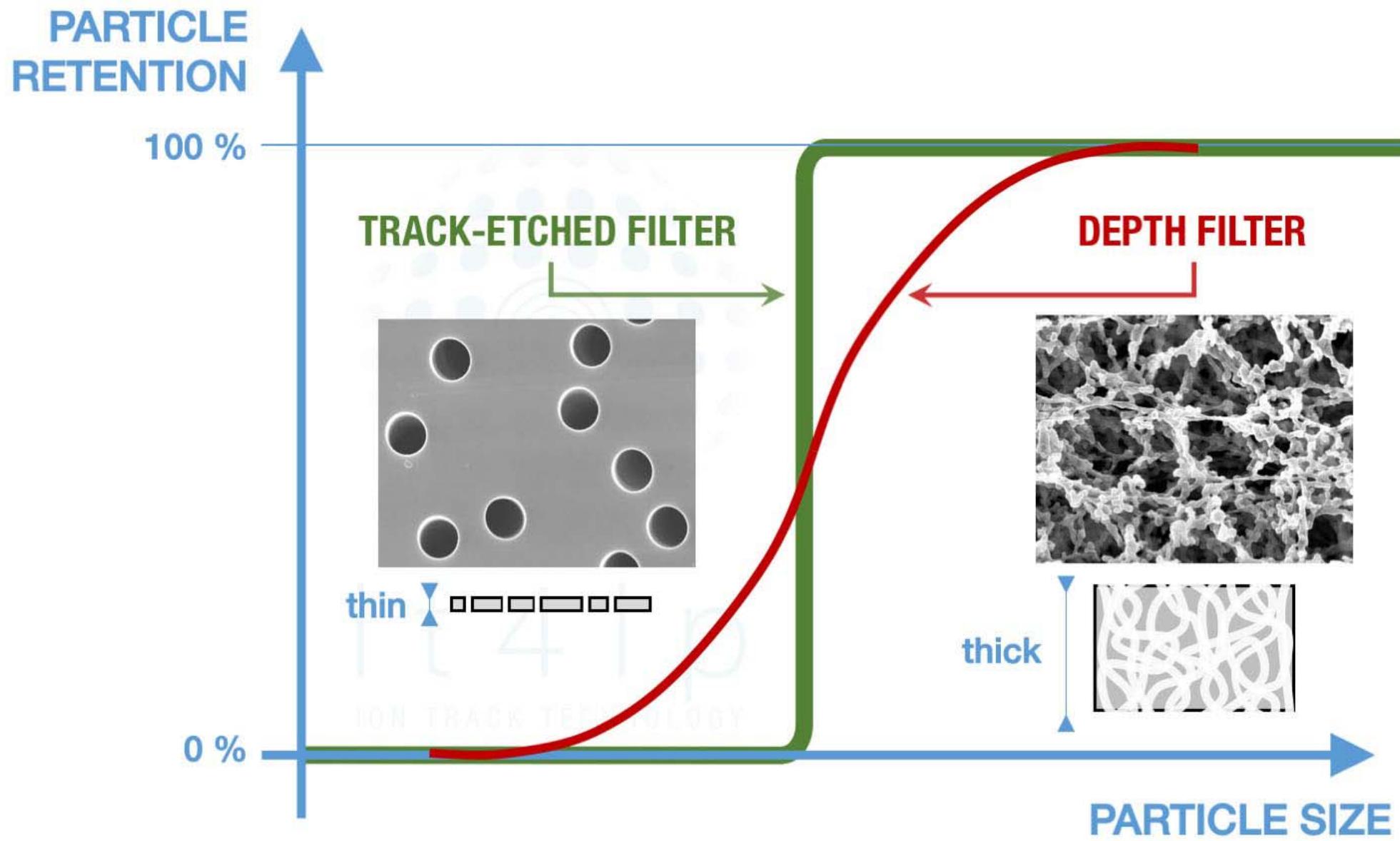
Hollow fibres – wet spinning



Schematic of a set-up for wet-spinning of hollow fibres
(B: bore injection medium, liquid or gas; C: coagulation bath; G: quench bath)

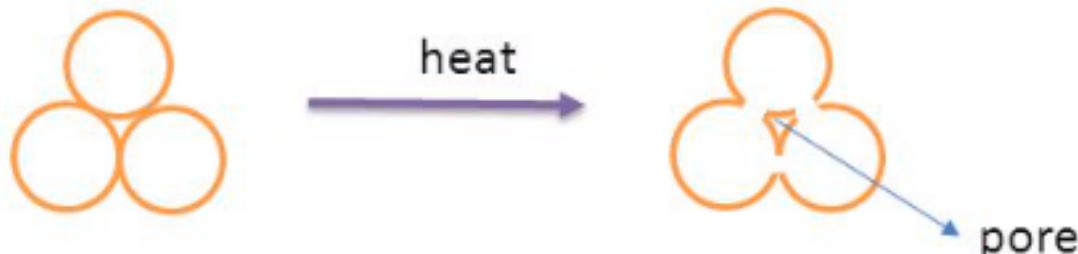
Track-etching process





Sintering

- Simple technique allowing porous membrane to be obtained from organic as well as from inorganic materials
- The method involves compressing a powder consisting of particles of a given size and sintering at elevated temperatures.
- The required temperature depends on the material used.
- A wide range of different materials can be used such as powders of polymers (polyethylene, polytetrafluoroethylene, polypropylene), metals (stainless steel, tungsten), ceramics (aluminium oxide, zirconium oxide), graphite (carbon) and glass (silicates).
- The pore size of resulting membrane ($0.1\text{-}10\mu\text{m}$) is determined by the particle size and particle distribution.
- The porosity of porous polymeric membrane is generally low (10-20 %)
- Only microfiltration membrane can be prepared by this technique.



Membrane characterization

Real retention & Observed retention

Molecular weight cut-off

Membrane permeability

Pore size distribution

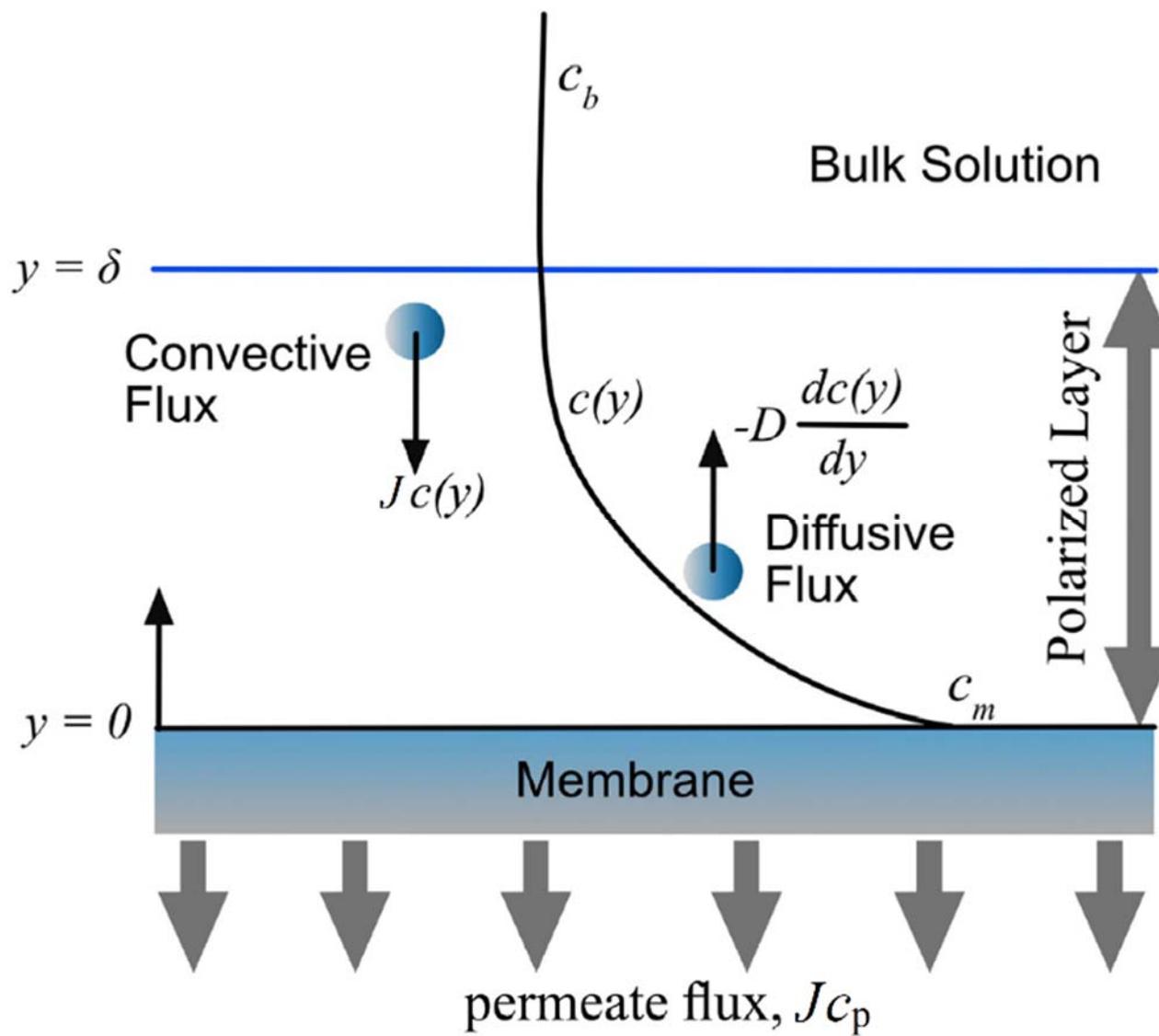
Porosity

Mechanical strength

Surface energy (hydrophilicity?)

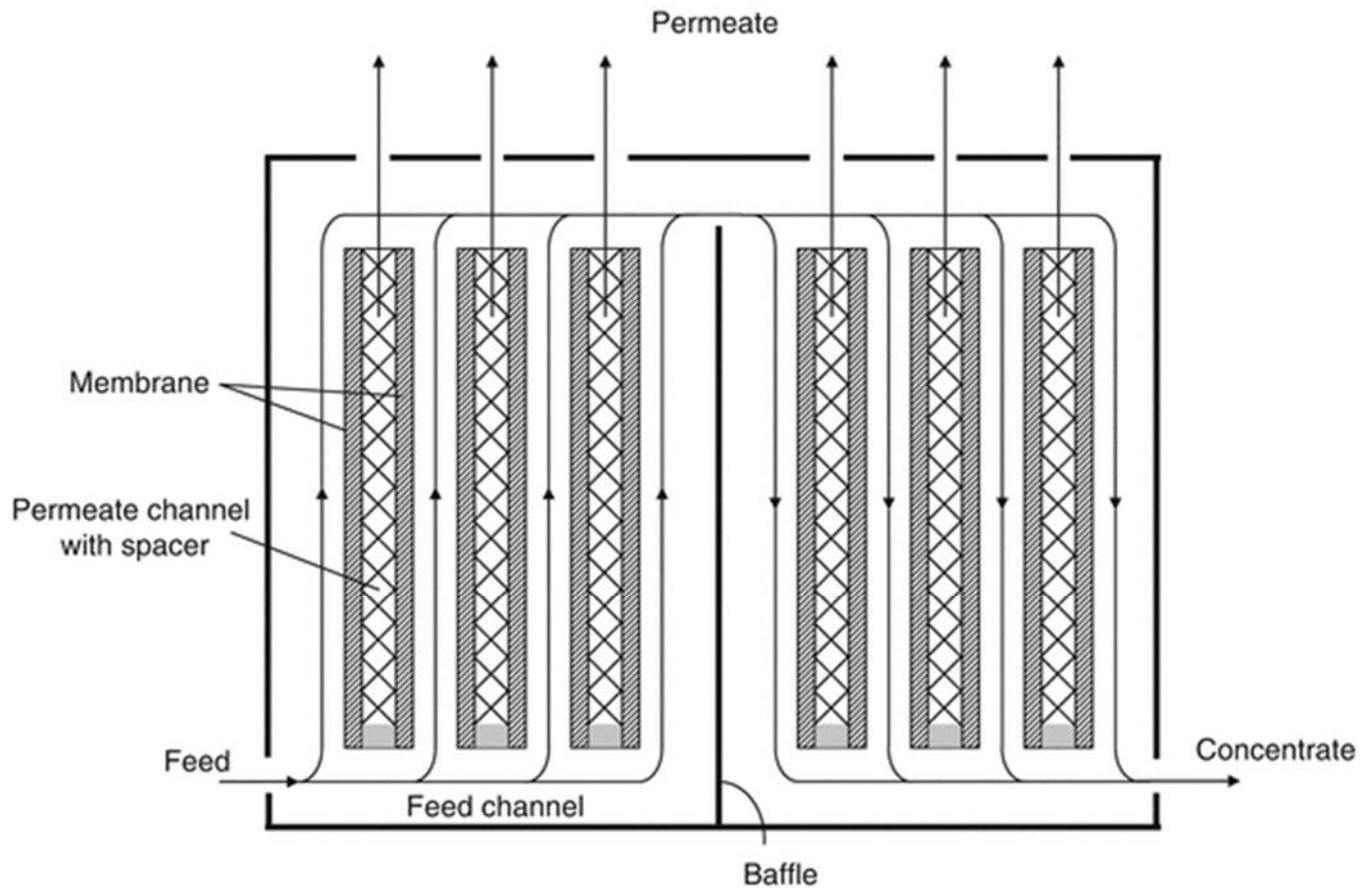
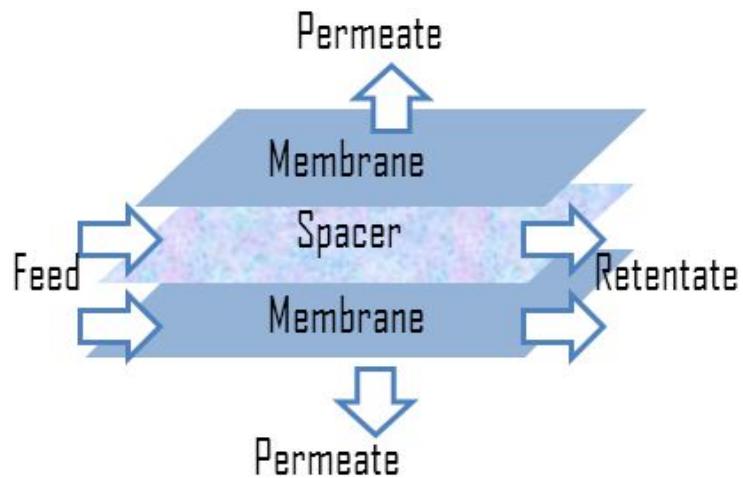
Chemical stability

