



Spring Semester course

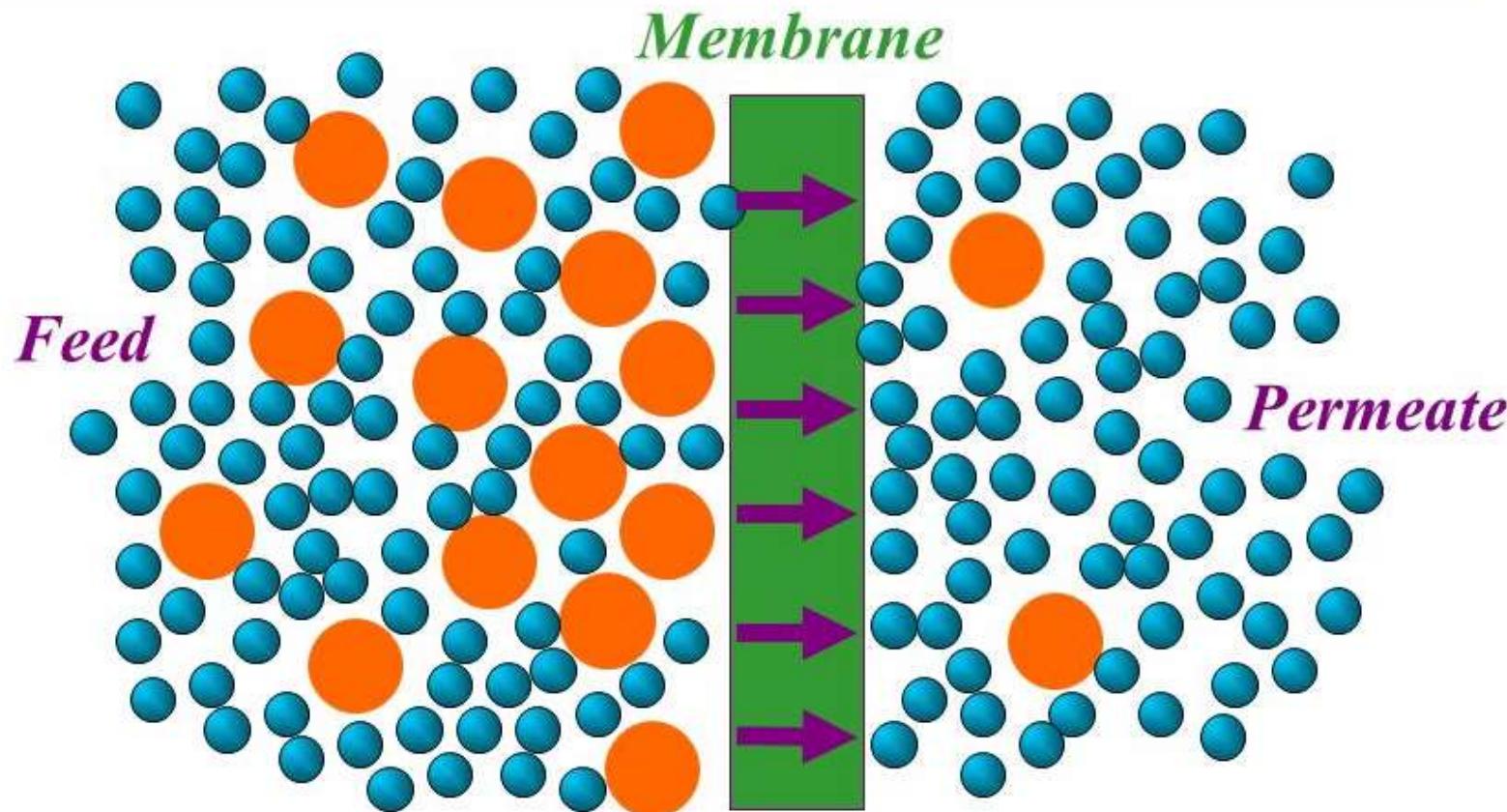
CH31010: Mass Transfer II

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IIT Kharagpur, Kharagpur, India

L5: Membrane Separation

Membrane Separation

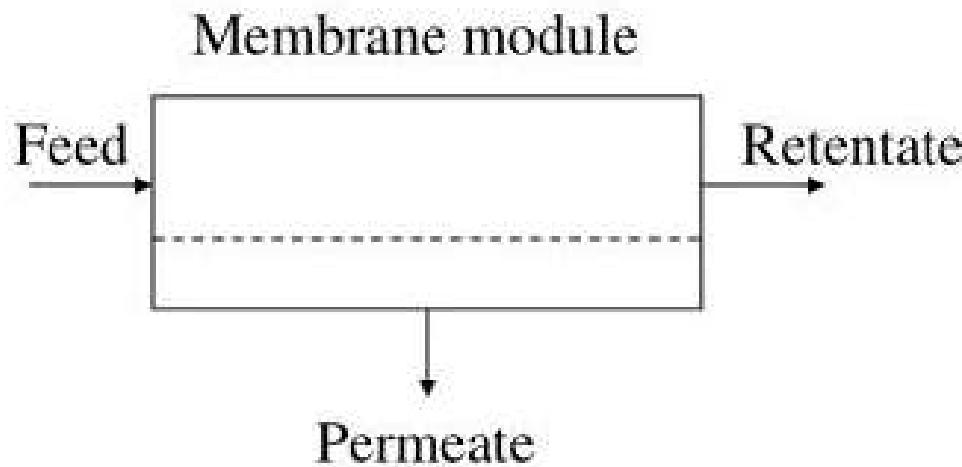


*Particle or
Solute Molecule*



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

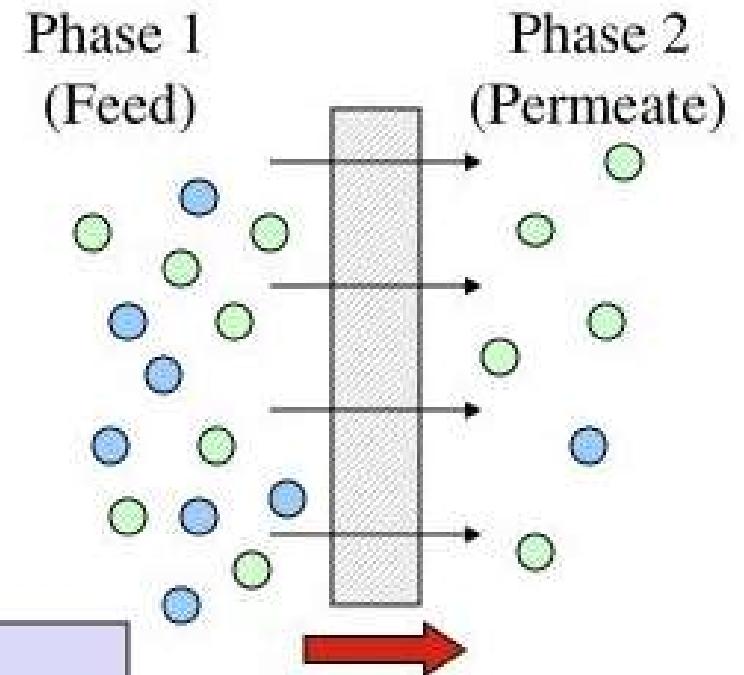
Reverse Osmosis

Molecular sieving

Gas separation

Membrane contactors

Pervaporation



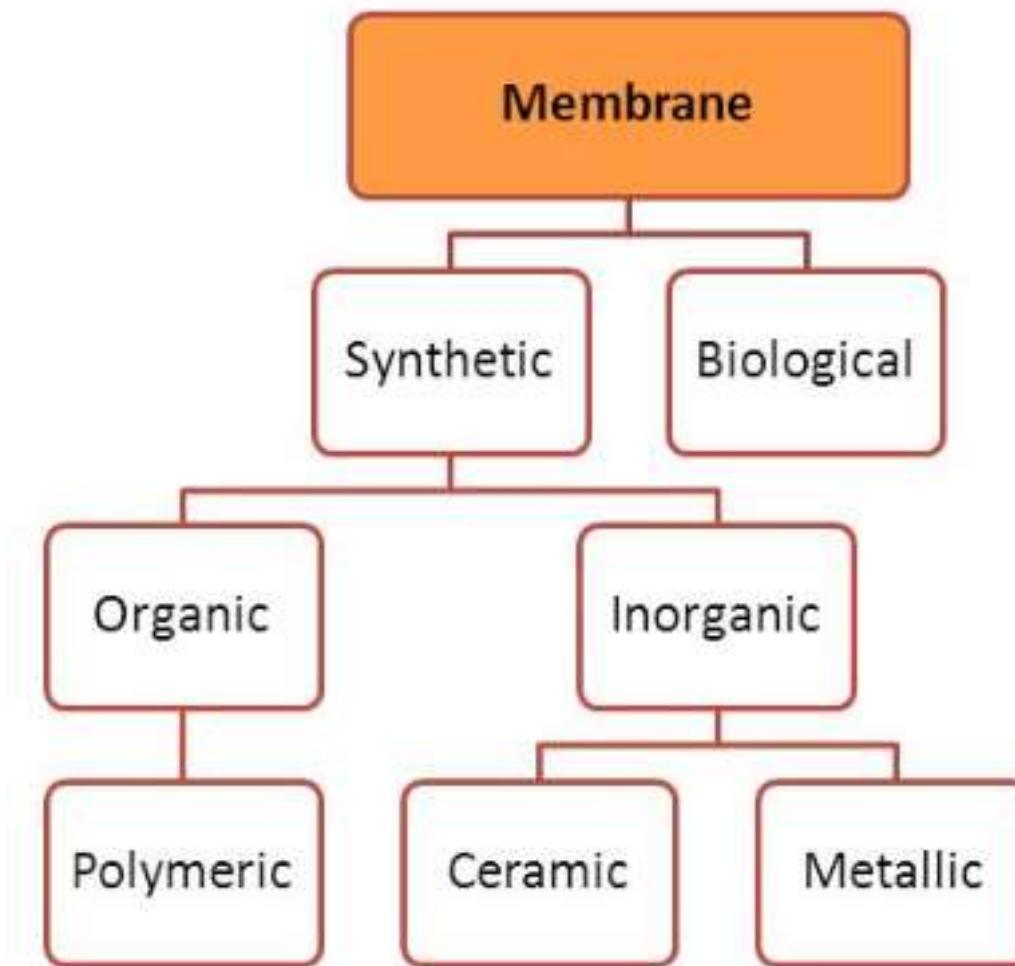
Flux
Selectivity

	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	10^7
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



