Lecture 2

Separation Theory, Membrane Operations, Preparation of Membranes

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Presentation Menu

- Definition of separation
- Particle separation
- Solute separation
- Models for solute transport and separation
- Donnan equilibria for rejections of ions
- Membrane operations
- Preparation of membranes

Important definitions

Separation - Global

- Membrane separation or rejection, R
- c_p = concentration of permeate
- c_f = concentration of feed

$$R = 1 - \left(\frac{c_p}{c_f} \right)$$

Membrane separation

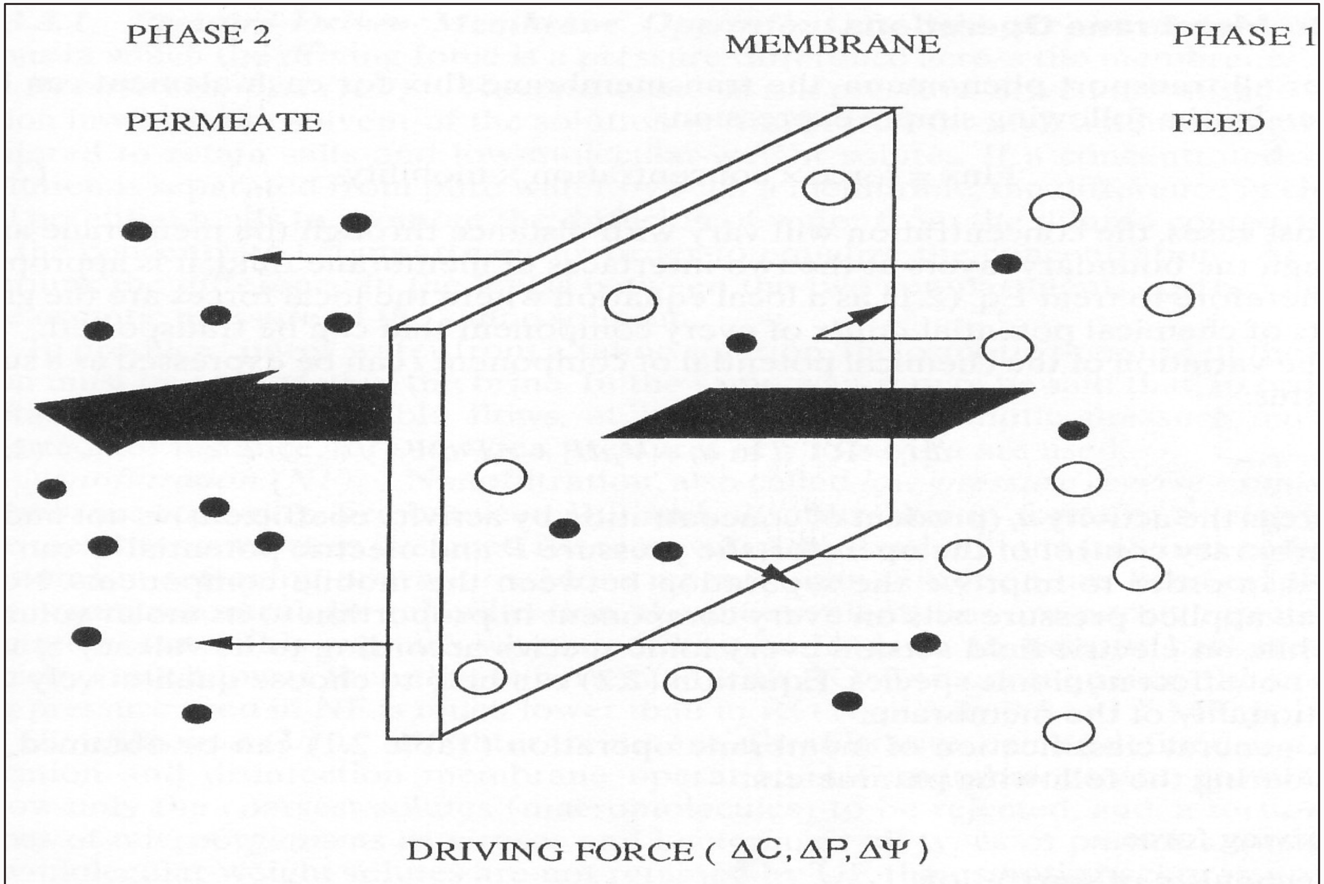
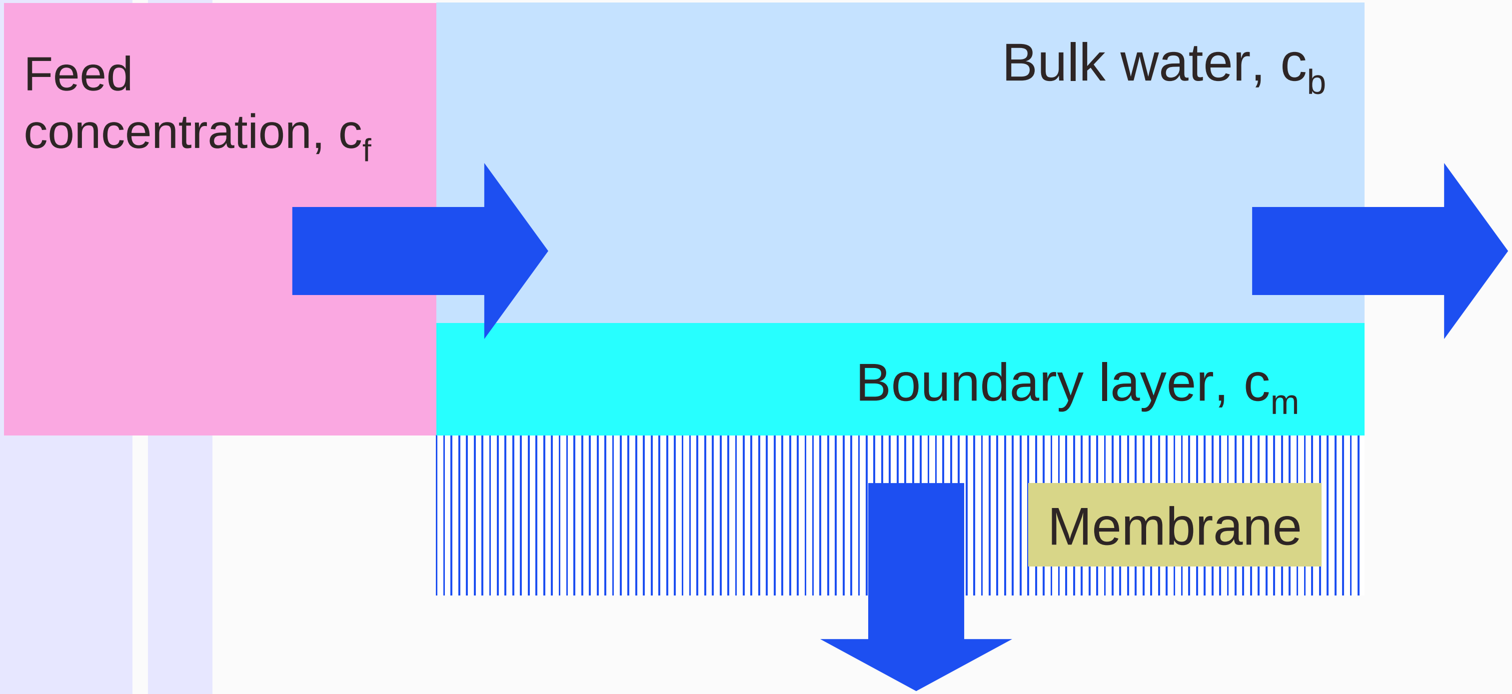