Schematic of the major mass transport phenomena in membrane science



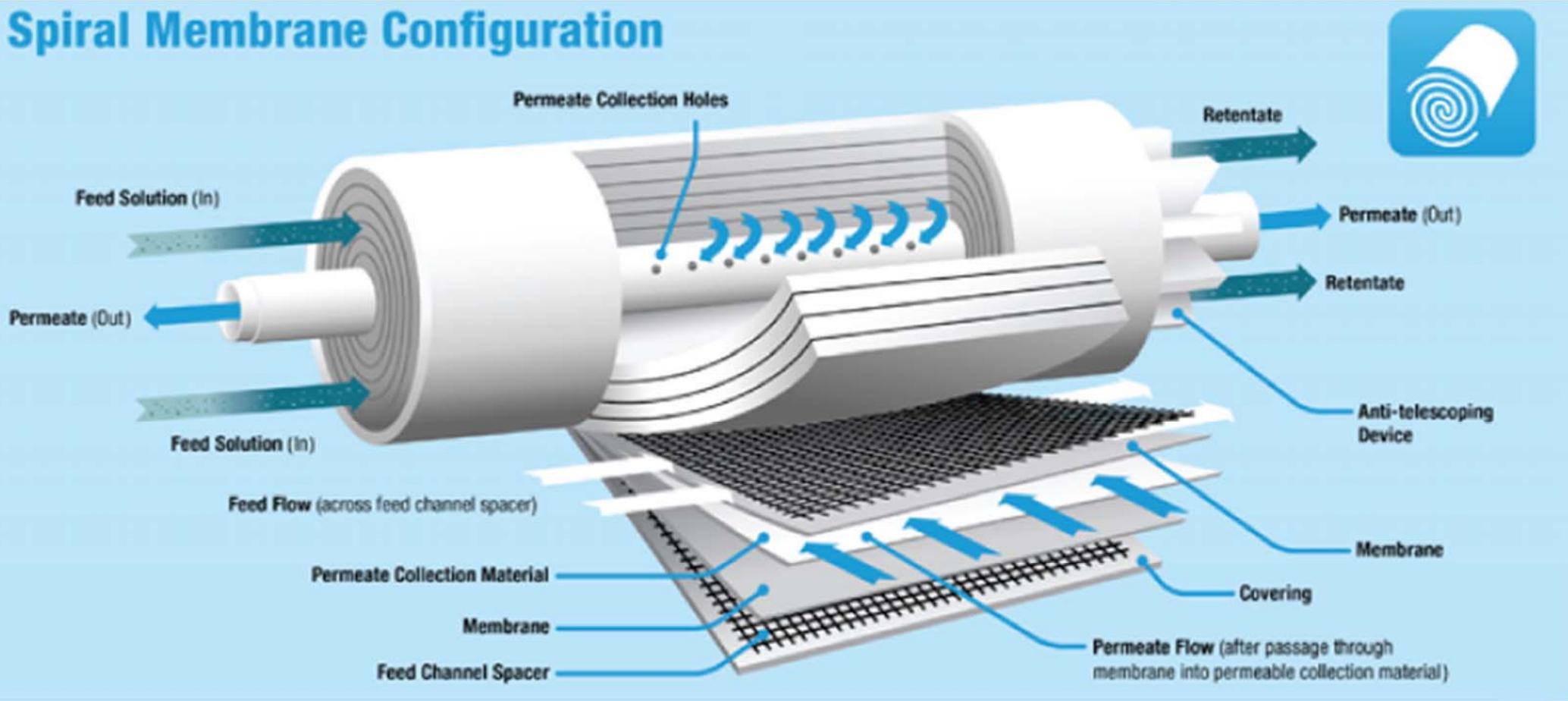
Membrane modules

Plate & frame module

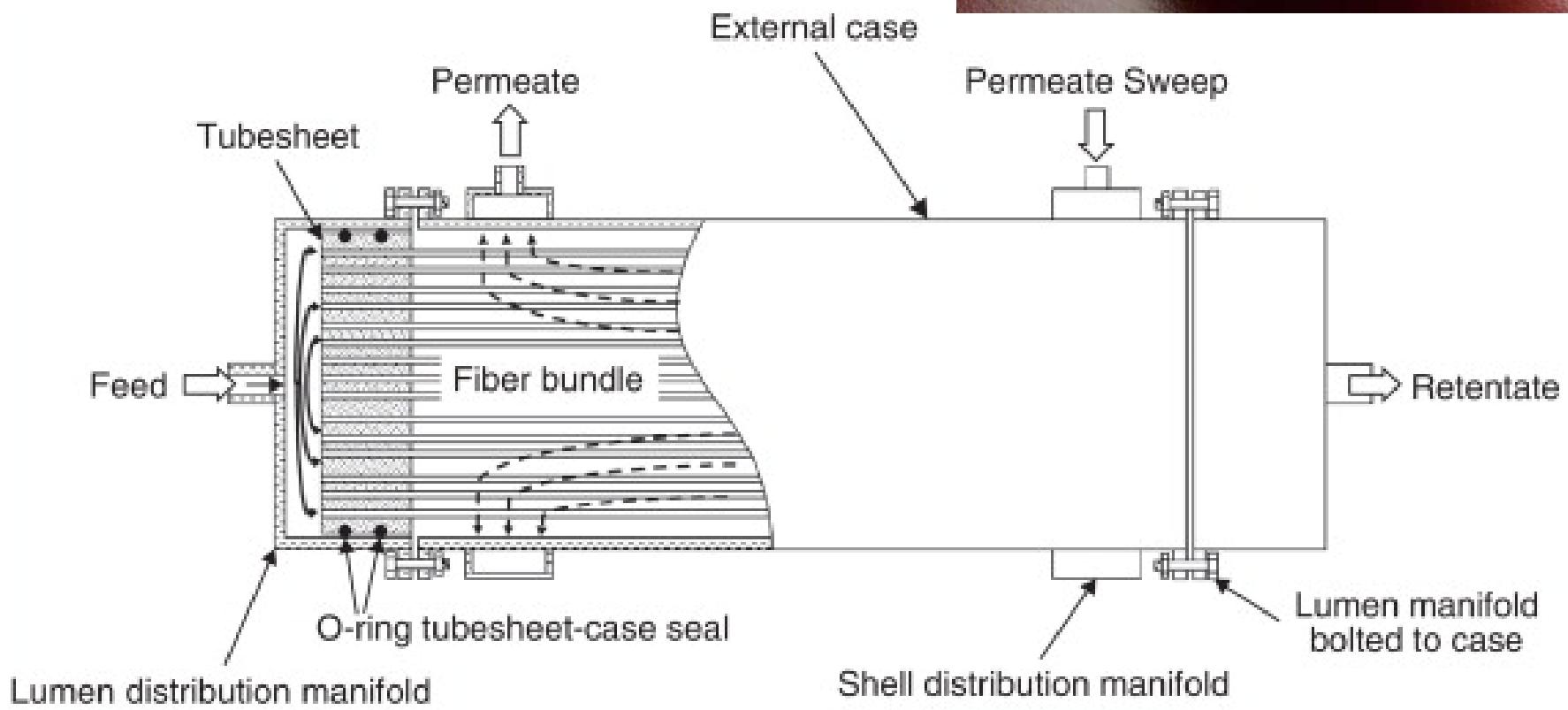
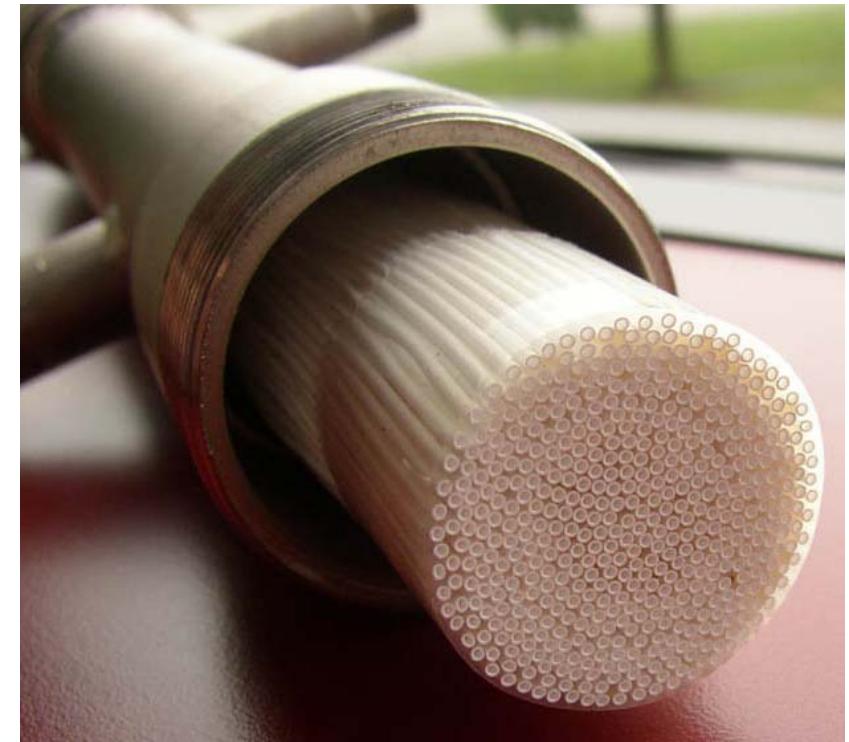


Sets of two membranes are placed in a sandwich-like fashion with their feed sides facing each other. In each feed and permeate compartment thus obtained a suitable spacer is placed. The number of sets needed for a given membrane area furnished with sealing rings and two end plates then builds up to a plate-and-frame stack.

Spiral Membrane Configuration



Hollow fibre module



ADVANTAGES AND DISADVANTAGES OF MEMBRANE MODULES

SPIRAL-WOUND

ADVANTAGES

- Low manufacturing cost
- Relatively easy to clean by both chemical and hydraulic methods.
- Has a very broad range of applications
- High packing density

HOLLOW FIBER

DISADVANTAGES

- It can not be used on highly turbid feed waters without extensive pretreatment.
- Susceptible to plugging by particulates
- Extremely susceptible to fouling due to very small spacing between fibers.
- Difficult to clean.
- Requires extensive pretreatment.

TUBULAR

- Can be operated on extremely turbid feed waters.
- Relatively easy to clean either mechanically or hydraulically.
- Can process high suspended solid feed with minimal pretreatment.

PLATE AND FRAME

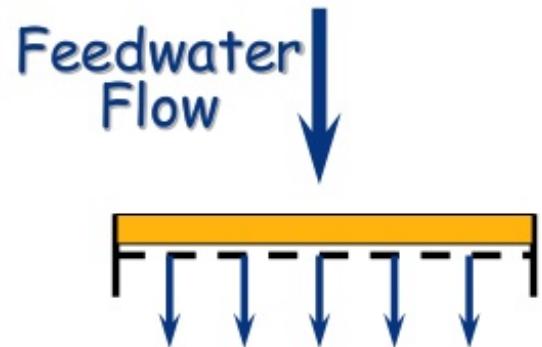
- Moderate membrane surface.
- Well-developed equipment.

- High capital cost.
- Relative high volume required per unit membrane area.

- Expensive to operate for large scale.
- Susceptible to plugging by particulates at flow stagnation points.
- Potentially difficult to clean.

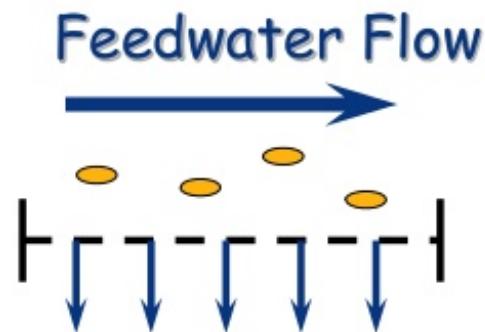
Flow arrangements

TYPICAL FILTRATION



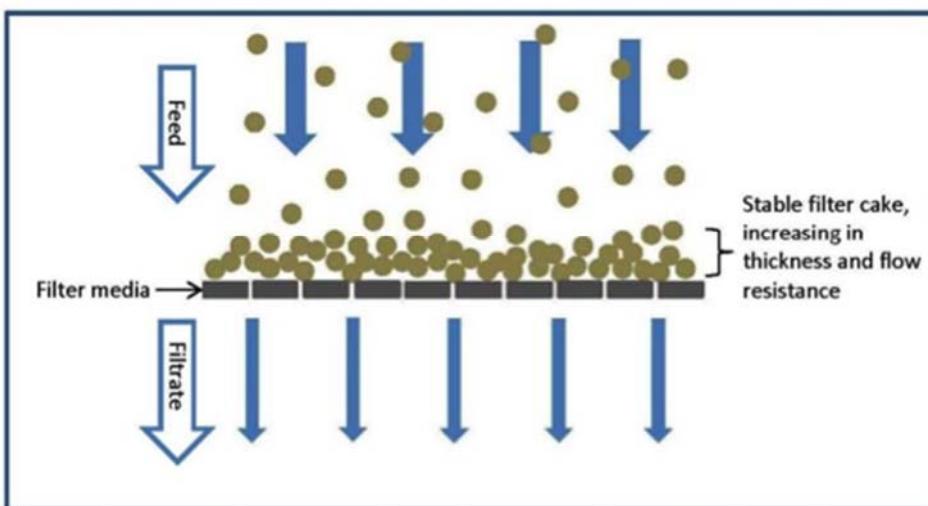
Solids on surface quickly foul the membrane