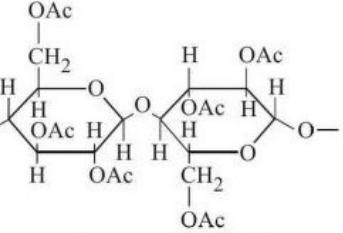
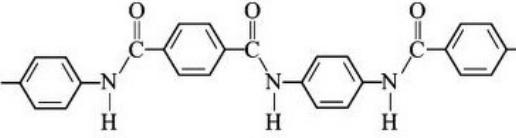
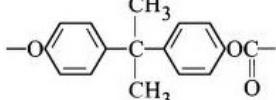
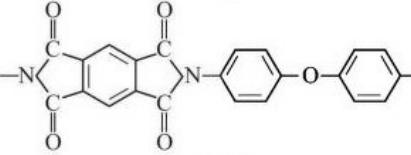
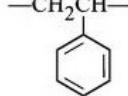
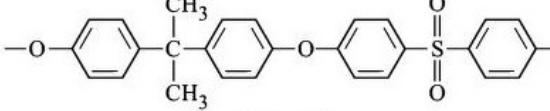
Membrane materials

Polymer (organic) >>> Inorganic

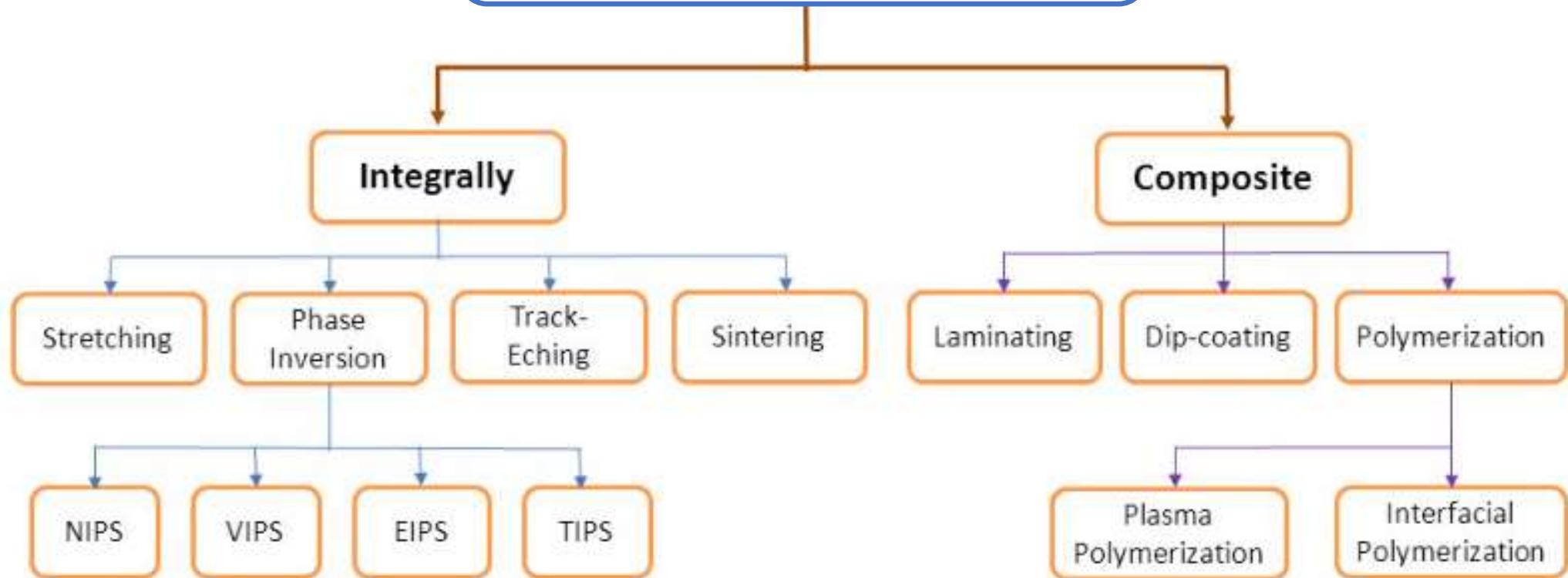
- (i) many different types of polymeric material are commercially available,
- (ii) a large variety of different selective barriers, i.e., porous, nonporous, charged and affinity, can be prepared by versatile methods,
- (iii) production of large membrane area with consistent quality is possible in technical 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

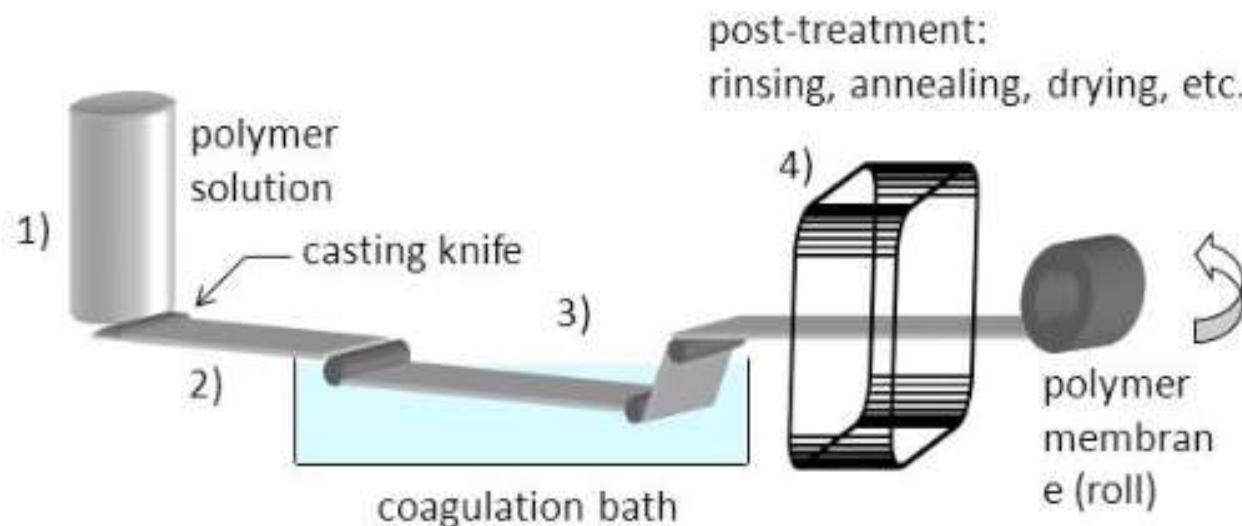
Polymer	Type	Representative repeat unit/formula	Tg, °C	M.P., °C
Cellulose triacetate	Crystalline			300
Polyisoprene (natural rubber)	Rubbery	$\left[\text{CH}_2\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2 \right]_n$	-70	
Aromatic polyamide	Crystalline			275
Polycarbonate	Glassy		150	
Polyimide	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		$\left[(\text{CF}_2\text{--CF}_2)_m \text{--} \underset{\substack{ \\ \text{O} \\ \\ \text{F}}}{\text{CF}} \text{--} \text{CF}_2 \right]_n$ $(\text{CF}_2\text{--C}(\text{CF}_3)\text{--O}_p)\text{--CF}_2\text{--CF}_2\text{--SO}_3\text{H}$		

Membrane preparation



Phase inversion

Schematic depiction of the continuous manufacturing process of polymeric membranes



Factors:

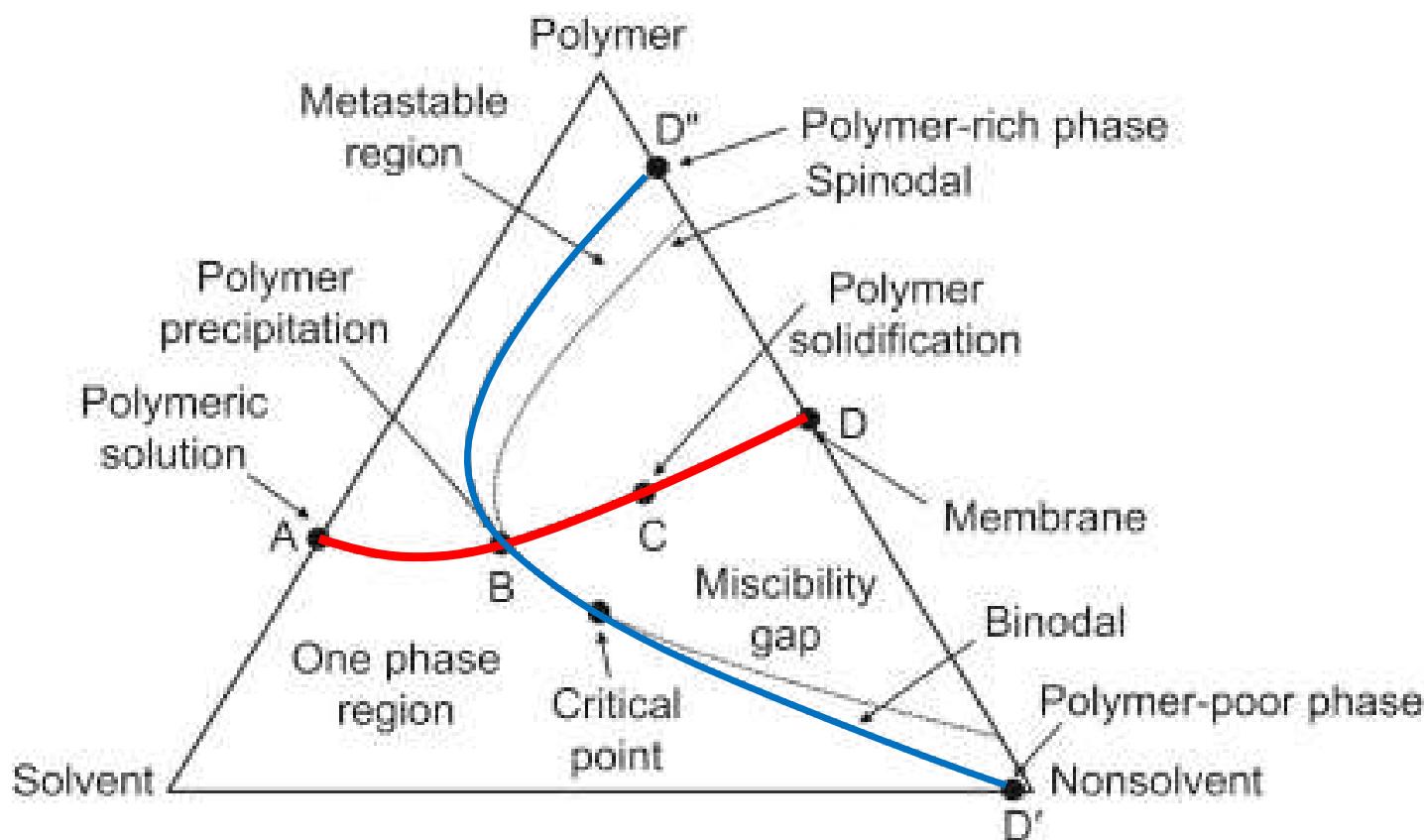
- (i) Thermodynamic aspects.
- (ii) The rate of precipitation in the liquid film; the mass-transfer (non-solvent in-flow, and solvent out-flow) can have tremendous influence: Instantaneous liquid-liquid demixing, which will result in a porous membrane, delayed onset of liquid-liquid demixing, which can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