CROSS-FLOW FILTRATION

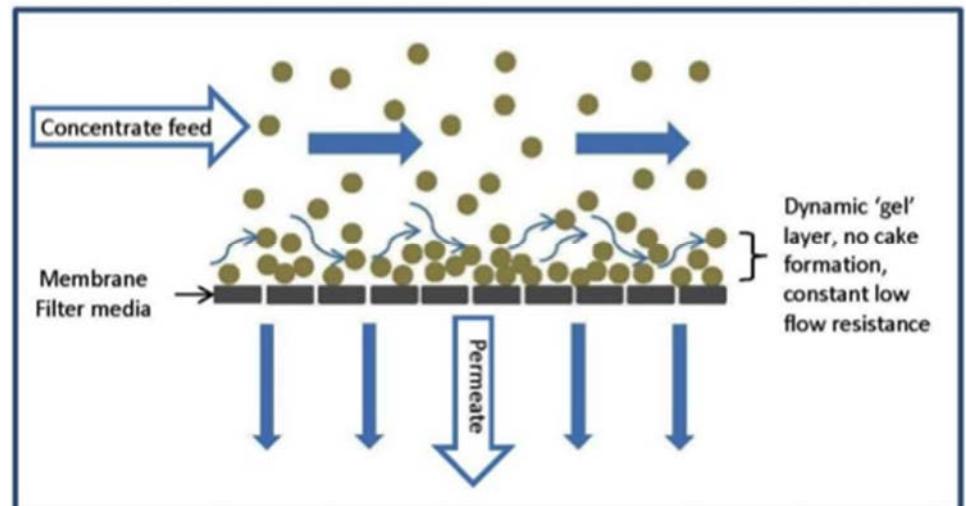


Solids are swept away by continuous flow

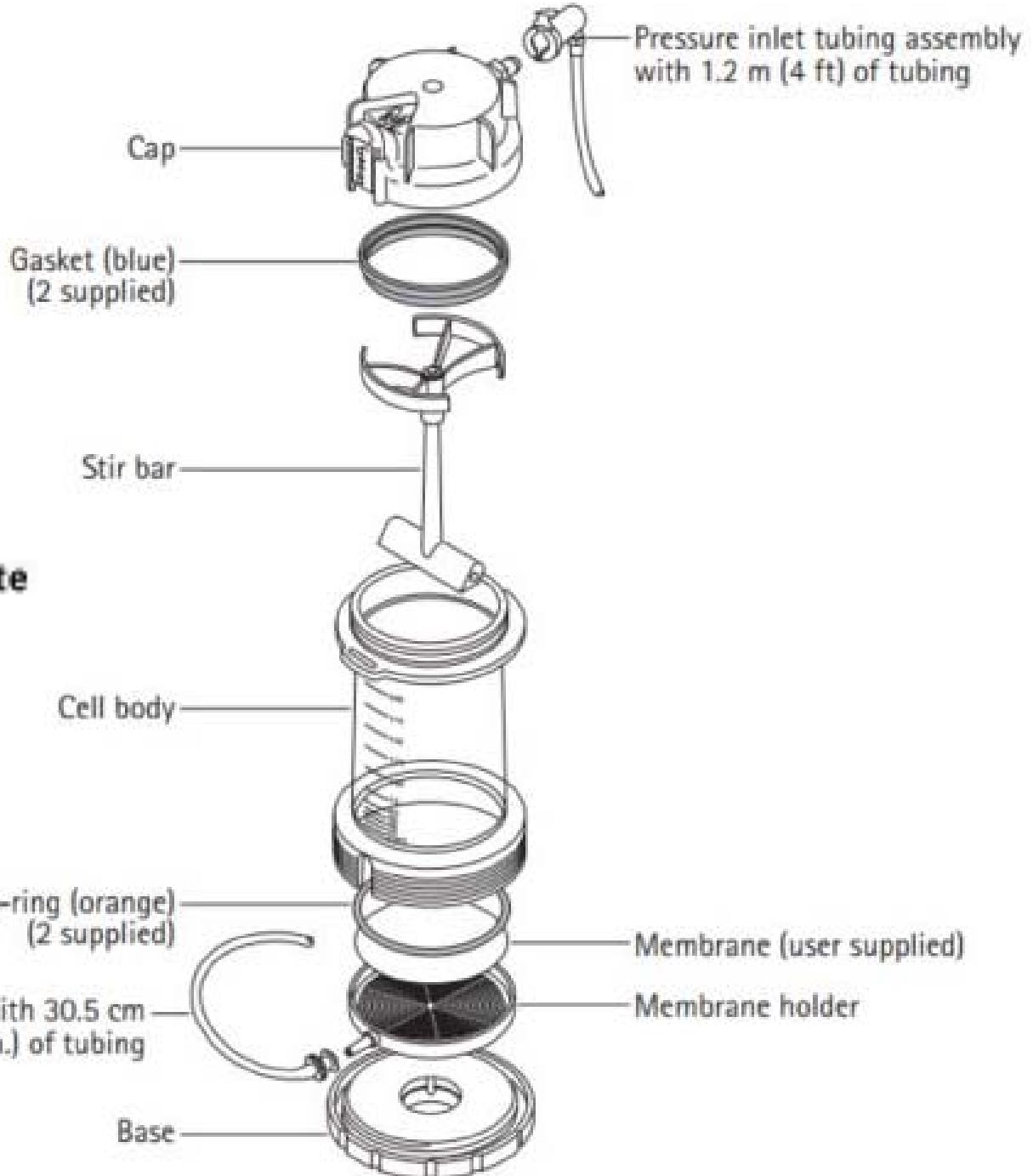
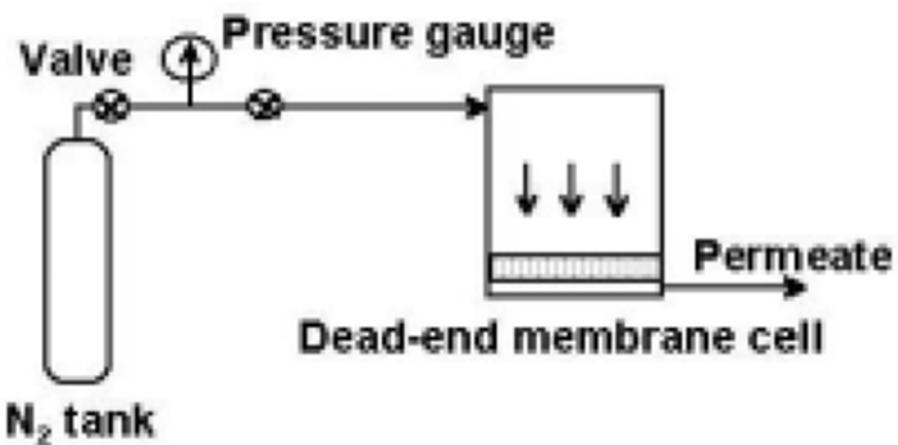
Dead-end filtration



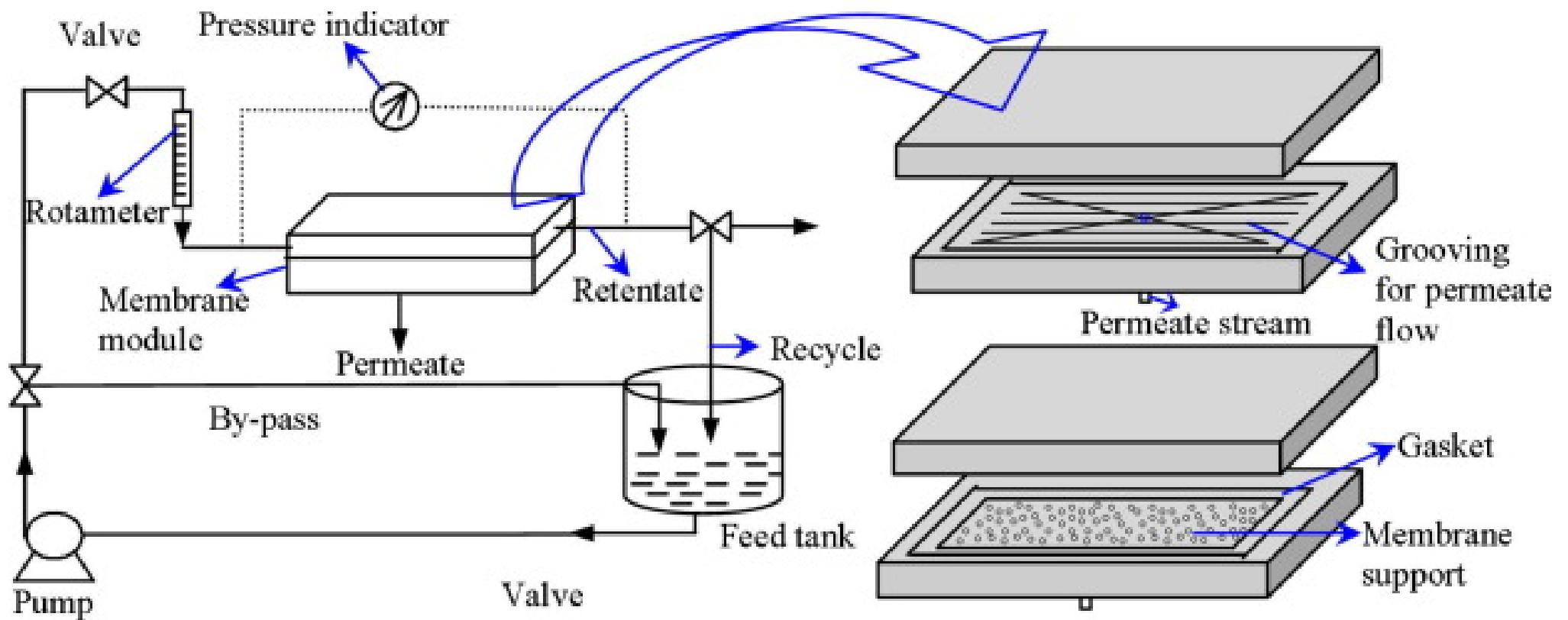
Cross flow filtration



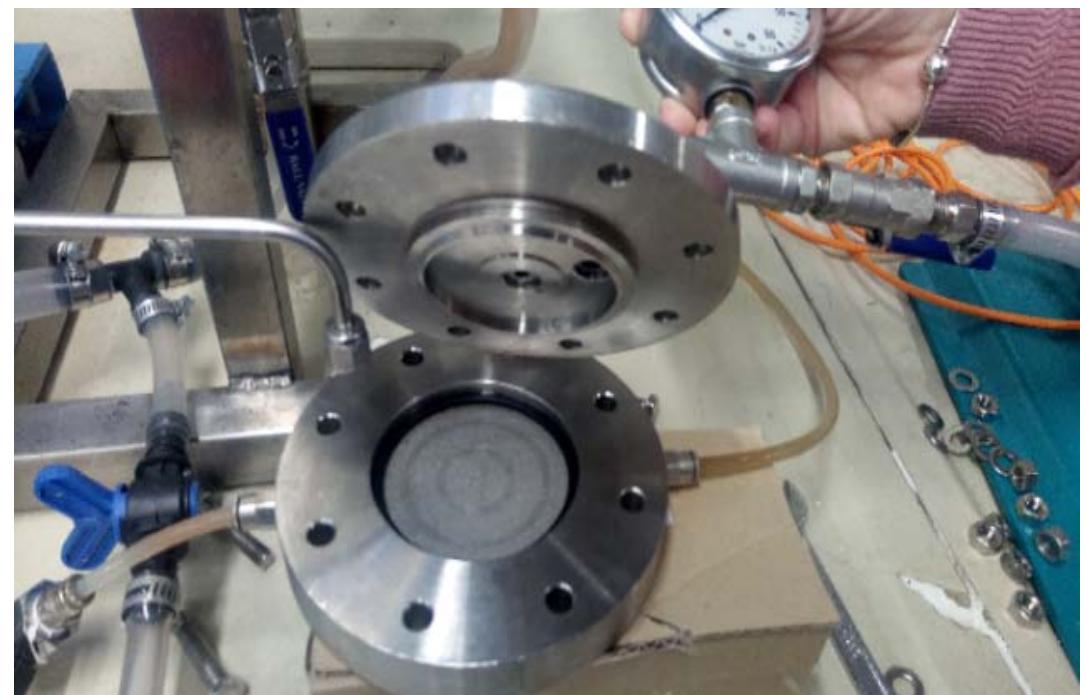
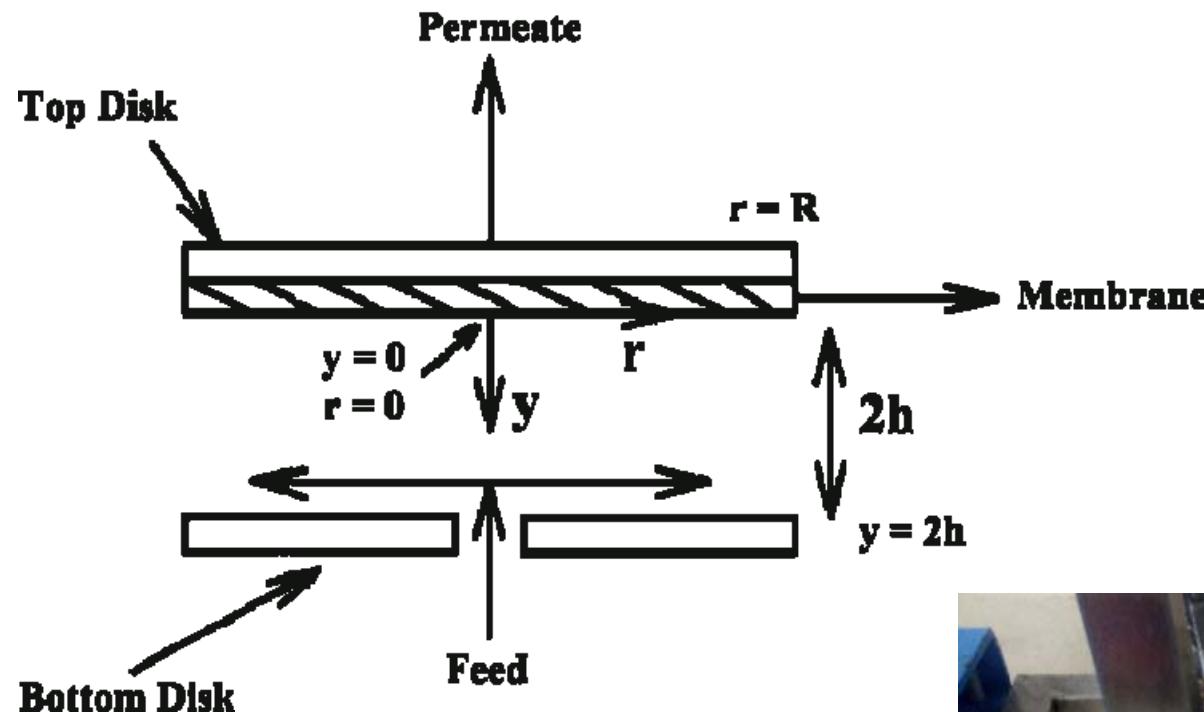
Batch cell setup



Cross flow flat setup



Radial cross flow cell



Pressure driven membrane processes

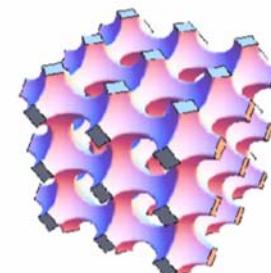
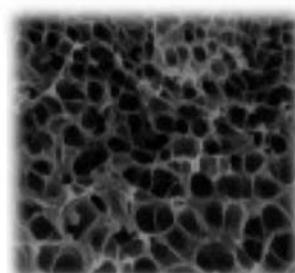
Flow through membrane – theory

1. Darcy law
2. Sampson + Poiseuille flow
3. Kozeny-Karman type

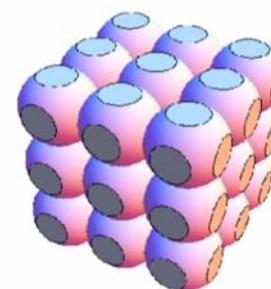
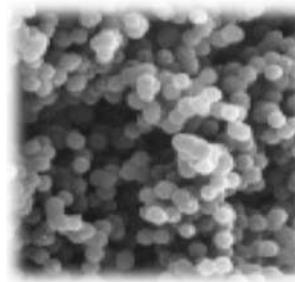
[Refer to the notes]

Effect of membrane morphology

Branched matrix type



Assembly of particles
(packed bed)



Sometimes the membrane structure or morphology resembles more like an *assembly of particles with void spaces* which is similar to a very thin ‘packed bed’. The pressure drop–flow relation (Noble and Stern, 1995) for such a membrane is given by the well-known Kozeny–Karman equation.

$$J_w = \frac{d_s^2 \varepsilon^3}{180 \mu (1 - \varepsilon)^2} \frac{\Delta P}{l_m} \quad (d_s \text{ is the ‘equivalent particle diameter’})$$

Selectivity – Ferry equation

Based on volume exclusion on the rejection of a rigid sphere by a cylindrical pore

$$S = (1 - \lambda)^2 [2 - (1 - \lambda)^2]$$

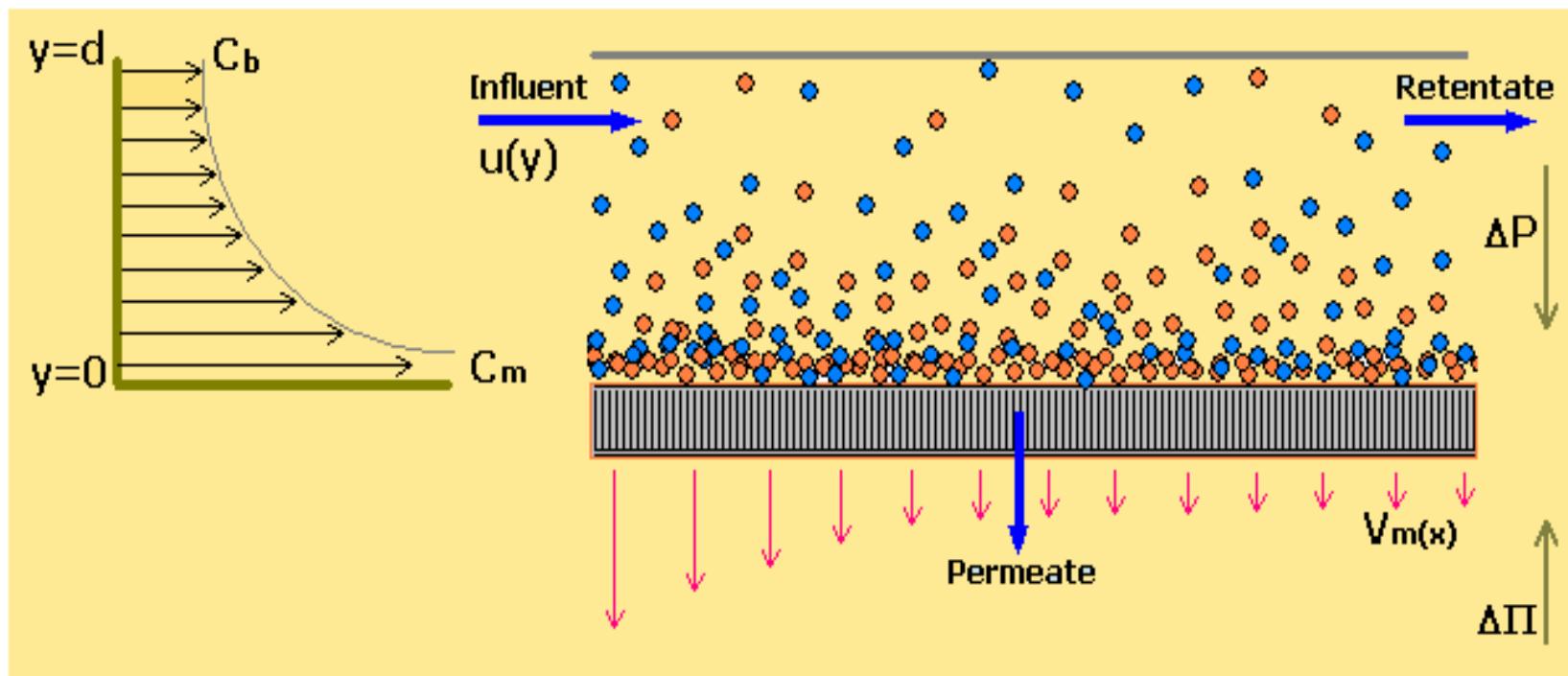
S:: ratio of the concentration outside of the pore to the concentration inside the pore

λ : size ratio of the solute rejected and the membrane pore radius

J.D. Ferry, Statistic evaluation of sieve constants in ultrafiltration, J. Gen. Physiol.
20 (1936) 95-104.

Theory of pressure driven membrane processes

Concentration polarization in the reversible accumulation of the rejected solute in the fluid phase at the membrane-fluid interface as the solvent passes through the membrane. When the solvent (water) flows through the membrane, the solutes are left behind (being rejected) at the feed side surface of the membrane. This results in increase of the solute concentration in the close vicinity of the membrane.



Description of the concentration polarization

$$J_w C_p = J_w C - \left(-D \frac{dC}{dz} \right)$$

Solute flux through the membrane Convective flux towards the membrane surface Flux of back diffusion of the solute to the bulk of the liquid

where

J_w = solvent flux

C_p = solute concentration in the permeate

D = diffusivity of the solute

C = local concentration of the solute in the film.

The following boundary conditions may be specified.

$$z = 0, \quad C = C_m$$

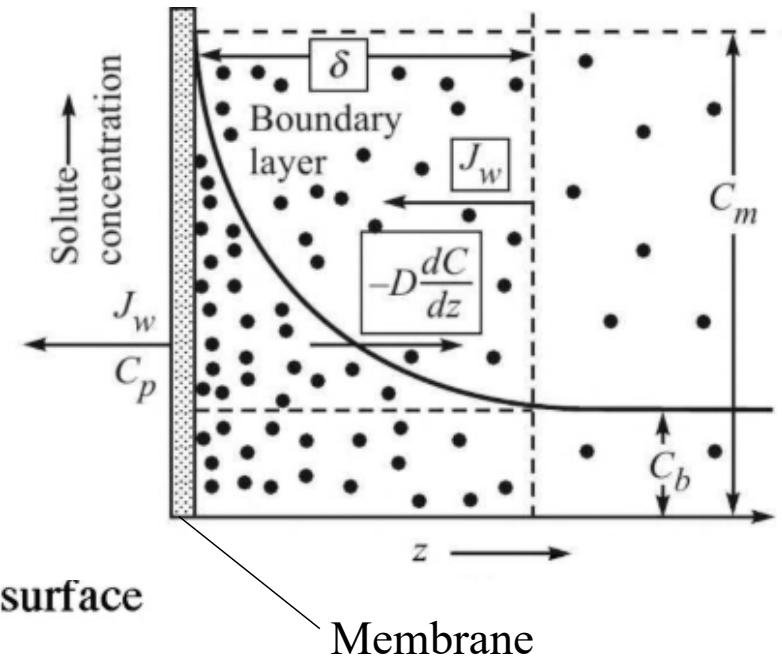
$$z = \delta, \quad C = C_b$$

where

δ = film or ‘boundary layer thickness’ at the membrane surface

C_b = solute concentration in the bulk solution

C_m = solute concentration in the liquid at the membrane surface.



Consequences of Concentration Polarization

$C_m \uparrow \rightarrow \Pi_m \uparrow \rightarrow (\Delta P - \Delta \Pi) \downarrow \rightarrow V_w \downarrow$

$C_m \uparrow \rightarrow \mu \uparrow \rightarrow \text{Resistance} \uparrow \rightarrow V_w \downarrow$

$C_m \uparrow \rightarrow \text{May form Gel} \rightarrow V_w \downarrow$

$C_m \uparrow \rightarrow \text{Clogging} \rightarrow L_p \downarrow \rightarrow V_w \downarrow$

Control of concentration polarization is crucial

Modeling steps

- Solution of fluid dynamics and mass transfer outside the membrane
- To obtain appropriate transport law inside porous membrane

Coupling of above two → System performance

Estimation of concentration polarization (Film theory)

Net flux towards membrane = 0 at steady state.

$$V_w C - \left(-D \frac{dc}{cy} \right) - V_w C_p = 0$$

Integrate using the limits at $y = 0, C = C_m$ and at $y = \delta, C = C_0$

$$\frac{C_m - C_p}{C_0 - C_p} = \exp\left(\frac{V_w}{k}\right), \quad k = \frac{D}{\delta}$$

Flow through porous medium (simple Darcy law):

$$\Delta\pi = \pi_m - \pi_p$$

$$V_w = L_p (\Delta P - \Delta\pi) \quad \pi = 84837C \text{ for NaCl} \quad \text{where } \pi \text{ is in Pa and } C \text{ in kg/m}^3$$

Using definition of real retention

$$R_r = 1 - \frac{C_p}{C_m}$$

$$\text{So, } \Delta\pi = b(C_m - C_p)$$

Combining the previous equations

$$V_w = L_p [\Delta P - b R_r C_0 \frac{e^{V_w/k}}{R_r + (1 - R_r) e^{V_w/k}}]$$

where the mass transfer coefficient (k) can be estimated from different correlations.

Mass transfer correlations (Leveque relationships)

For rectangular channel (flat sheet):

$$Sh = \frac{kd}{D} = 1.86(\text{Re } Sc \frac{d}{L})^{1/3}$$
$$= 0.023(\text{Re})^{0.8} (Sc)^{0.33}$$

for laminar flow, $\text{Re} < 2100$

for turbulent flow, $\text{Re} > 4000$

For cylindrical tube (hollow fibre):

$$Sh = \frac{kd}{D} = 1.62(\text{Re } Sc \frac{d}{L})^{1/3}$$
$$= 0.023(\text{Re})^{0.8} (Sc)^{0.33}$$

for laminar flow, $\text{Re} < 2100$

for turbulent flow, $\text{Re} > 4000$

For radial cross flow cell:

$$Sh = \frac{kd}{D} = 1.47 \left(\text{Re } Sc \frac{d}{L} \right)^{1/3}$$
$$= 0.023 \text{Re}^{0.8} Sc^{0.33}$$

for laminar flow

for turbulent flow

Simplifications: for $\pi = bC$

Case 1: No concentration polarization

$$C_m = C_0; \quad e^{\nu_w/k} = 1$$

$$\nu_w = L_p(\Delta P - b R_r C_0)$$

Case 2: Low polarization

$$e^{\nu_w/k} = 1 + \frac{\nu_w}{k}$$

Substitute it here

$$\nu_w = L_p \left[\frac{\Delta P - b R_r C_0}{R_r + (1 - R_r)e^{\frac{\nu_w}{k}}} \right]$$

Quadratic in ν_w to be solved

Case 3: Low polarization; $c_p = 0$, perfectly rejecting membrane, $R_r = 1.0$

$$V_w = \frac{\Delta P - bC_0}{\frac{1}{L_p} + \frac{bC_0}{k}}$$

Simplified 1D modeling

Steady state film theory Equation

$$v_w = k \ln \left(\frac{c_m - c_p}{c_0 - c_p} \right)$$

Osmotic pressure relation $v_w = L_p (\Delta P - \Delta \pi)$

~~Solution diffusion model for RO~~ $v_w c_p = B (c_m - c_p)$

For UF/MF $R_r = 1 - \frac{c_m}{c_p}$

Iterative solution !

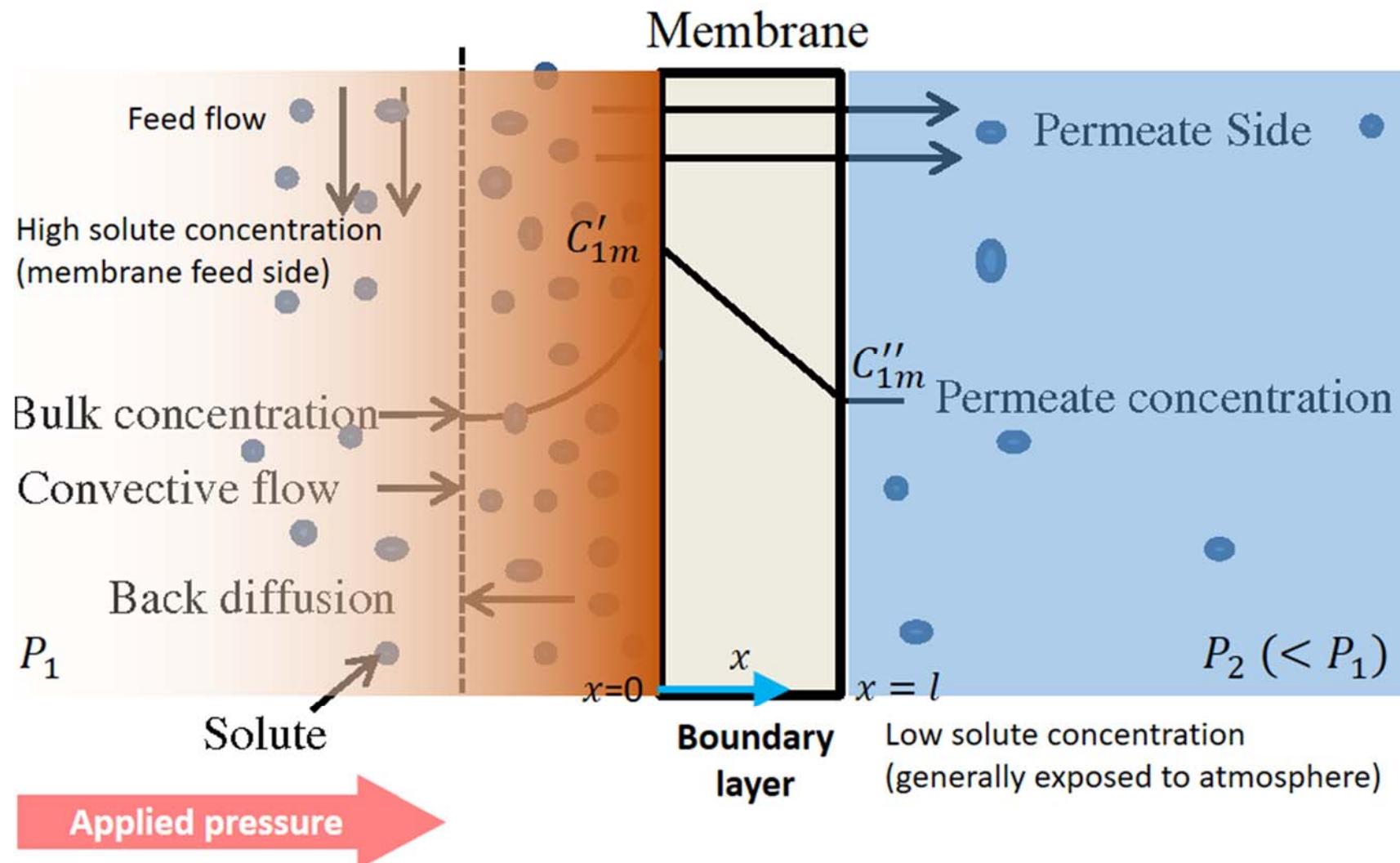
Shortcomings of the 1-D model

- Overlooks developing mass transfer boundary layer
- Overlooks property variation
- Sherwood number from heat-mass transfer analogy for impervious conduit

Modelling of RO systems

1. Osmotic pressure model (solution-diffusion)
2. Kedem-Katchalsky model

Principle of reverse osmosis



Solution diffusion model

The solute flux is

$$JC''_{1m} = B(C'_{1m} - C''_{1m})$$

The above equation is known as **solution diffusion model**.