Types of phase inversion

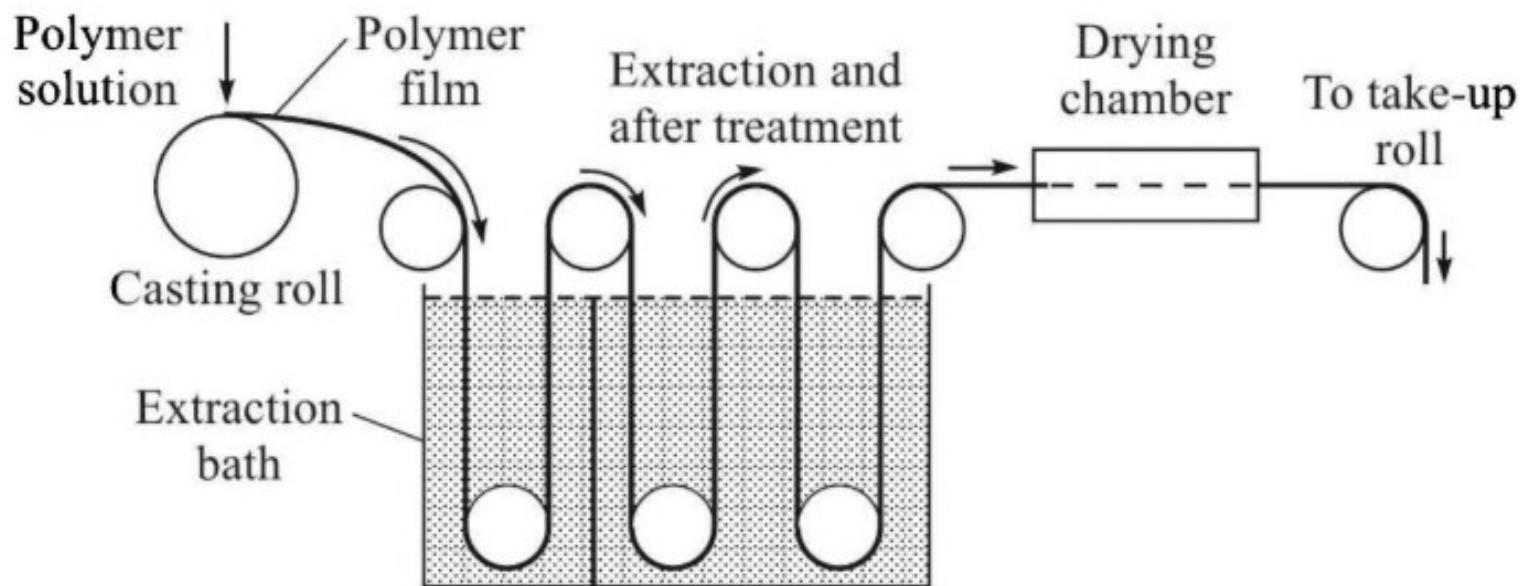
- ***Nonsolvent induced phase separation (NIPS)*** – the polymer solution is immersed in a nonsolvent coagulation bath (typically water); demixing and precipitation occur due to the exchange of solvent (from polymer solution) and nonsolvent (from coagulation bath), i.e., the solvent and nonsolvent must 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)

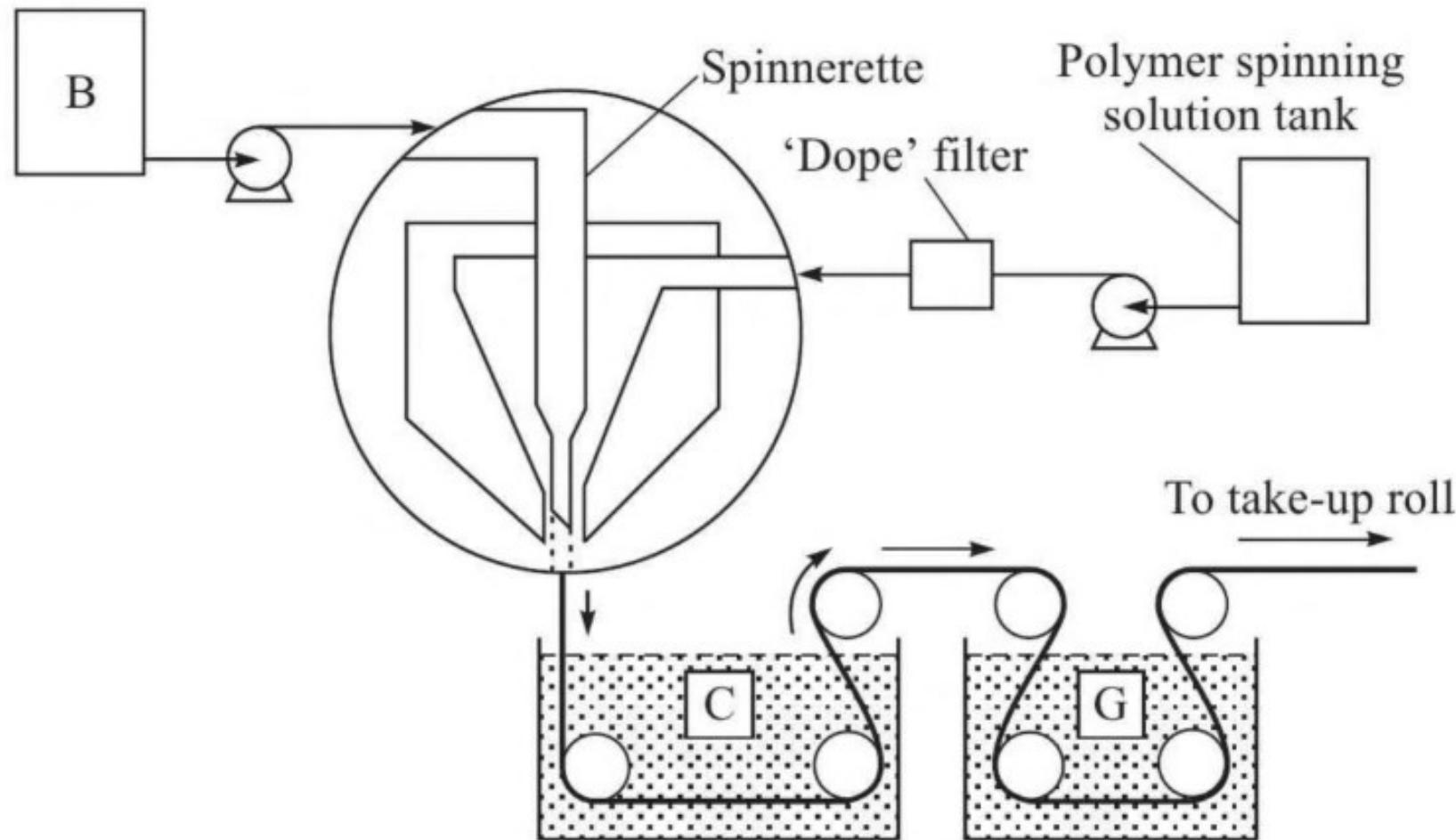


Fabrication of flat sheet membranes



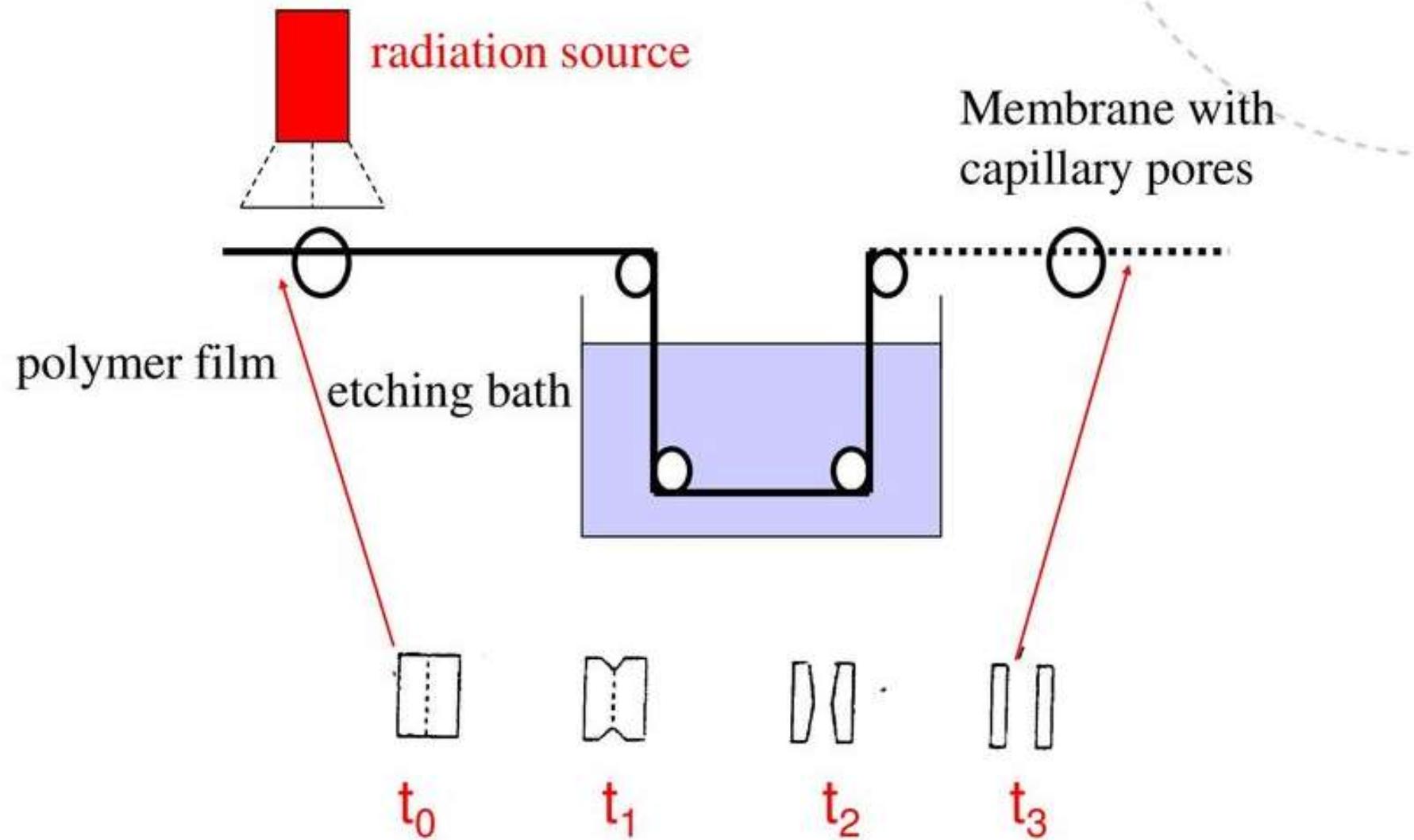
Schematic of a set-up for preparation of microporous membranes by the polymer precipitation technique.