Combining the above equation with the definition of real retention, the permeate flux can be expressed in terms of retention as

$$J = B \left(\frac{1}{1 - R_r} - 1 \right)$$

where R_r is the real retention of the solute, defined as $R_r = 1 - \frac{C''_{1m}}{C'_{1m}}$

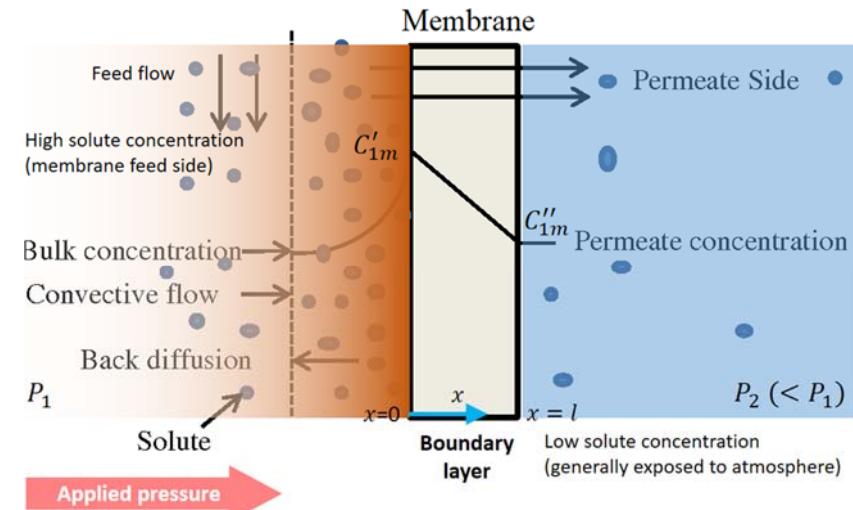
The solvent flux (J), in terms of volumetric flux and membrane permeability (L_p) is

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

The above equation is the Darcy's law and is also known as **osmotic pressure model**.

Combining the above two equations, R_r can be expressed in terms of operating pressure

$$R_r = \frac{L_p (\Delta P - \Delta \pi)}{L_p (\Delta P - \Delta \pi) + B}$$



Kedem-Katchalsky equation

The solvent flux is presented as

$$J = L_p(\Delta P - \sigma \Delta \pi)$$

where σ is reflection coefficient.

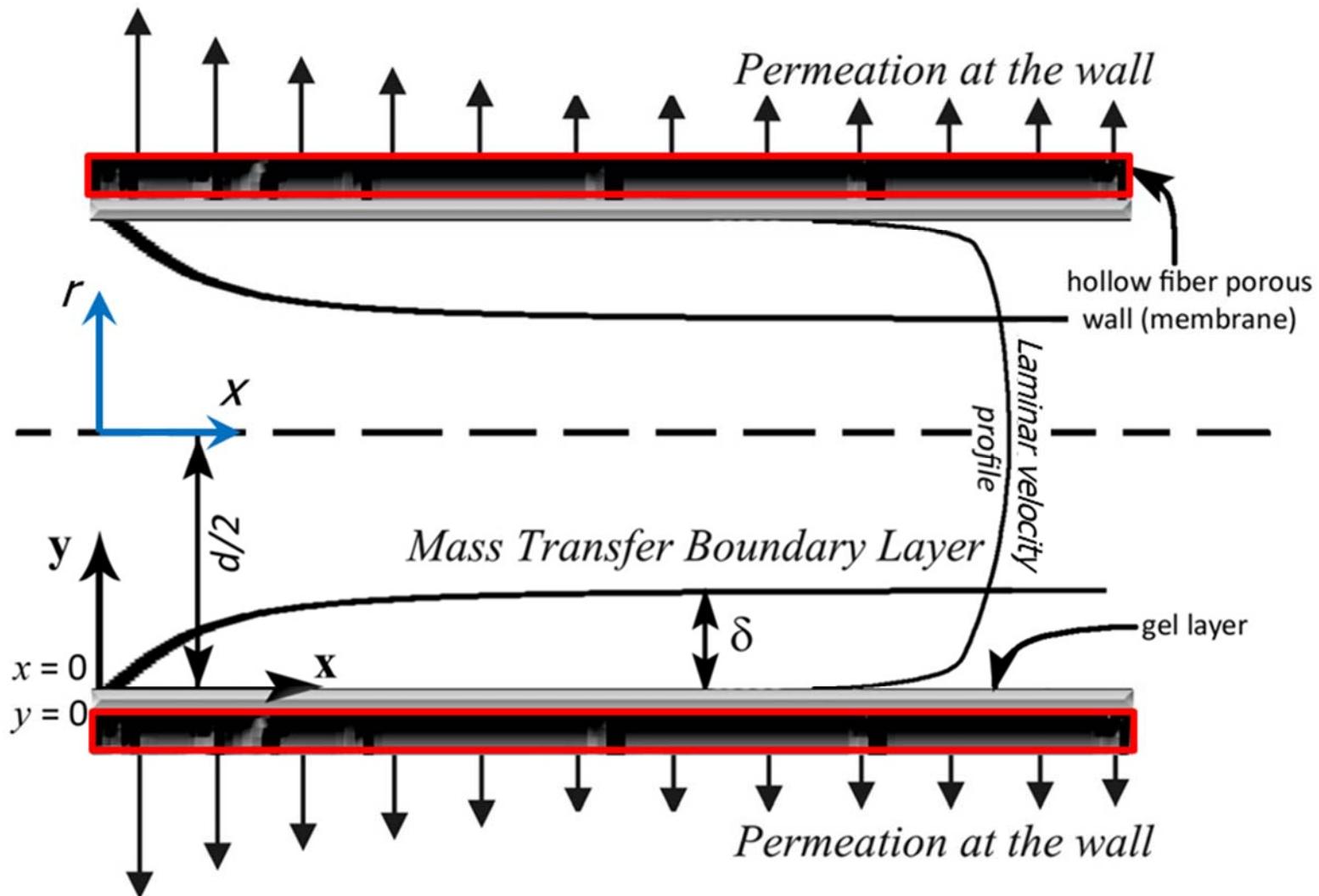
In this case, the solute transport through the membrane is modified by incorporating the convective transport of the solutes through the pores, in addition to the diffusive transport. Thus, this model is more applicable for more porous membrane.

The solute flux is written as,

$$JC_p = (C_m - C_p)\chi + (1 - \sigma)C_{avg}J$$

where $C_{avg} = \frac{C_m - C_p}{\ln(C_m/C_p)}$

Developing mass transfer boundary layer (2D analysis)



Key assumptions:

- (i) steady state, fully developed, laminar flow;
- (ii) permeation rate is negligible compared to cross flow rate and hence the parabolic velocity profile remains intact;
- (iii) there is no adsorption of solute on the membrane surface.

Mass transport equation in the thin concentration boundary layer:

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}$$

It is assumed that the velocity field in the **rectangular channel** is parabolic and the hydrodynamics is fully developed:

$$u(y) = \frac{3}{2} u_0 \left[1 - \left(\frac{y-h}{h} \right)^2 \right]$$

Can you derive the (laminar) velocity field with a leaking / permeating boundary?

For a thin mass transfer boundary layer where the fluid flow is important, one can neglect the $O(y^2)$ terms.

Thus, $u(y) = \frac{3u_0y}{h}$ [for rectangular channel]

Further, it can be assumed that the y-component velocity is constant

$$v = -J(x)$$

Thus, $\frac{3u_0y}{h} \frac{\partial c}{\partial x} - J \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}$

Boundary conditions are @ $x=0, c = C_0$

@ $y=\delta (\rightarrow \infty), c = C_0$

@ $y=0, Jc + D \frac{\partial c}{\partial y} = JC_p$

Solution using similarity technique

The main PDE can be evaluated at the edge of the BL,

since $\frac{\partial C}{\partial y} = 0$

$$\text{So, } \frac{3u_0 y}{h} \frac{\partial C}{\partial x} = D \frac{\frac{\partial^2 C}{\partial y^2}}{y^2}$$

From a scaling analysis, $\frac{3u_0 \delta}{h} \frac{\Delta C}{x} \approx D \frac{\Delta C}{\delta^2}$

$$\Rightarrow \delta = \left[\frac{h D x}{3 u_0} \right]^{1/3}$$

The similarity parameter is thus, $\eta = \frac{y}{\delta} = \left[\frac{u_0}{h D} \right]^{1/3} \frac{y}{x^{1/3}}$

Transforming the PDE $\frac{3u_0y}{h} \frac{\partial c}{\partial x} - J \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}$

in terms of η ,

Steps!

$$\frac{\partial c}{\partial x} = \frac{dc}{d\eta} \left(-\frac{1}{3} \left(\frac{u_0}{hD} \right)^{1/3} \frac{y}{x^{1/3}} \right) \frac{1}{x} = \left(-\frac{y}{3x} \right) \frac{dc}{d\eta}$$

$$\frac{\partial c}{\partial y} = \left(\frac{u_0}{hD} \right)^{1/3} \frac{1}{x^{1/3}} \frac{dc}{d\eta}$$

$$\frac{\partial^2 c}{\partial y^2} = \left(\frac{u_0}{hD} \right)^{2/3} \frac{1}{x^{2/3}} \frac{dc}{d\eta^2}$$

Thus, $\left[-\eta^2 - \left(\frac{hx}{u_0 D^2} \right)^{1/3} \right] \frac{dc}{d\eta} = \frac{dc}{d\eta^2}$

The perm. flux J is inversely proportional to the thickness of the BL,

$$J \propto \frac{1}{\delta} \propto \frac{1}{x^{1/3}}$$

Thus, $J x^{1/3} \rightarrow \text{const.}$

One can also write, $J \left(\frac{h x}{U_b D^2} \right)^{1/3} = \text{const. (say } A \text{)}$

$$\therefore \frac{d\tilde{c}}{d\eta^2} = [-\eta^2 - A] \frac{d\tilde{c}}{d\eta} \quad \begin{bmatrix} \text{Non-dimensionalising} \\ \tilde{c} = c/c_0 \end{bmatrix}$$

$$\text{Integrate once} \Rightarrow \frac{d\tilde{c}}{d\eta} = k_3 \exp\left(-\eta^3/3 - An\right)$$

$$\text{Further integration} \Rightarrow \tilde{c} = k_3 \int_0^\eta \exp\left(-\eta^3/3 - An\right) d\eta + k_4$$

Boundary conditions:

$$@ \eta=0, \frac{d\tilde{C}}{d\eta} + A \tilde{C}_m R_r = 0$$

$$@ \eta \rightarrow \infty, \tilde{C} = 1$$

It may be noted that @ $\eta=0$, $\tilde{C} = \tilde{C}_m = K_4$

$$\text{Thus, } k_3 = - \frac{A R_r}{1 - A R_r I}$$

$$k_4 = \tilde{C}_m = \frac{1}{1 - A R_r I}$$

where $I = \int_0^\infty \exp\left[-\frac{\eta^3}{3} - An\right] d\eta$

Nondimensionalising the Darcy equation,

$$Pe_w(\tilde{x}) = B \left(1 - \frac{\Delta \pi}{\Delta P}\right) \quad \text{where } B = L_p d e \Delta P / D$$

$$\Delta \pi \rightarrow f(cm)$$

$$Pe_w = \frac{U_w de}{D} = 4^{1/3} A \left(Re Sc \frac{de}{L} \right)^{1/3} \tilde{x}^{-1/3}$$

$$\text{So, } A = \frac{Pe_w \tilde{x}^{1/3}}{\left(4 Re Sc de/L\right)^{1/3}}$$

Solution Scheme

1. Guess the value of \tilde{c}_m @ a specific x .
2. Calculate P_{ew}, A
3. Evaluate I
4. Compute $\tilde{c}_m (= k_4)$
5. Compare \tilde{c}_m with the guess value @ step 1.
If not $<$ tolerance, use this as new guess
in step 1.
6. If converged, move to the next axial
location until $\tilde{x} \rightarrow 1$.

Length averaged (non-dimensional) perm. flux ,

$$\overline{P_{ew}} = \int_0^1 P_{ew}(\tilde{x}) d\tilde{x} = 4^{1/3} A \left(Re Sc \frac{de}{L} \right)^{1/3} \int_0^1 \tilde{x}^{-1/3} d\tilde{x}$$

$$= 2.38 A \left(Re Sc \frac{de}{L} \right)^{1/3}$$

Define suction parameter $\alpha = \frac{\overline{P_{ew}}}{\left(Re Sc \frac{de}{L} \right)^{1/3}}$

So, $A = 0.42 \alpha$

Substituting this in the definition of I ,

$$I = \int_0^\infty \exp \left[-\frac{n^3}{3} - 0.42 \alpha n \right] dn$$

Mass transfer coefficient

From definition, $k(c_m - c_0) = -\left(\frac{\partial c}{\partial y}\right)_{y=0}$

Thus, $k(\tilde{c}_m - 1) = -D \left(\frac{u_0}{hDx}\right)^{1/3} \left(\frac{dc}{d\eta}\right)_{\eta=0}$

Substituting $\tilde{c}_m = k_4$ and $\left(\frac{dc}{d\eta}\right)_{\eta=0} = k_3$

$$\Rightarrow k = -\frac{k_3}{k_4 - 1} \left(\frac{u_0 D^2}{hx}\right)^{1/3} = \frac{1}{I} \left(\frac{u_0 D^2}{hx}\right)^{1/3}$$

$$Sh(\tilde{x}) = \frac{kde}{D} = \frac{4^{1/3}}{I} \left(Re Sc \frac{de}{L}\right)^{1/3} x^{-1/3}$$

$$\overline{Sh} = \int_0^1 Sh(\tilde{x}) d\tilde{x} = \frac{2.38}{I} \left(Re Sc \frac{de}{L}\right)^{1/3}$$

For no wall suction, $\overline{P_{ew}} = 0$ (no permeation)

$$I = \int_0^\infty \exp\left(-\frac{\eta^3}{3}\right) d\eta = 1.288$$

$$\text{Thus, } \overline{Sh} = 1.85 \left(Re Sc \frac{de}{L}\right)^{1/3} \quad \xleftarrow{\text{Classical Leveque soln !}}$$

For $\overline{P_{ew}} \neq 0$

One can numerically calculate I as a function of λ ,
and can fit for polynomial function (choose polynomial
order depending on accuracy of fitting)

$$\overline{Sh} = 1.85 \left(Re Sc \frac{de}{L}\right)^{1/3} \left[1 + 0.32\lambda + 0.02\lambda^2 + O(\lambda^3) \text{ & higher} \right]$$

[rectangular channel]