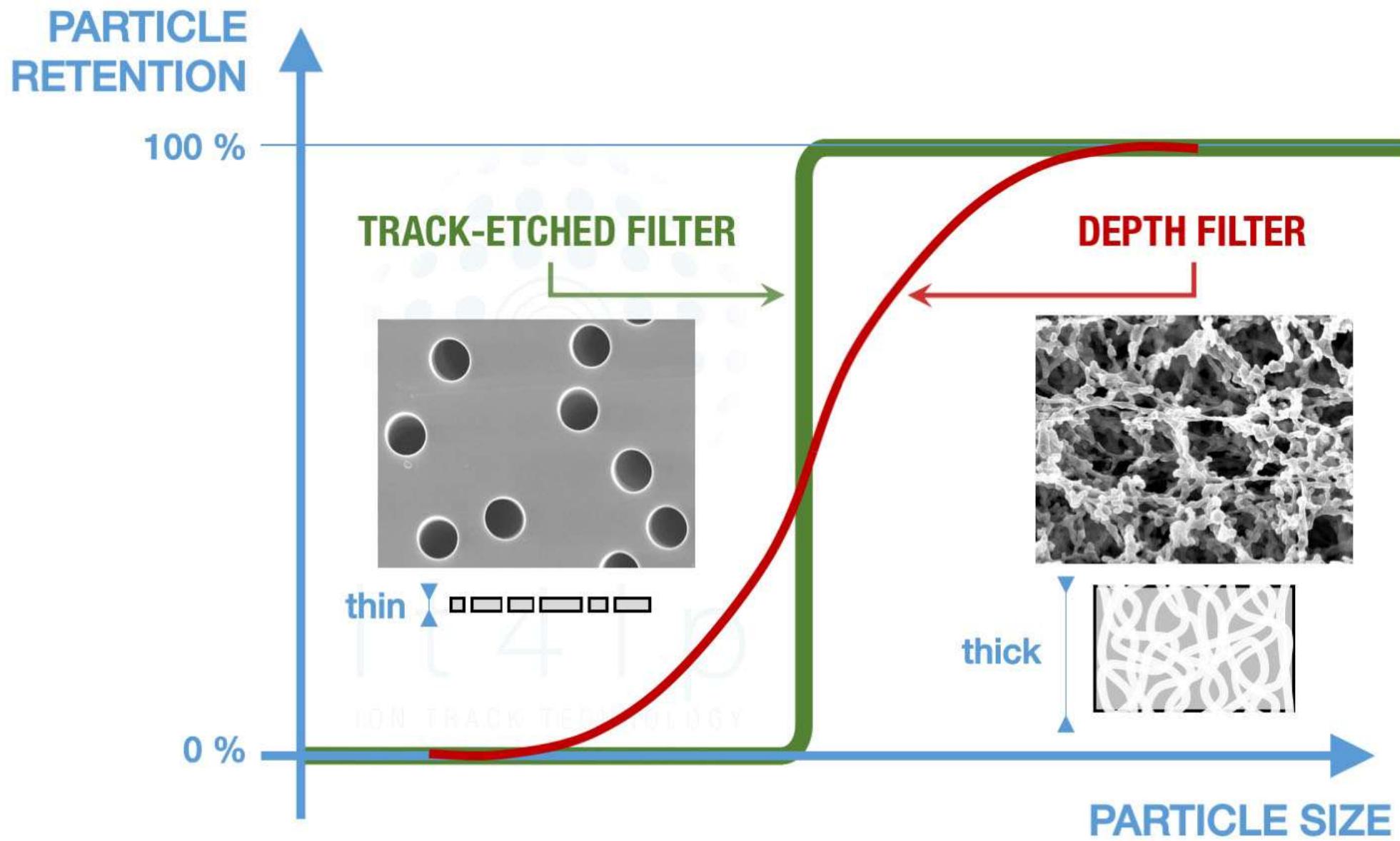
Hollow fibres – wet spinning



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

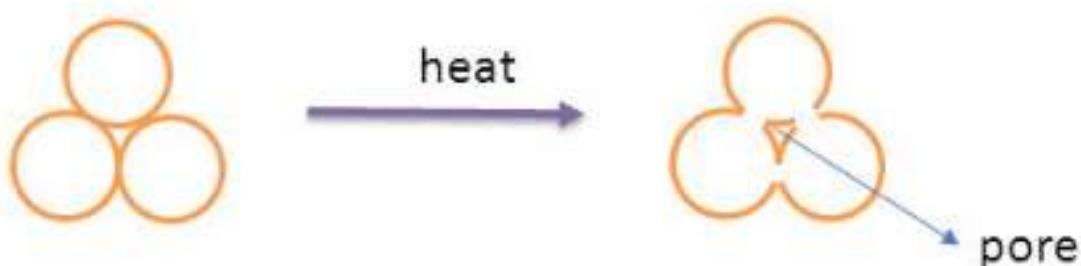
Track-etching process





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

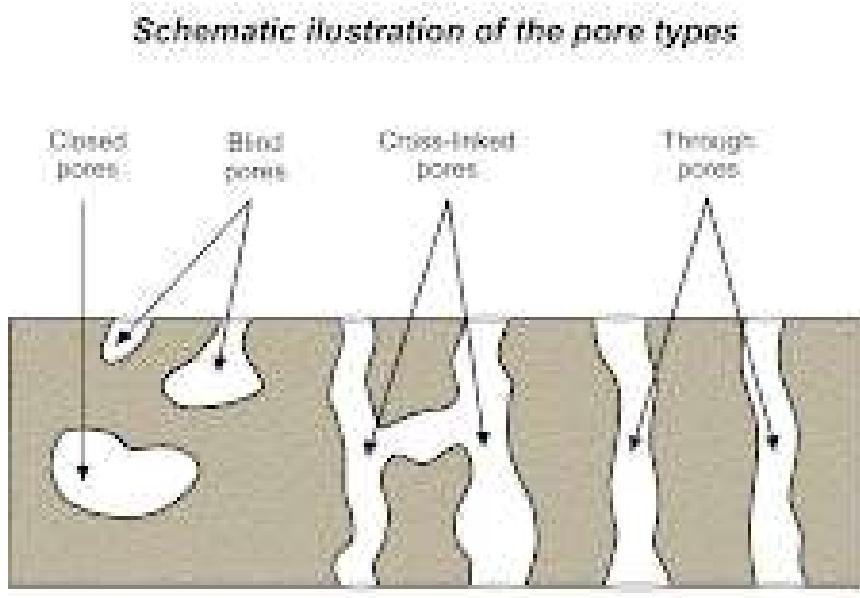
Mechanical strength

Surface energy (hydrophilicity?)

Chemical stability

Principle of mercury porosimetry

The technique involves the intrusion of a non-wetting liquid (often mercury) at high pressure into the porous material. The pore size is inversely proportional to the external pressure needed to force the liquid into a pore.



Mercury drop in contact with porous material

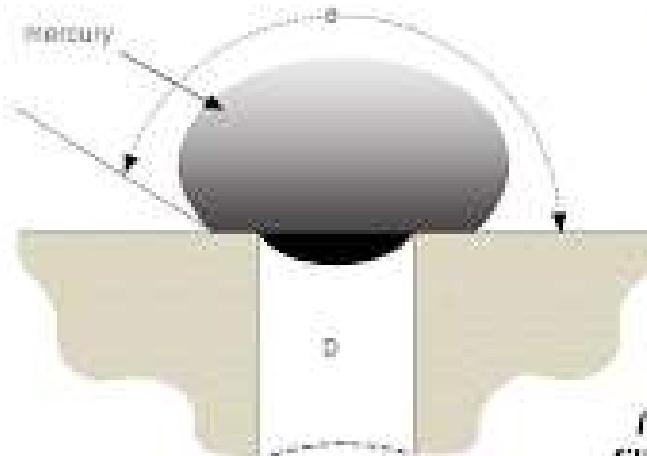


Illustration of the mercury filling the sealed sample cup with sample present.

Washburn Equation: $P_L - P_G = -\frac{2\gamma \cos \theta}{r_P}$

Principle of BET analysis

Multi-layer adsorption according to Brunnauer, Emmett und Teller

$$\frac{1}{v[(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c}$$

v = adsorbed gas quantity

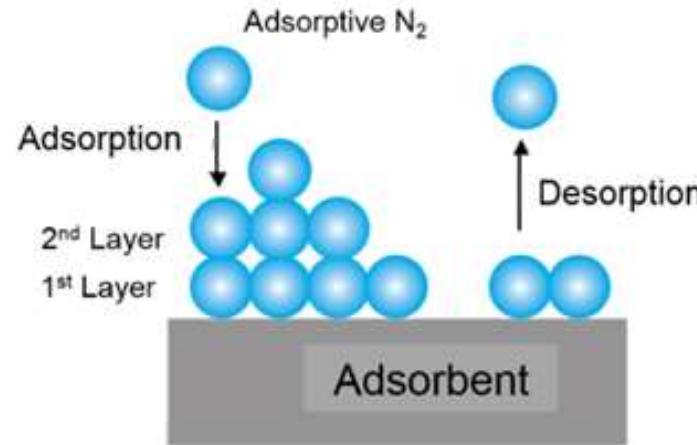
p_0 = saturation pressure of adsorbate

p = equilibrium pressure of adsorbate

c = BET constant = $\exp\left(\frac{E_1 - E_L}{RT}\right)$

E_1 = heat of adsorption for the first layer

E_L = heat of vaporization



Equilibrium

Rate of adsorption equals rate of desorption.

From the monolayer adsorbed gas volume (v_m), we can determine the total and specific surface area

S_t = total surface area of sample material

v_m = monolayer absorbed gas volume

N = Avogadro's number = 6.02×10^{23} molecules/mol

s = cross-sectional area of adsorbed gas molecule

V = molar volume of adsorbed gas

S_{BET} = specific surface area

a = mass of sample

$$S_t = \frac{v_m s N}{V} \quad S_{BET} = \frac{s_t}{a} [\text{m}^2/\text{g}]$$

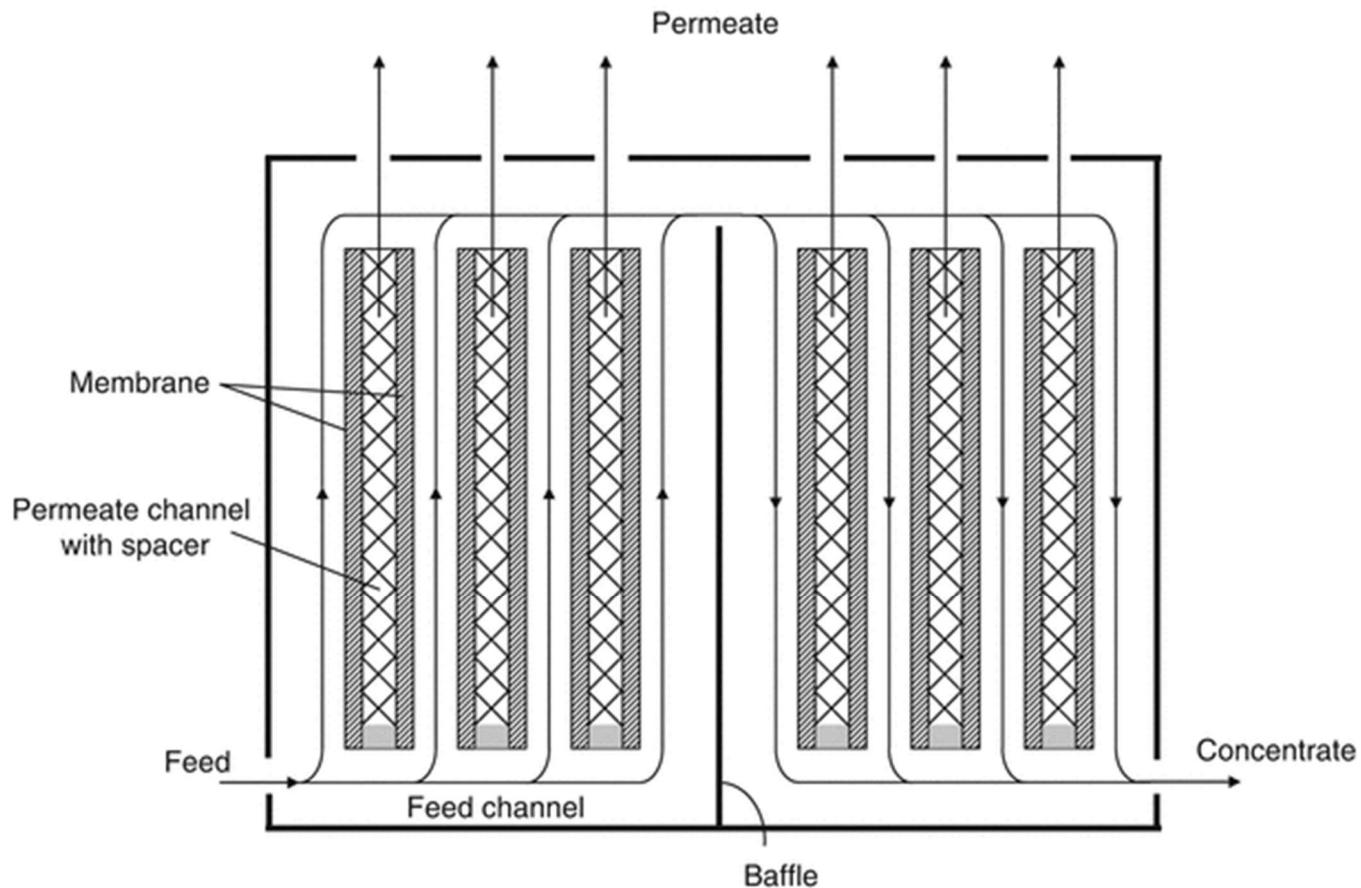
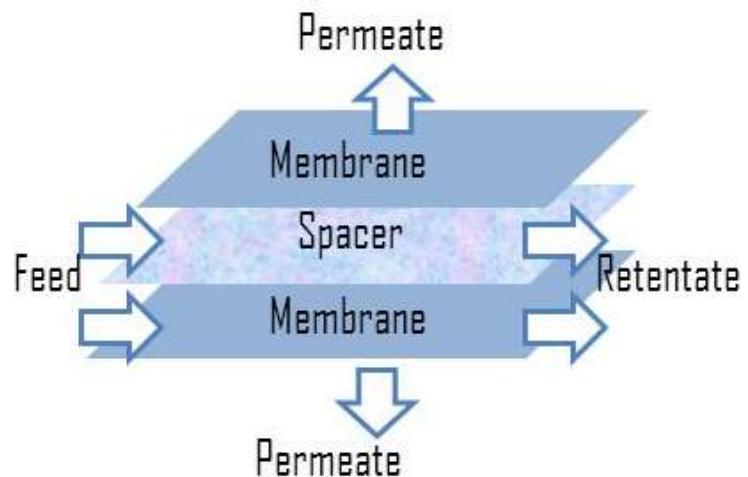
Capillary condensation:

The relative pressure where the pore condensation occurs depends on the pore radius, $\log\left(\frac{p}{p_0}\right) = -\frac{2\gamma L}{r_p R_g T}$

[Kelvin Equation]