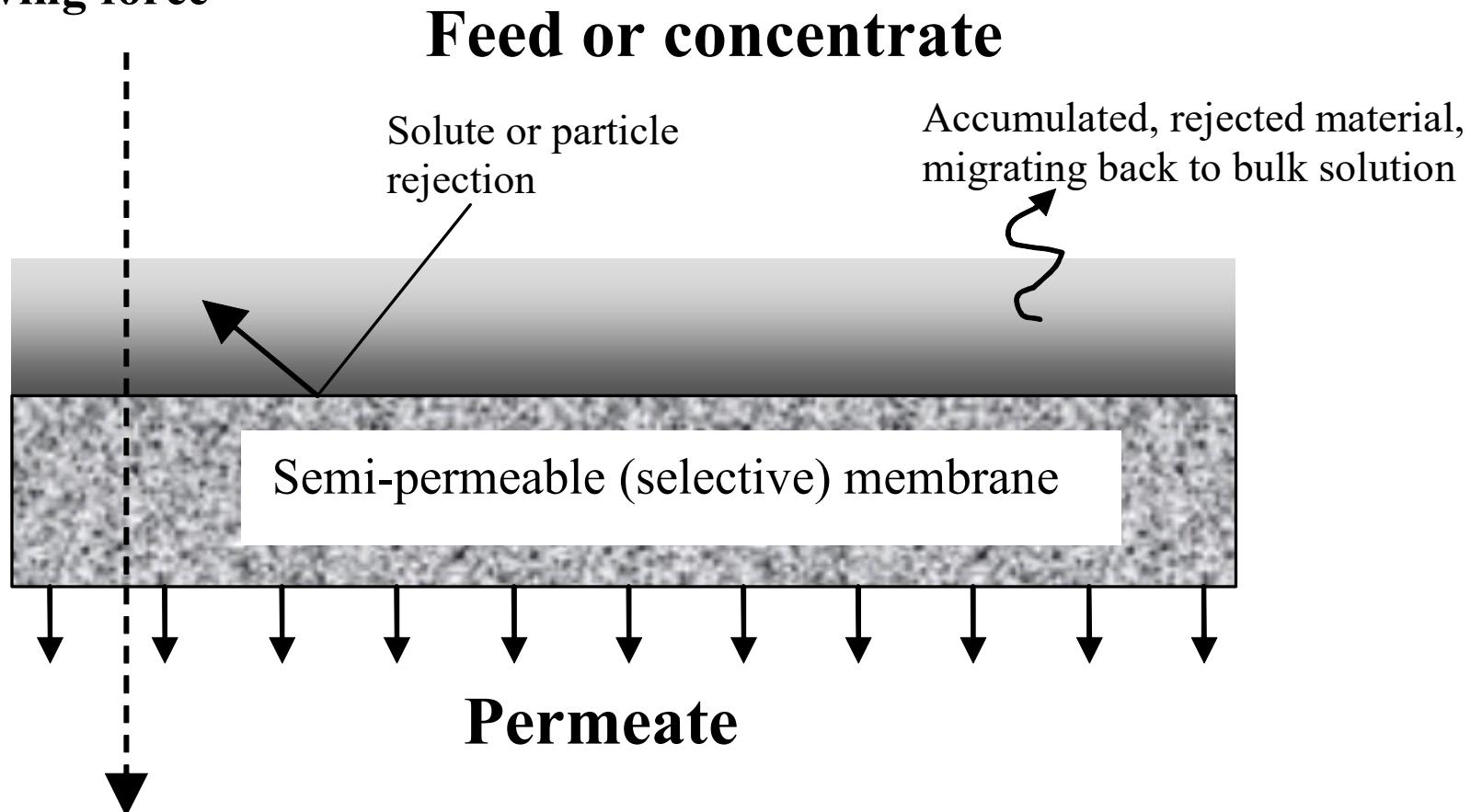
Modelling of UF and MF systems

Define concentration polarization

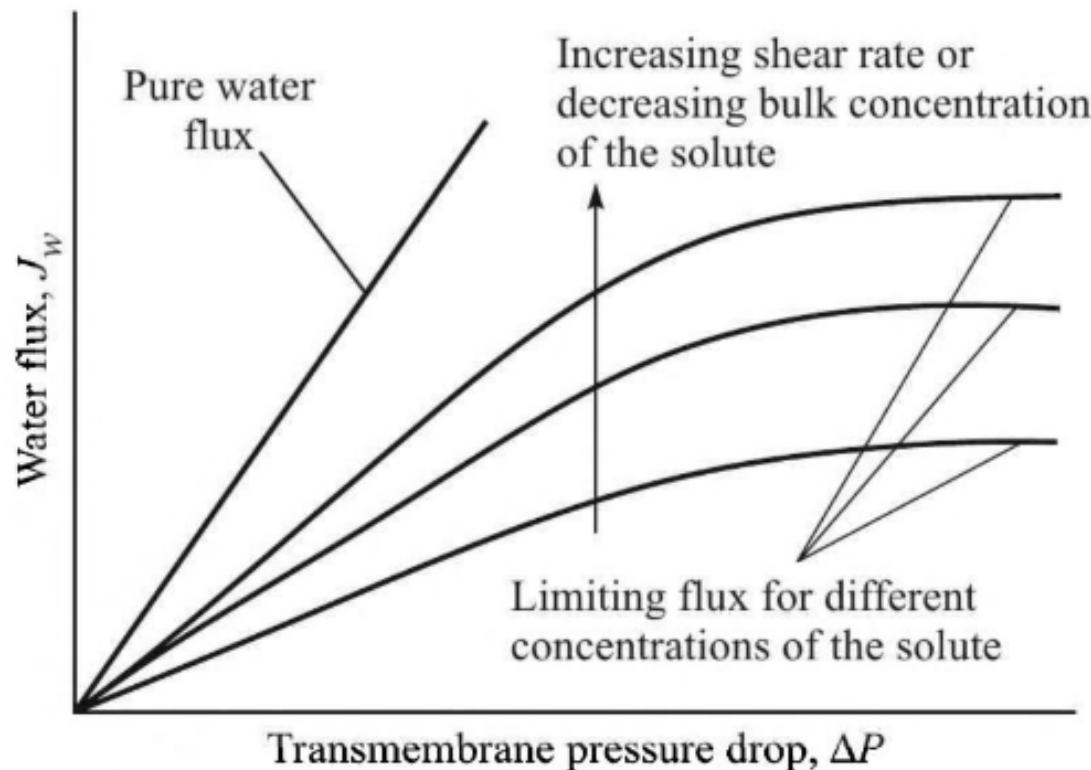
1. Film theory models
2. 2D modelling

Gel layer controlling

Physical, chemical,
and/or electrical
driving force



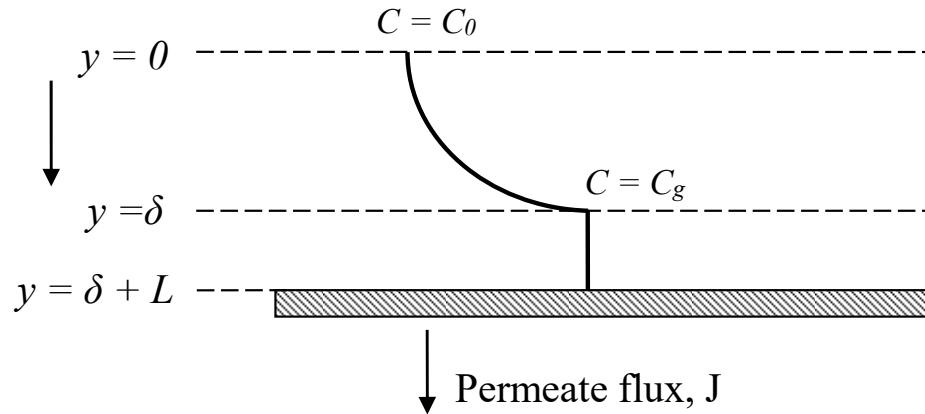
Limiting flux



$$J_{\infty} = \frac{\Delta P}{\mu(R_m + R_g)} = k_L \ln \left(\frac{C_g - C_p}{C_b - C_p} \right)$$

If the solute rejection is high (i.e. $C_p \ll C_b$ and C_s),

$$J_{\infty} = k_L (\ln C_g - \ln C_b)$$



Solute balance in the concentration boundary layer over the gel,

$$\text{Solute balance : } \rho_g \frac{dL}{dt} = Jc - D \frac{\partial c}{\partial y}$$

non-homogeneous ODE

Boundary conditions : @ $y=0, c = c_0$

@ $y=\delta, c = c_g$

$$\text{Thus, } \rho_g \frac{dL}{dt} = J \frac{c_g - c_0 \exp(J/\kappa)}{1 - \exp(J/\kappa)}$$

$$J = \frac{\Delta P}{\mu(R_m + R_g)}$$

Gel resistance

$$R_g = \alpha(1 - \varepsilon_g) \rho_g L$$

α : sp. gel layer resistance $\Rightarrow \alpha = \frac{180(1 - \varepsilon_g)}{\varepsilon_g^2 \rho_g d_p^2}$

ε_g : gel porosity

ρ_g : gel layer density

L : gel layer thickness

(from kozemny karman equation)

Solution of these two equations simultaneously -

Estimation of sp. cake resistance (α)

O experiments need to be conducted in dead-end (unstirred) batch cell.

$$J = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta P}{\mu(R_m + R_g)} = \frac{J_0}{1 + \frac{R_g}{R_m}}$$

Solute mass balance in the gel layer leads to

$$LA(1 - \epsilon_g) P_g = C_0 V \quad (\text{for completely rejecting membrane})$$

Since $R_g = \alpha(1 - \epsilon_g) \epsilon_g L \equiv \frac{\alpha C_0 V}{A}$

$$\therefore \frac{1}{A} \frac{dV}{dt} = \frac{J_0}{1 + \left(\frac{\alpha C_0}{A R_m}\right)V}$$

On integration $t \in (0, t)$

$$V + \left(\frac{\alpha C_0}{2 A R_m} \right) V^2 = J_0 A t$$

On rearranging, $\frac{t}{V} = \frac{1}{A J_0} + \left(\frac{\alpha C_0}{2 A^2 J_0 R_m} \right) V$

Plot of $(\frac{t}{V})$ with $V \rightarrow$ slope gives an estimate on α

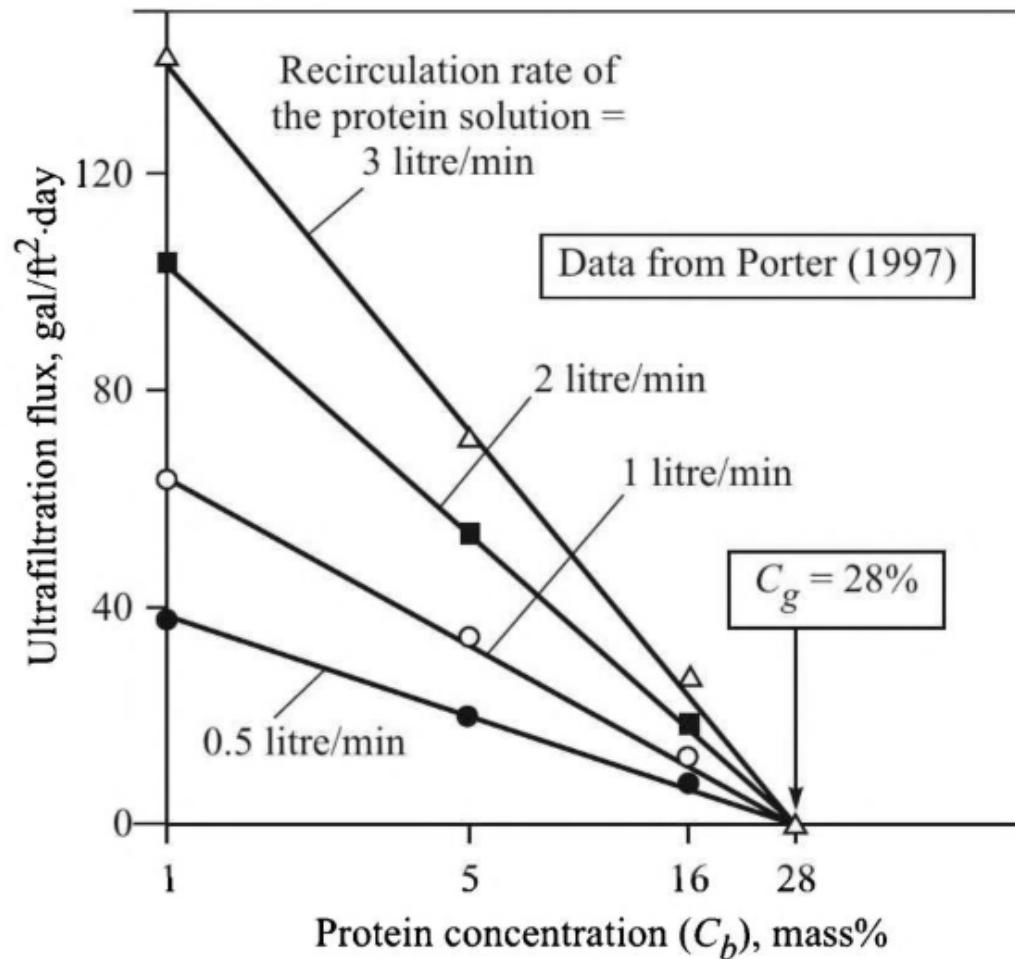
Typically $\alpha = \alpha_0 (\Delta P)^n$

for $n=0 \rightarrow$ cake/gel is incompressible

$n < 1 \rightarrow$ compressible
 $\neq 0$

Estimation of C_g

$$\mathcal{J} = k_L \ln \left(\frac{C_g}{C_b} \right)$$



Estimation of ϵ_g and d_p

$$\text{Vol. of one molecule} : V_0 = \frac{\pi}{6} d_p^3$$

$$\text{Vol. of one mole} = N_A V_0 = \frac{\pi N_A}{6} d_p^3$$

$$\text{No. of moles/m}^3 \text{ of soln.} = 10^3 C_g / M_w$$

$$\therefore \text{Vol. of cake in } 1 m^3 \text{ of soln.} = 10^3 \frac{C_g}{M_w} N_A \frac{\pi}{6} d_p^3$$

$$\text{gel porosity, } \epsilon_g = 1 - 10^3 \frac{C_g}{M_w} N_A \frac{\pi}{6} d_p^3$$

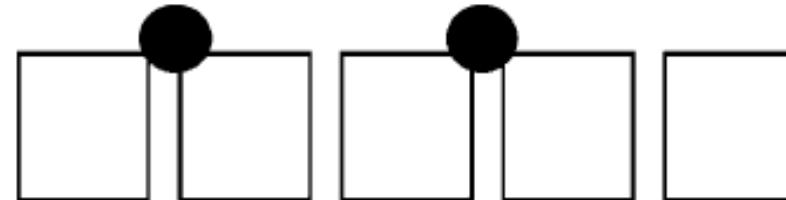
$$\text{From the prev. eqn. of } \alpha = \alpha_0 (\Delta P)^n = 180 \frac{(1-\epsilon_g)}{\epsilon_g^2 d_p^2 \rho}$$

Substitute ϵ_g in terms of d_p

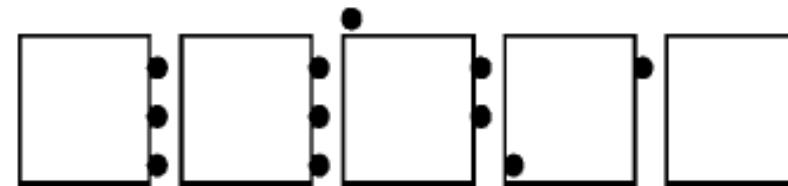
For compressible cake, $d_p (\Delta P) \rightarrow$ soft spheres/particles

Dead end filtration: Mechanisms of membrane fouling

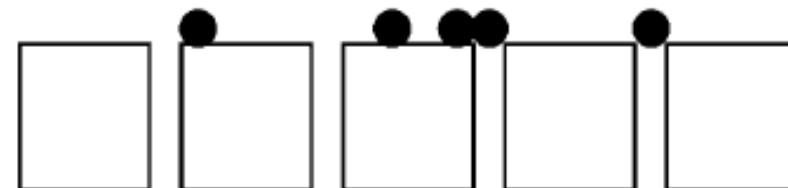
Complete pore blocking



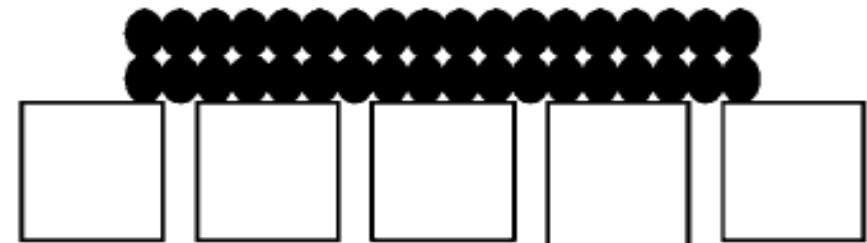
Intermediate pore blocking



Standard pore blocking



Blocking due to cake formation



Primary pore blocking models

- Hermia (J. Hermia, Trans. Int. J. Chem. Eng., 60, 1982, 183-187)
- Unstirred batch cell experiments
- Derived all the characteristic equations of blocking models, occurring one mechanism at a time

Mathematical description

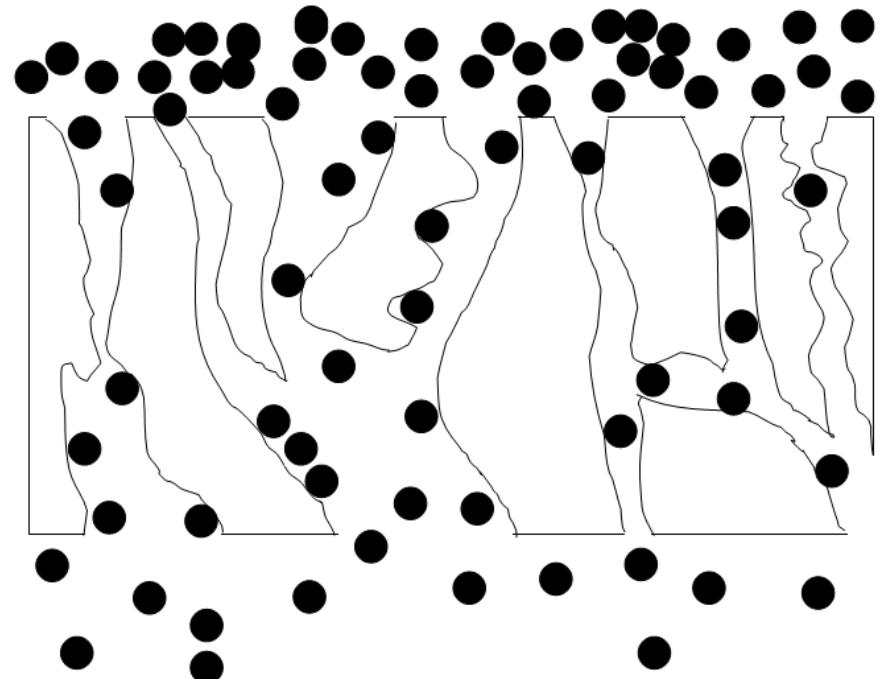
$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n$$

n = 2 for complete pore blocking

**n = 1 for intermediate pore
blocking**

n = 3/2 for standard pore blocking

n = 0 for cake filtration



The above equation can be transformed in terms of the flux

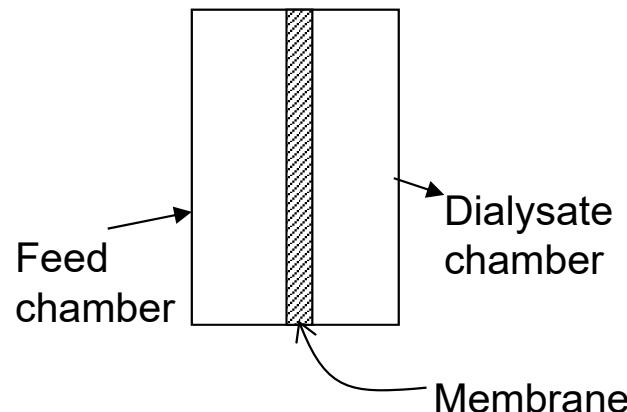
$$\frac{dJ}{dt} = -kJ(JA_0)^{2-n}$$

where $J = \frac{1}{A_0} \frac{dV}{dt}$

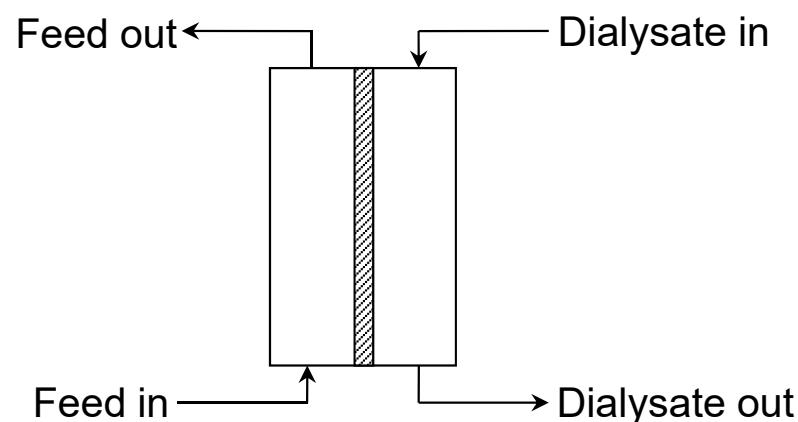
Different fouling mechanisms in UF / MF

Mechanism	n	Models
Complete pore blocking	2.0	$J(t) = J_0 \exp(-k_1 t)$
Intermediate pore blocking	1.0	$J(t) = \left(\frac{Q}{A_0} \right) \frac{1}{1 + k_2 t}$
Standard blocking	1.5	$J(t) = \frac{J_0}{(1 + Bt)^2}$
Cake formation	0	$\frac{1}{J(t)^2} = \frac{1}{J_0^2} + k_c t$

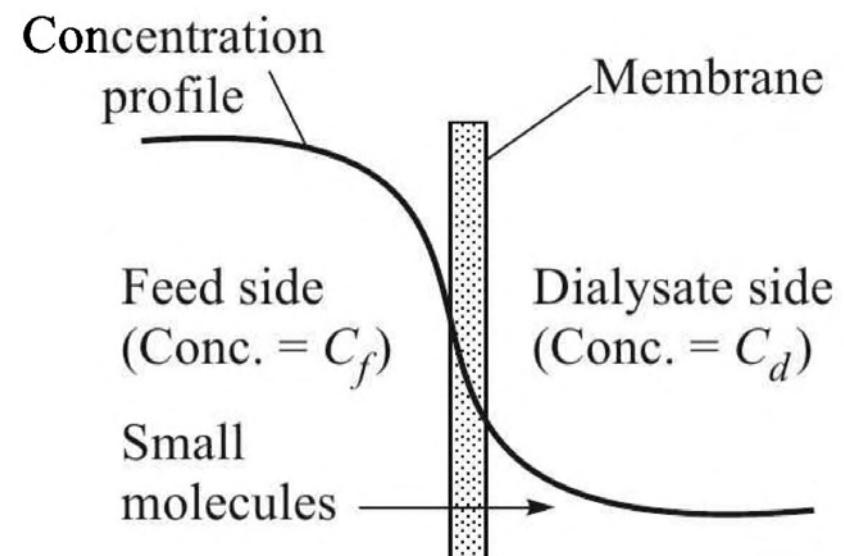
Concentration driven membrane processes



Batch dialyser



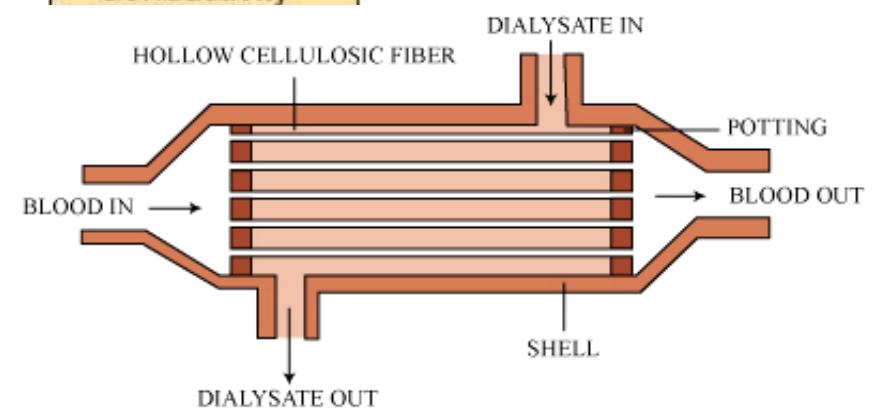
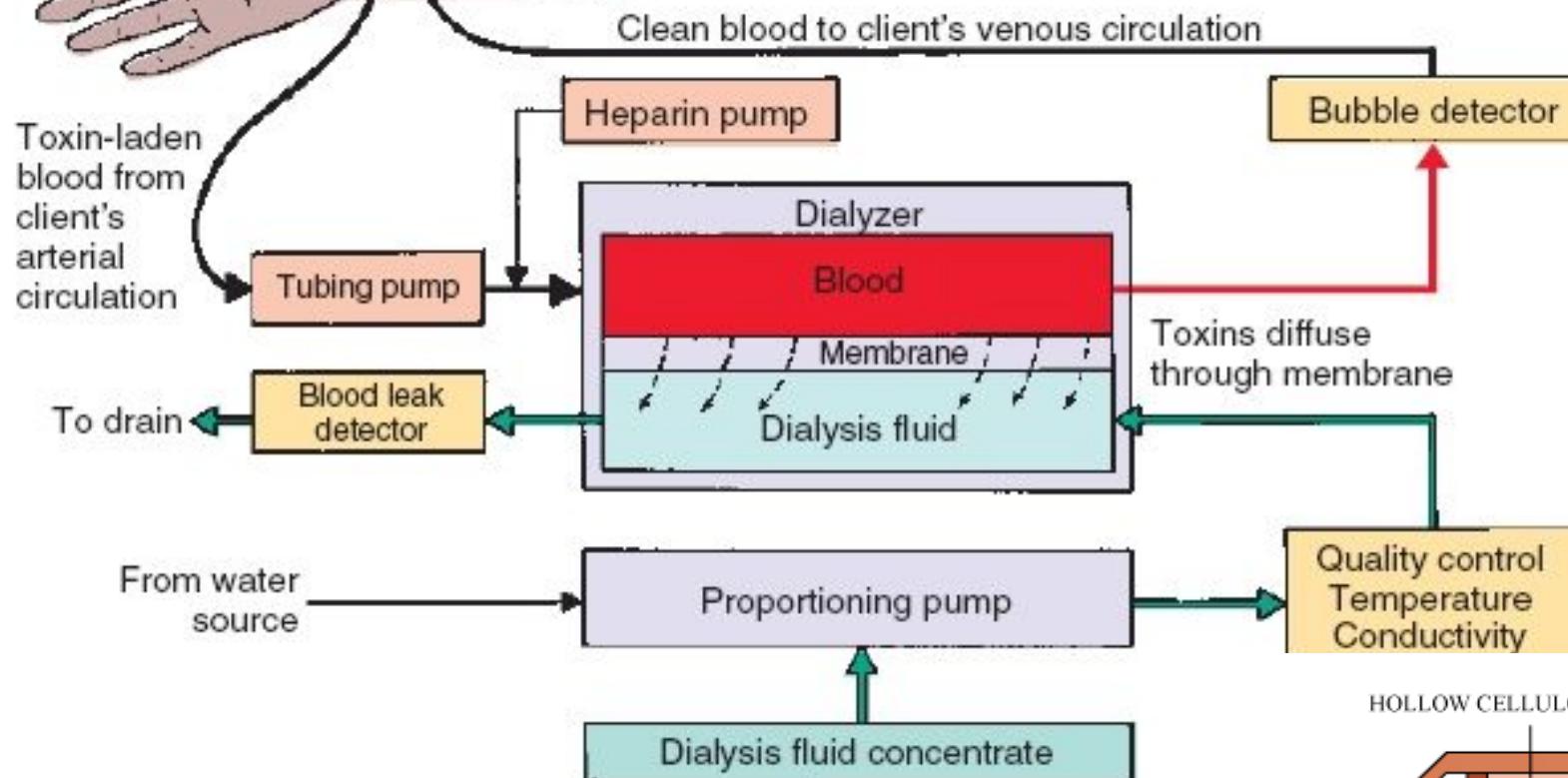
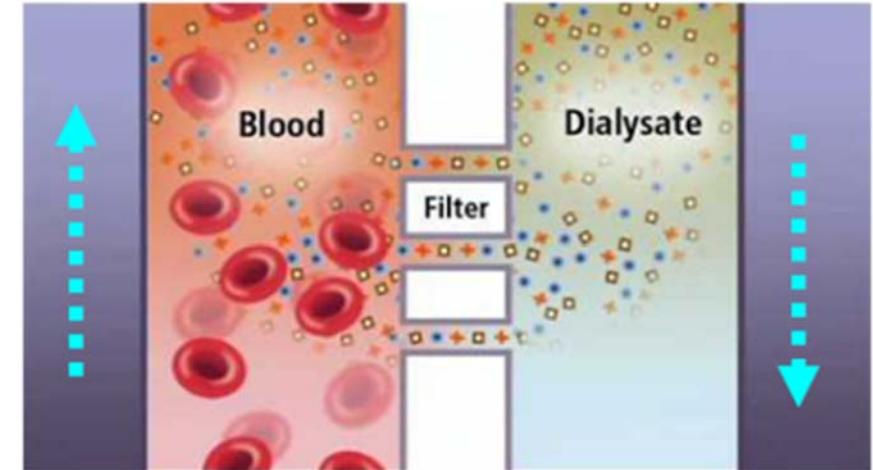
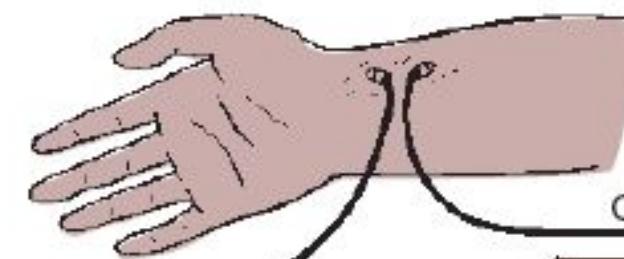
Continuous dialyser