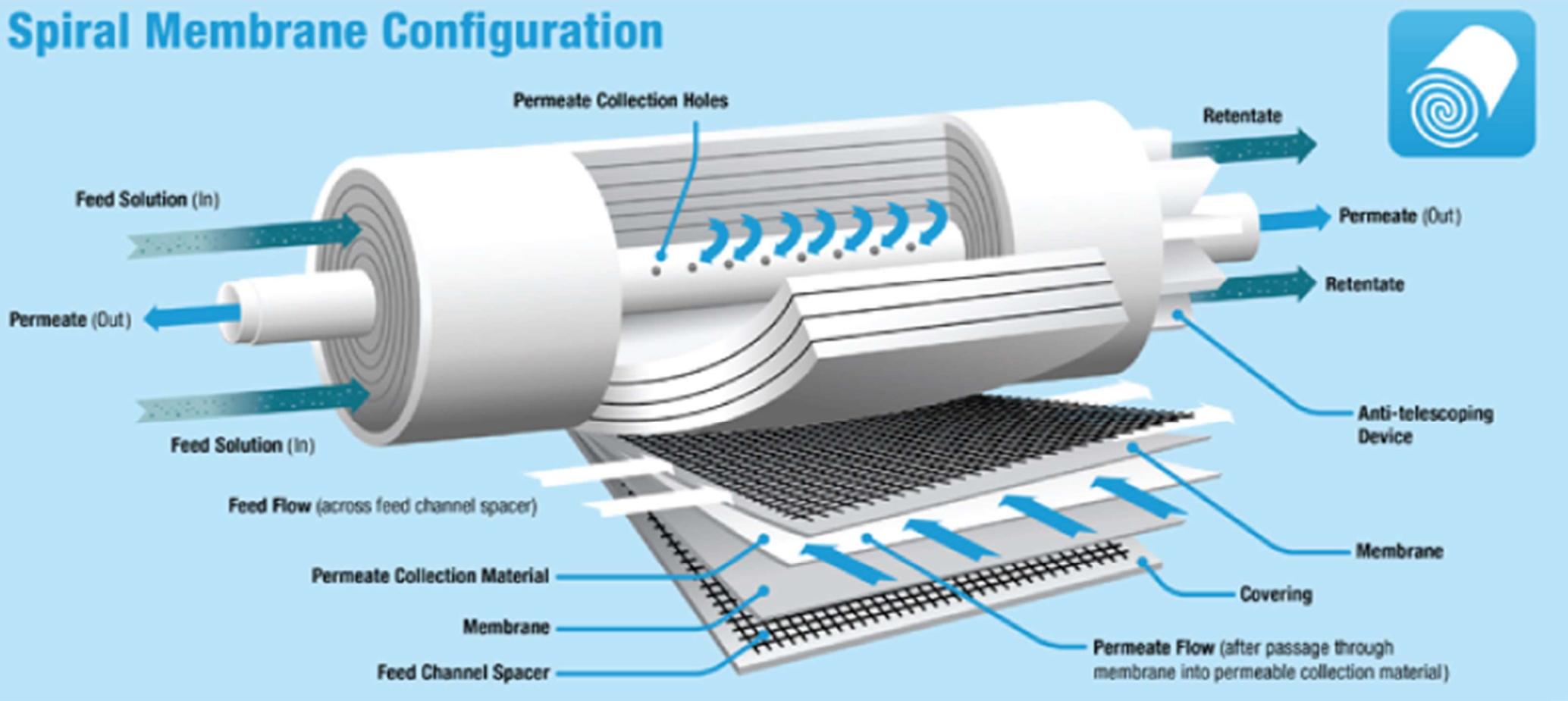
Membrane modules

Plate & frame module

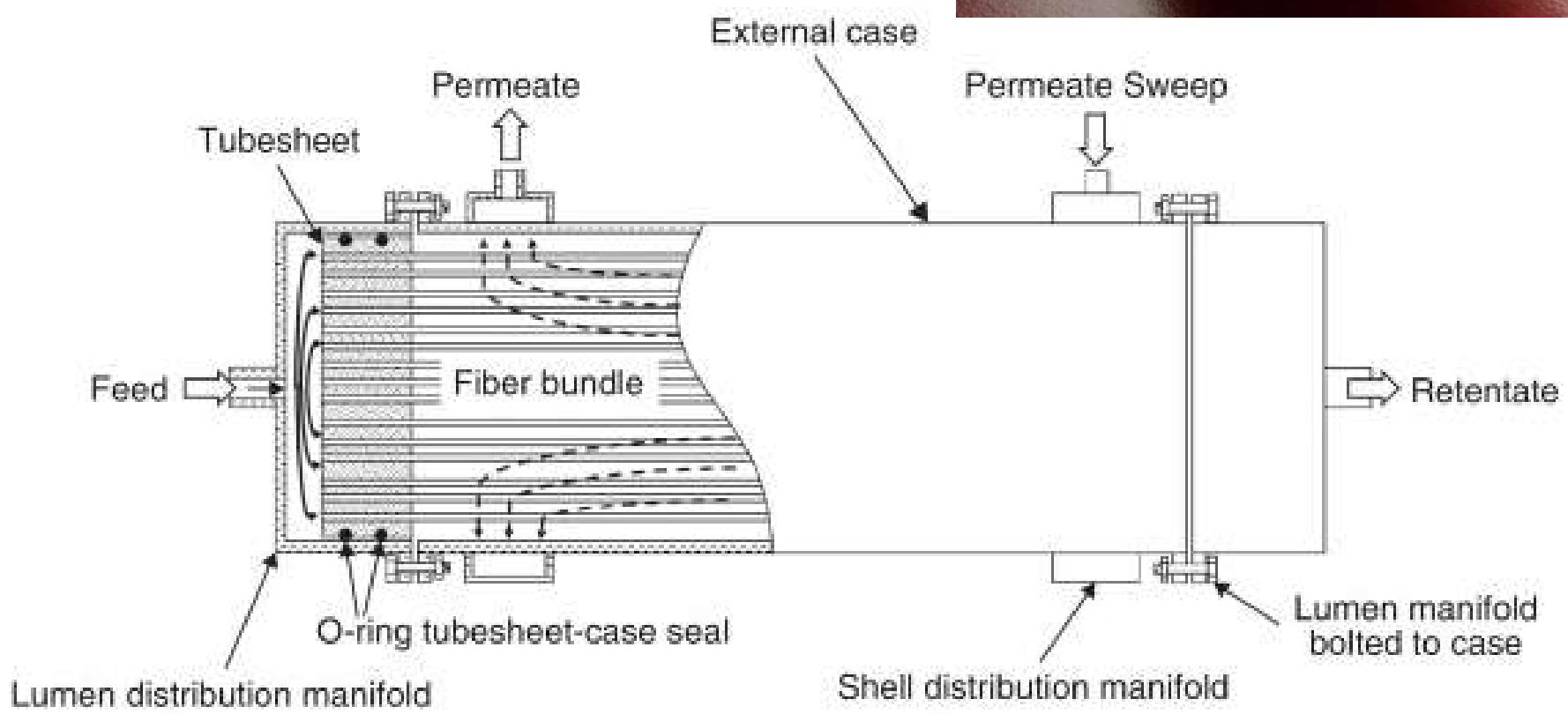


Sets of two membranes are placed in a sandwich-like fashion with their feed sides facing each other. In each feed and permeate compartment thus obtained a suitable spacer is placed. The number of sets needed for a given membrane area furnished with sealing rings and two end plates then builds up to a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

Spiral Membrane Configuration



Hollow fibre module

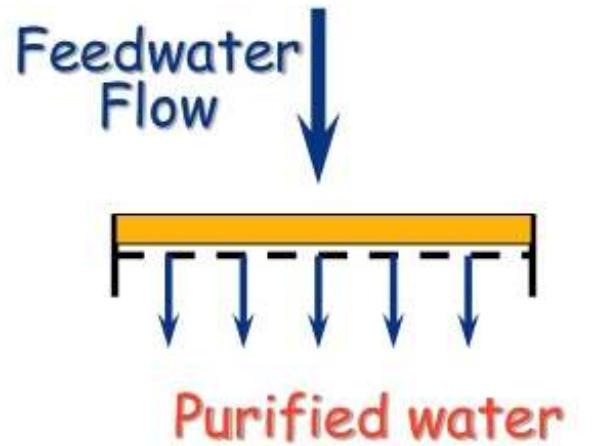


ADVANTAGES AND DISADVANTAGES OF MEMBRANE MODULES

	ADVANTAGES	DISADVANTAGES
SPIRAL-WOUND	<ul style="list-style-type: none">• Low manufacturing cost• Relatively easy to clean by both chemical and hydraulic methods.• Has a very broad range of applications• High packing density	<ul style="list-style-type: none">• It can not be used on highly turbid feed waters without extensive pretreatment.• Susceptible to plugging by particulates
HOLLOW FIBER	<ul style="list-style-type: none">• Relatively low manufacturing cost.• Compact• High packing density• Modes energy requirement	<ul style="list-style-type: none">• Extremely susceptible to fouling due to very small spacing between fibers.• Difficult to clean.• Requires extensive pretreatment.
TUBULAR	<ul style="list-style-type: none">• 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.	<ul style="list-style-type: none">• High capital cost.• Relative high volume required per unit membrane area.
PLATE AND FRAME	<ul style="list-style-type: none">• Moderate membrane surface.• Well-developed equipment.	<ul style="list-style-type: none">• Expensive to operate for large scale.• Susceptible to plugging by particulates at flow stagnation points.• Potentially difficult to clean.

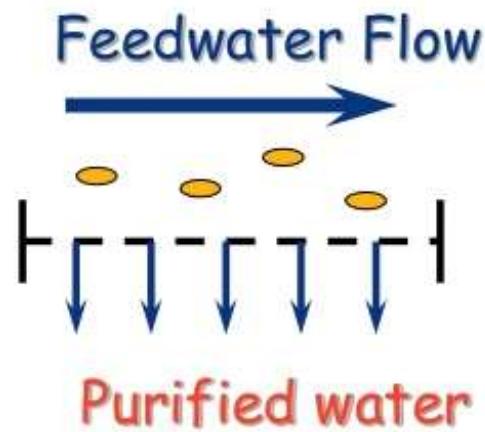
Flow arrangements

TYPICAL FILTRATION



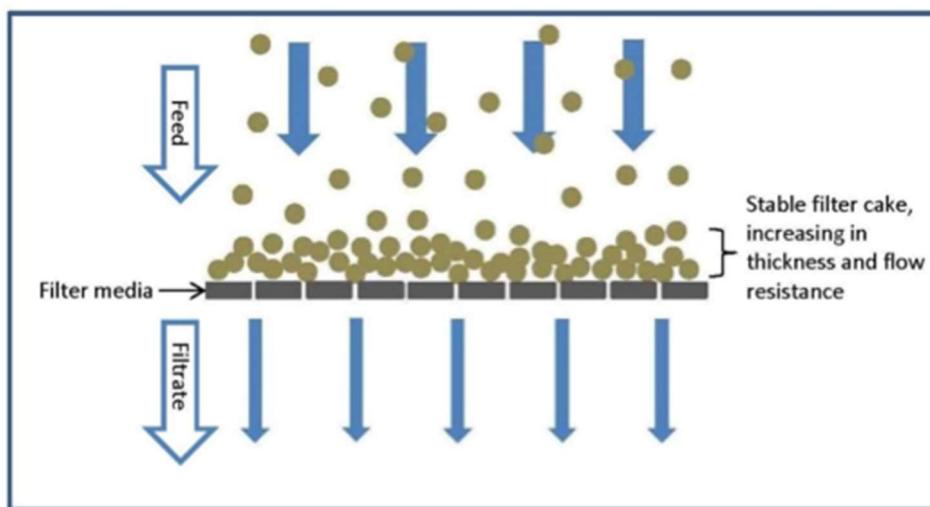
Solids on surface quickly foul the membrane