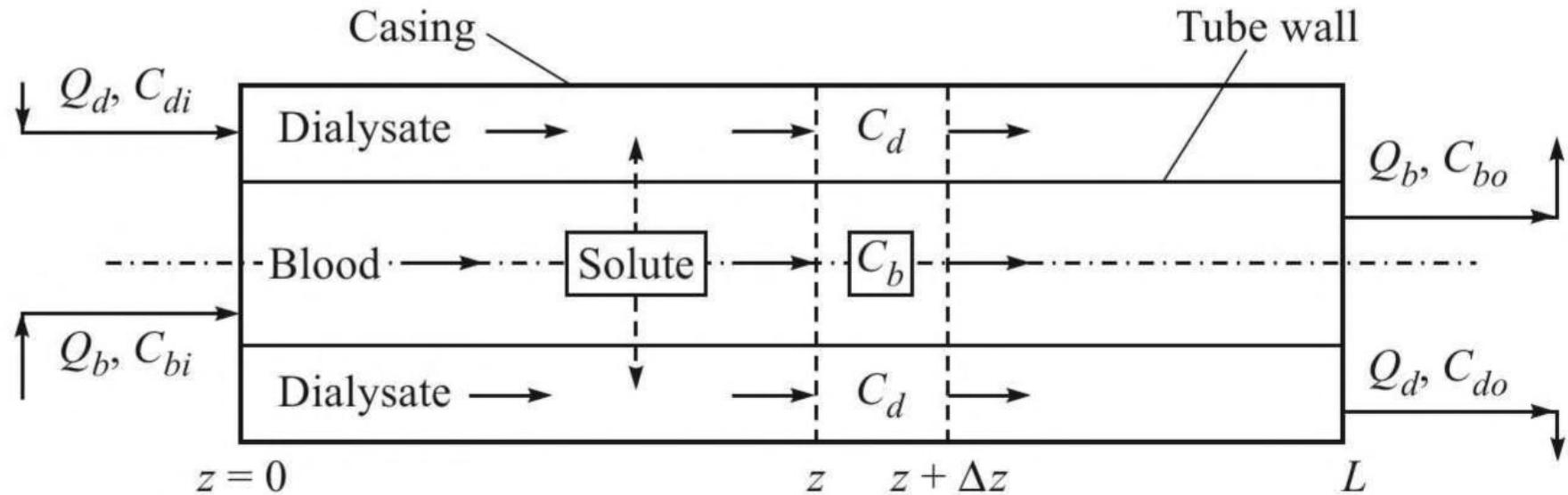
Dialysis : schematic

$$\frac{1}{k_{overall}} = \frac{1}{k_f} + \frac{L}{D_{im}} + \frac{1}{k_d}$$

Haemodialysis



Solute transport in dialysis / haemodialysis



Steady-state solute mass balance from blood to dialysate

$$Q_b C_b|_z - Q_b C_b|_{z+\Delta z} = K_L (B' \Delta z) (C_b - C_d) \Rightarrow -Q_b \frac{dC_b}{dz} = K_L B' (C_b - C_d)$$

$$Q_d C_d|_z - Q_d C_d|_{z+\Delta z} = -K_L (B' \Delta z) (C_b - C_d) \Rightarrow -Q_d \frac{dC_d}{dz} = -K_L B' (C_b - C_d)$$

B' \equiv perimeter of the tubes K_L \equiv overall mass tr. coeff.

From the 2 mass balance equations, we can write

$$Q_b \frac{dC_b}{dz} + Q_d \frac{dC_d}{dz} = 0$$

Assumptions: Flowrates Q_b & Q_d are const.

$$\Rightarrow Q_b C_b + Q_d C_d = \text{const.} = Q_b C_{bi} + Q_d C_{di}$$

$$\therefore C_d(z) = C_{di} + \underbrace{\left(\frac{Q_b}{Q_d} \right)}_{\xi_f} [C_{bi} - C_b]$$

$$\therefore \text{From the eqn: } -Q_b \frac{dC_b}{dz} = k_L B' (C_b - C_d)$$

$$\begin{aligned} \Rightarrow -Q_b \frac{dC_b}{dz} &= k_L B' \left[C_b - (C_{di} + \xi_f (C_{bi} - C_b)) \right] \\ &= k_L B' \left[(1 + \xi_f) C_b - (C_{di} + \xi_f C_{bi}) \right] \end{aligned}$$

On integration from $z=0, L$, $C = (C_{bi}, C_{bo})$

$$-\int_{C_{bi}}^{C_{bo}} \frac{dC_b}{(1+\xi)C_b - (C_{di} + \xi C_{bi})} = \int_0^L \frac{k_L B' I}{Q_b} dz$$

$$\Rightarrow \ln \left[\frac{(1+\xi)C_{bo} - (C_{di} + \xi C_{bi})}{(1+\xi)C_{bi} - (C_{di} + \xi C_{bi})} \right] = - (1+\xi) \underbrace{\frac{k_L B' L}{Q_b}}_{N_T: \text{no. of transfer units}} \xrightarrow{\substack{A_m \\ \text{Area of the dialyser}}}$$

Performance of a dialyser is measured by the clearance & dialysance

$$\dot{M} = Q_b (C_{bi} - C_{bo}) \rightarrow \text{mass of solute that is removed in the dialyser}$$

$$(CL) [C_{bi} - 0] = \dot{M} \rightarrow \text{mass flowrate of blood which will be completely free of the solute}$$

$$\Rightarrow CL = Q_b \left[1 - \frac{C_{bo}}{C_{bi}} \right]$$

This indicates the rate of the dialyser ability to completely clean the blood.

→ remove solutes (urea/creatinin)

Typically commercial dialysers have a CL of 50-100 ml/min

Dialysance : Solute removal capacity of the dialyser

$$DL = \frac{Q_b (C_{bi} - C_{bo})}{C_{bi} - C_{di}} = \frac{\dot{M}}{C_{bi} - C_{di}}$$

If the inlet dialysate fluid is free of solute, $C_{di} = 0$

then $CL = DL$

From the eqn. $\ln \left[\frac{(1+\xi_s)C_{bo} - (C_{di} + \xi_s C_{bi})}{(1+\xi_s)C_{bi} - (C_{di} + \xi_s C_{bi})} \right] = -(1+\xi_s)N_T$

we can write:
$$\frac{C_{bi} - C_{bo}}{C_{bi} - C_{di}} = \frac{1 - \exp[-(1+\xi_s)N_T]}{1 + \xi_s} = \frac{DL}{Q_b} = ER$$

ER for counter-current dialyser? Assignment

(Time of dialysis using a hollow-fibre haemodialyser) Blood from a patient's body is pumped through a cocurrent haemodialyser at a rate of 280 ml/min to reduce the urea concentration from 200 mg% to 20 mg%. The other undesirable substances are removed as well. The available membrane area is 1.15 m^2 , and the overall mass transfer coefficient is estimated to be $1.2 \times 10^{-6} \text{ m/s}$. The volume of blood in a normal human body is about 5 litre. If the flow rate of the dialysate fluid is maintained high ($Q_d \gg Q_b$), estimate the time of dialysis. Also the dialysate fluid is solute-free.

$$\text{Here } Q_b \ll Q_d \Rightarrow \xi = \frac{Q_b}{Q_d} \approx 0$$

Dialysate is also solute free $\rightarrow C_{di} = 0 \approx C_{do}$

$$\therefore ER = \frac{C_{bi} - C_{bo}}{C_{bi}} = 1 - \exp(-NT)$$

$$\Rightarrow C_{bi} - C_{bo} = C_{bi} [1 - \exp(-NT)]$$

The change in solute conc. in the body at time dt
is dC_{bi}

$$\therefore -V_L dC_{bi} = Q_b (C_{bi} - C_{bo}) dt$$

$$\Rightarrow -V_L \frac{dC_{bi}}{dt} = Q_b (C_{bi} - C_{bo})$$

Amt. of solute that is
removed/reduced from the
body (having blood V_L)

S_0 , in time t , the solute conc. changes from

$$c_1 \rightarrow c_2 (< c_1)$$

$$\Rightarrow - \int_{c_1}^{c_2} \frac{dc_{bi}}{c_{bi}} = \int_0^t \frac{Q_b}{V_L} [1 - \exp(-N_T)] dt$$

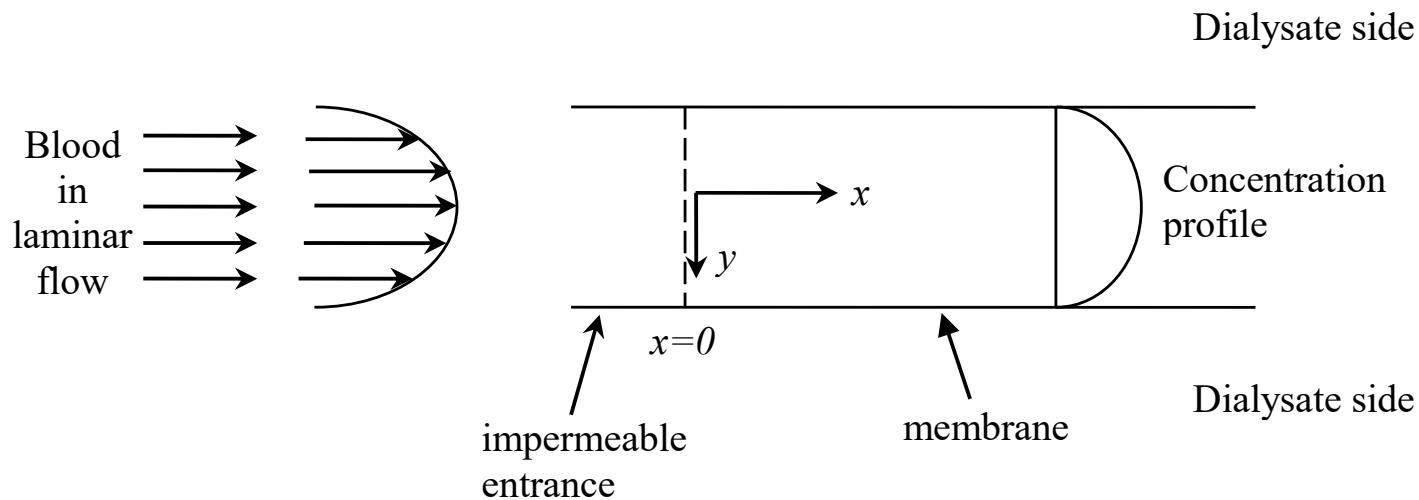
$$\Rightarrow t = \frac{V_L}{Q_b [1 - \exp(-N_T)]} \ln(c_1/c_2)$$

Use the numbers : $V_L = 5 \text{ lts}$. $c_1/c_2 = 200/20 = 10$

$$k_L = 1.2 \times 10^{-6} \text{ m/s}, \quad A_m = 1.15 \text{ m}^2 \quad Q_b = 280 \text{ mL/min}$$

$$\therefore t = 2 \text{ h } 40 \text{ min}$$

Detailed two dimensional analysis of Dialysis



We consider a Newtonian-laminar flow in a rectangular channel with the velocity profile

$$u(y) = \frac{3}{2} u_0 \left(1 - \frac{y^2}{h^2} \right)$$

At steady state, $-h \leq y \leq h$, the solute mass balance

$$u \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}$$

Boundary conditions : @ $x=0$, $c = C_0$
@ $y=0$, $\frac{\partial c}{\partial y} = 0$ (symmetry)

@ $y=h$, $-D \frac{\partial c}{\partial y} = k c$

typically referred to as
the membrane permeability

We can consider dialysate is extremely dilute, so
there is insignificant mass transfer resistance .

standard eigen value problem:

Can you solve this problem ?

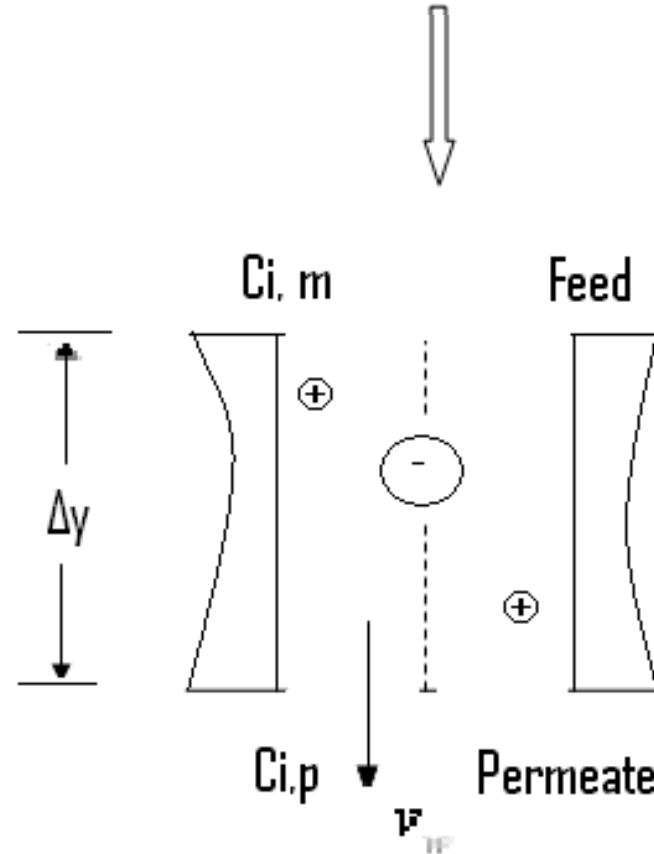
End sem

for some simplifications: say $u = u_0$ or $u = u_0 y$

Electrical potential driven membrane processes

Charge transport across membrane fuel cell / PEM

Pore flow model – charged / NF membranes



Model Equations

Film theory	$v_w = \ln \frac{C_m - C_p}{C_0 - C_p}$
Osmotic pressure model	$v_w = \frac{\Delta P - \Delta \pi}{\mu[R_m + k_0 C_m]}$
Transport through pore	$j_i = -D_{i,m} \frac{\partial c_i}{\partial y} + K_{i,c} c_i J_v - \frac{z_i c_i D_{i,m} F}{RT} \frac{\partial \psi_m}{\partial y}$
Solvent flux in pore	$j_i = J_v C_{i,p}$
Electro-neutrality in bulk	$I = \sum_i F z_i j_i = 0$
Electroneutrality in pore	$I = \sum_i z_i c_i + X = 0$

Hindered coefficients

$$K_{i,c} = \frac{v_i}{j_v} = -0.301\lambda_i + 1.022$$

$$K_{i,d} = \frac{D_{i,m}}{D_{i,\infty}} = -1.705\lambda_i + 0.946$$

Concentration equation in pore

$$\frac{d\xi_i}{d\eta} = \frac{Pe_i}{K_{i,d}} (K_{i,c}\xi_i - Y_{i,P}) - z_i \xi_i \frac{\sum_i \frac{z_i c_{i,0} Pe_i}{K_{i,d}} (K_{i,c}\xi_i - Y_{i,P})}{\sum_i z_i^2 c_{i,0} \xi_i}$$

Boundary conditions

$$\xi_i = 1 \quad \text{at} \quad \eta = 0$$

$$\xi_i = \frac{c_{i,\Delta y}}{c_{i,0}} = \frac{\Phi_i c_{i,p}}{\Phi_i c_{i,m}} = S_i \quad \text{at} \quad \eta = 1$$

$$\xi_i = \frac{c_i}{c_{i,0}}; \quad \eta = \frac{y}{\Delta y}; \quad Pe_i = \frac{J_v \Delta y}{D_{i,\infty}}; \quad S_i = \frac{c_{i,p}}{c_{i,m}}$$

Gas separation