CROSS-FLOW FILTRATION

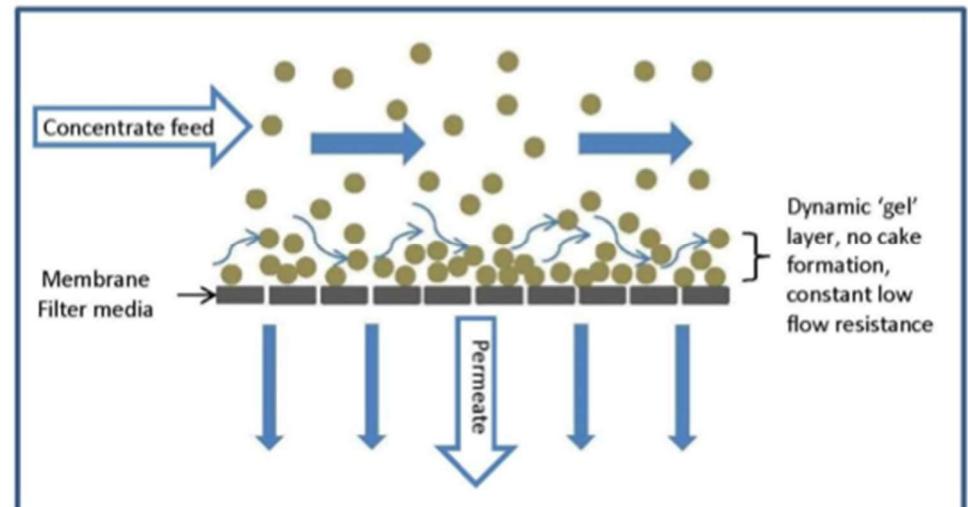


Solids are swept away by continuous flow

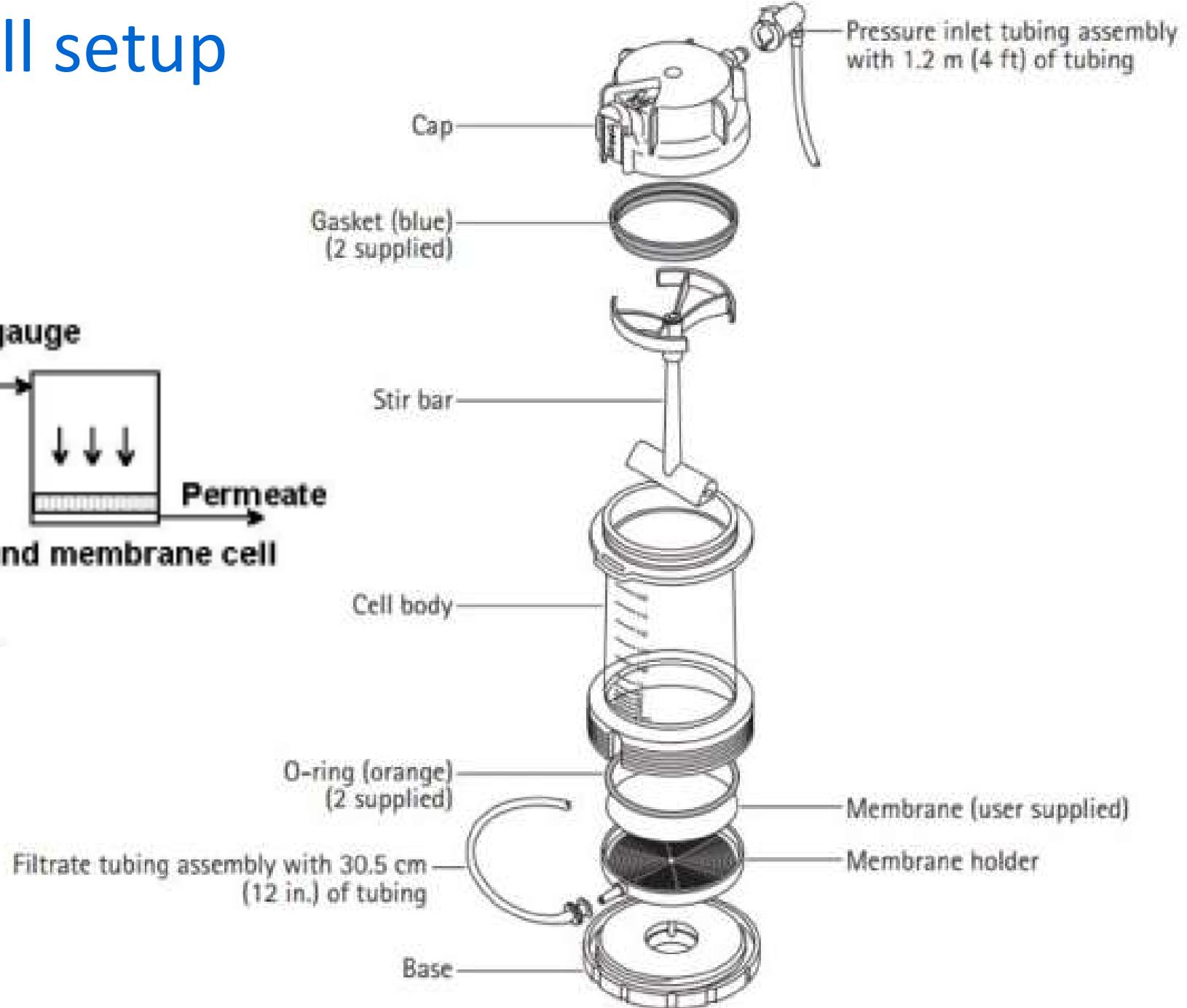
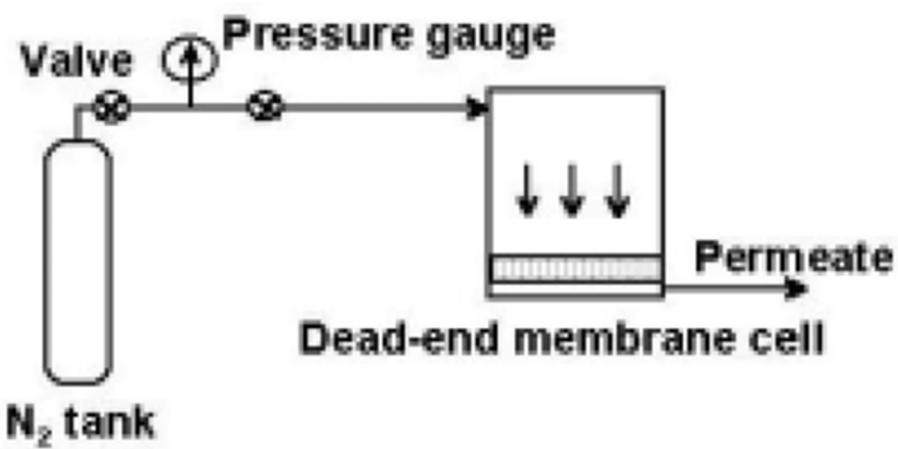
Dead-end filtration



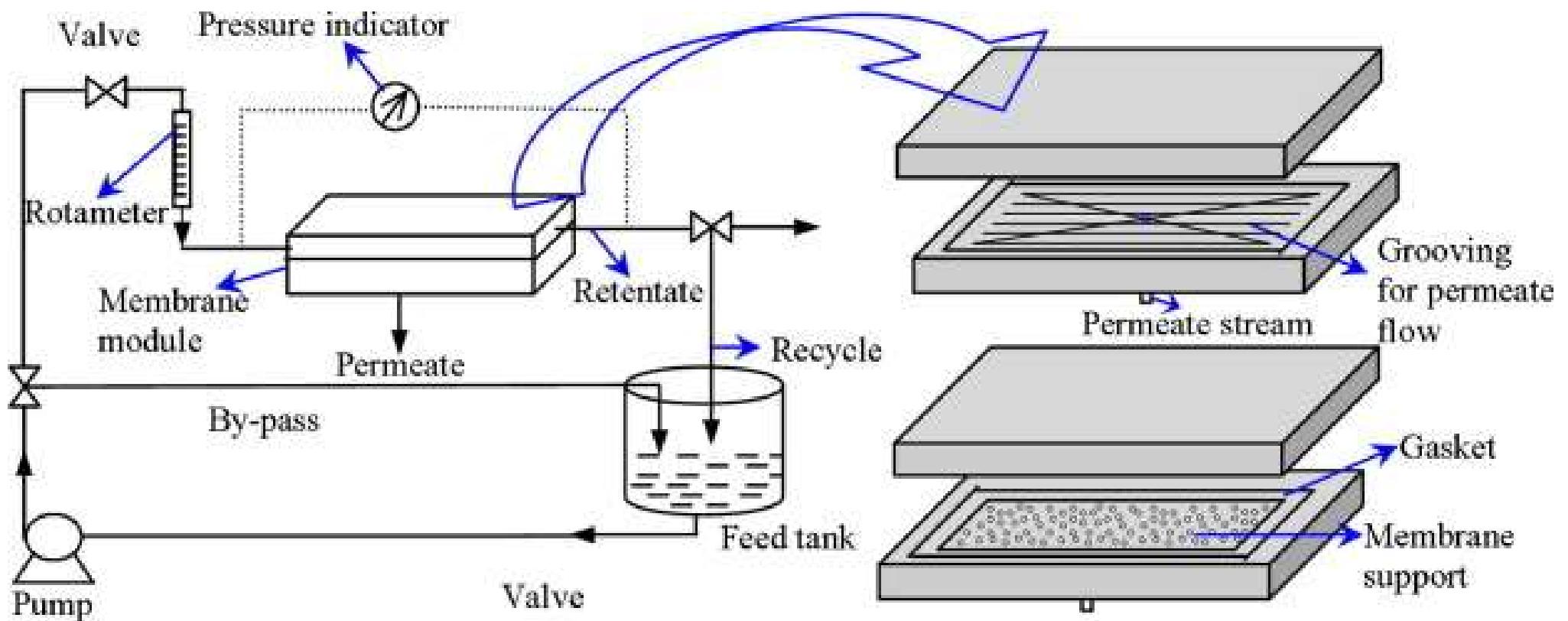
Cross flow filtration



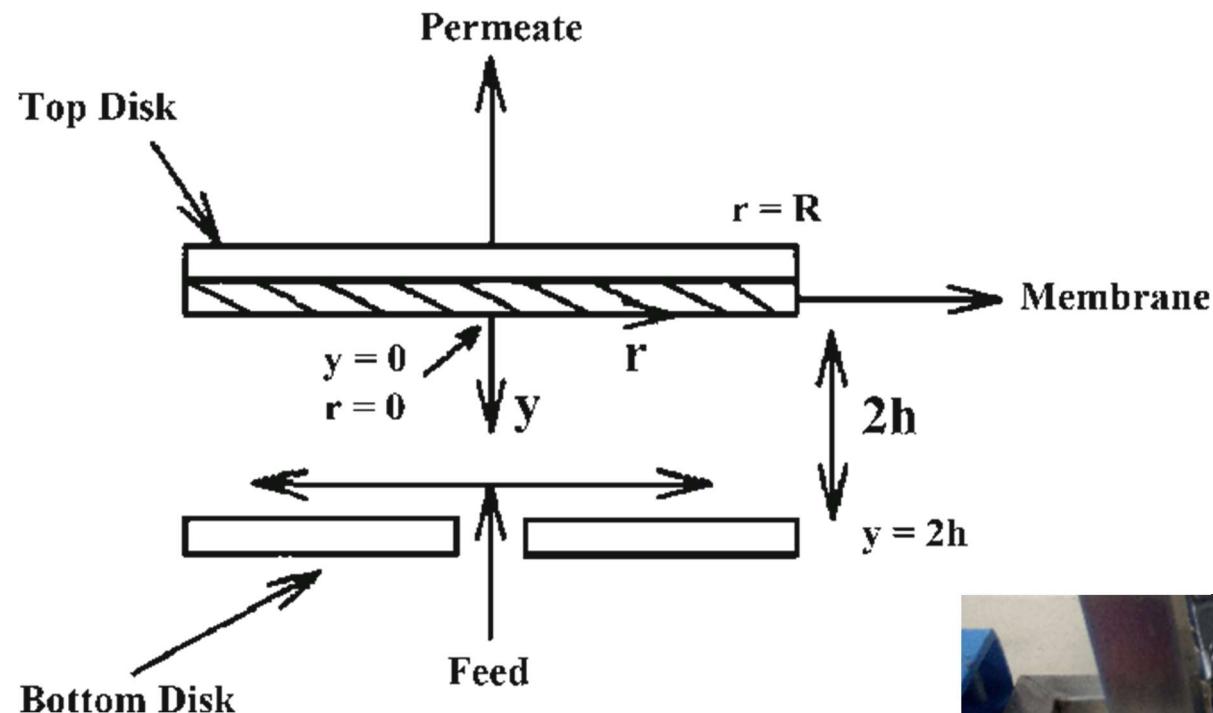
Batch cell setup



Cross flow flat setup



Radial cross flow cell



Pressure driven membrane processes

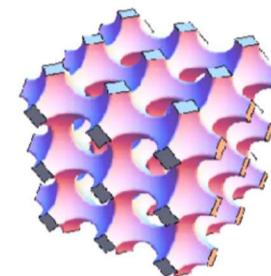
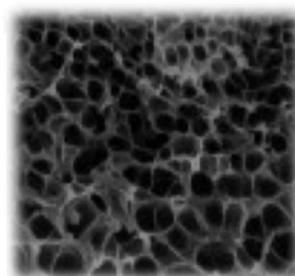
Flow through membrane – theory

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

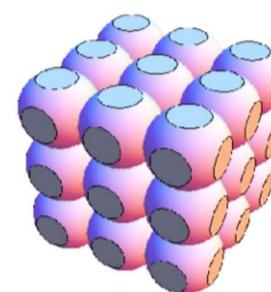
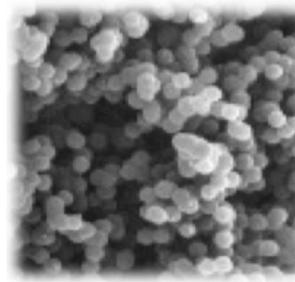
[Refer to the notes]

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

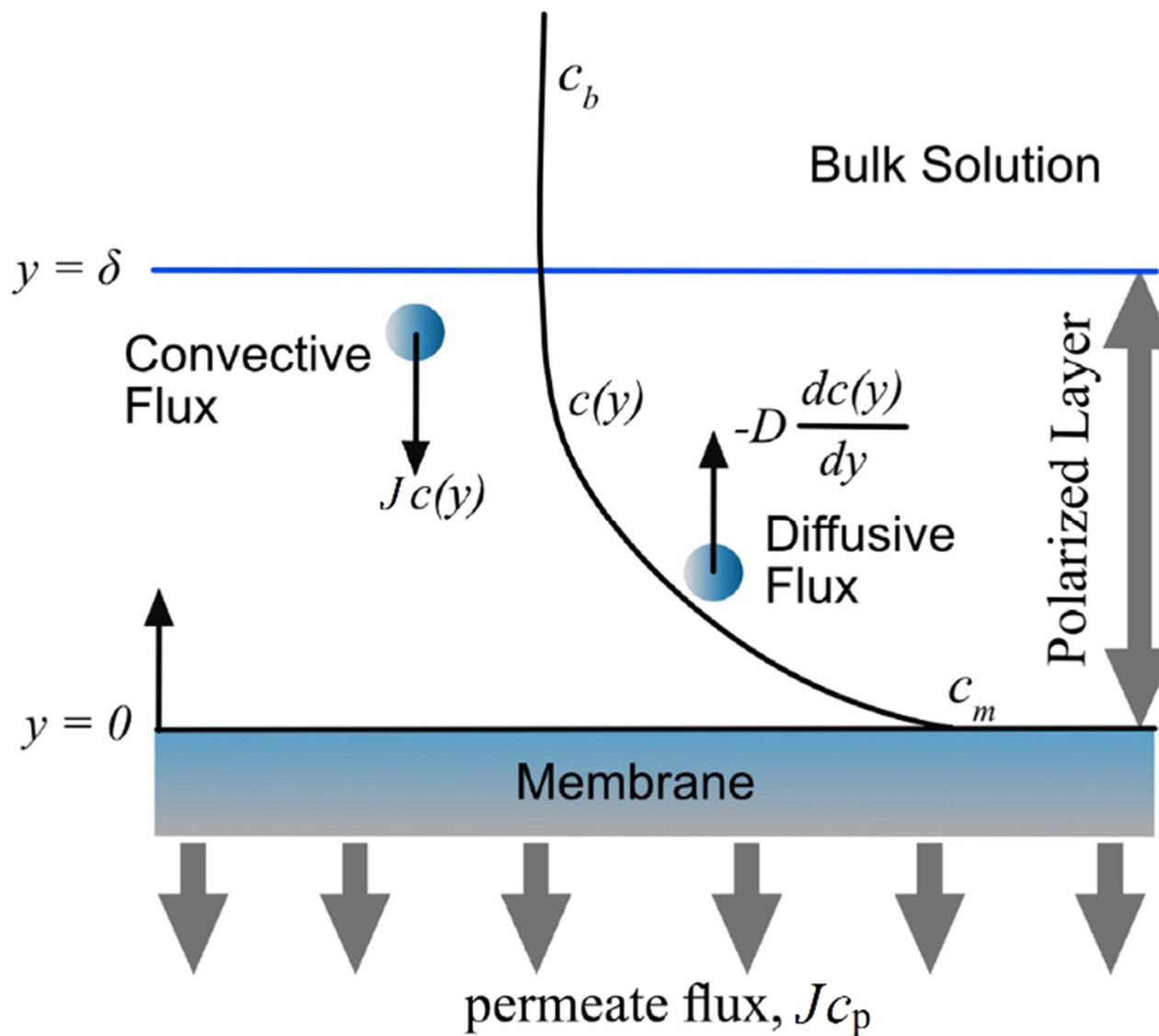
$$S = (1 - \lambda)^2 [2 - (1 - \lambda)^2]$$

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

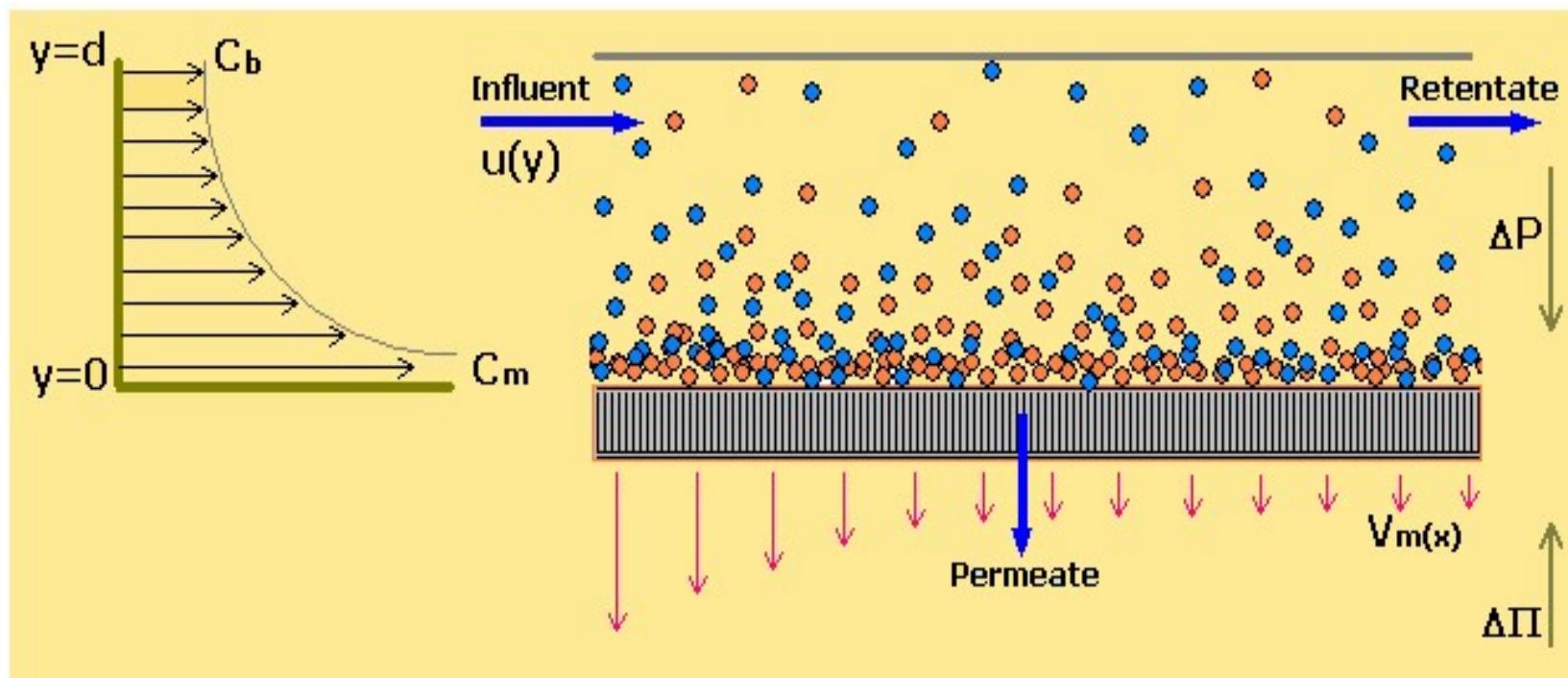
J.D. Ferry, Statistic evaluation of sieve constants in ultrafiltration, J. Gen. Physiol. 20 (1936) 95-104.

Schematic of the major mass transport phenomena in membrane science



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.

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

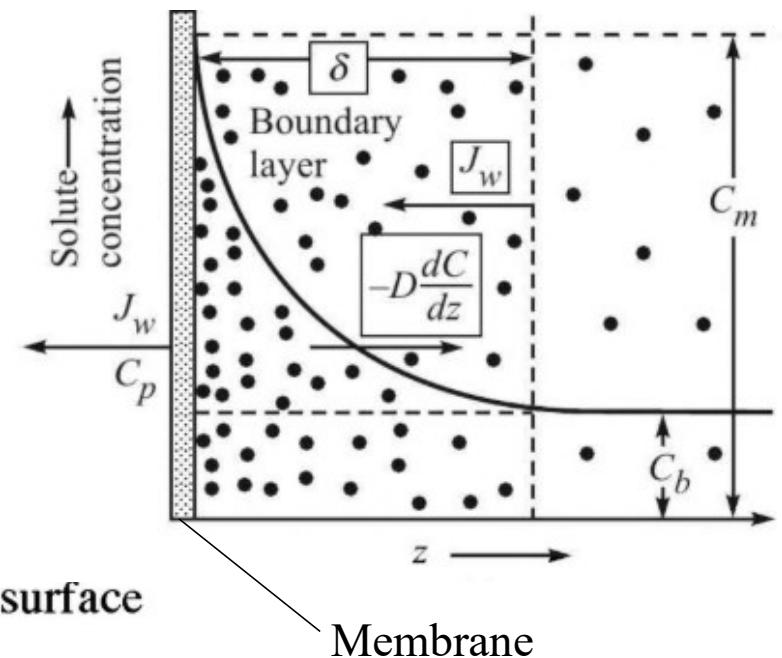
$$z = \delta, \quad C = C_b$$

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:

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

for laminar flow

for turbulent flow