FIGURE 2.1 Definition of a permselective membrane.

Concentrations at various locations in a membrane system



Feed concentration, c_f

Bulk water, c_b

Boundary layer, c_m

Membrane

Definition of concept

Separation – mass fraction

- Membrane separation or rejection based on mass fraction, R_{mass}
- c_p = concentration of permeate
- c_f = concentration of feed

$$R_{mass} = 1 - \left(\frac{c_p}{c_f} \right) r$$

The concentration of a contaminant in the permeate is likely to increase as system recovery increases, i.e. $C_p = f(r)$

Definition of concepts

Separation – local

- Membrane separation or rejection based on mass fraction, R_{local}
- c_p = concentration of permeate
- c_{wall} = concentration of membrane surface

$$R_{local} = 1 - \left(\frac{c_p}{c_{wall}} \right)$$

$$C_{wall} \geq C_{bulk} \geq C_f$$

Definition of concepts

Separation – Apparent

$$R_{apparent} = 1 - \left(\frac{c_p}{c_{bulk}} \right)$$

$$= 1 - (1 - R_{local})(PF)$$

- Apparent = rejection is expressed as a function of bulk concentration rather than concentration on membrane surface)
- PF = polarization factor; **$c_{wall} = (PF)\, c_{bulk}$**

Definition of concepts

Separation – Mass balance

If mass balance is performed over the membrane module, the following expression is derived relating the global to apparent rejection:

$$R = 1 - \left(\frac{c_p}{c_f} \right)$$

$$= 1 - \frac{1-(1-r)^{1-R_{apparent}}}{r}$$

Particle Separation

- Mechanical sieving at membrane surface
- Rejection of deformable drops
- Cake removal

Particle Separation

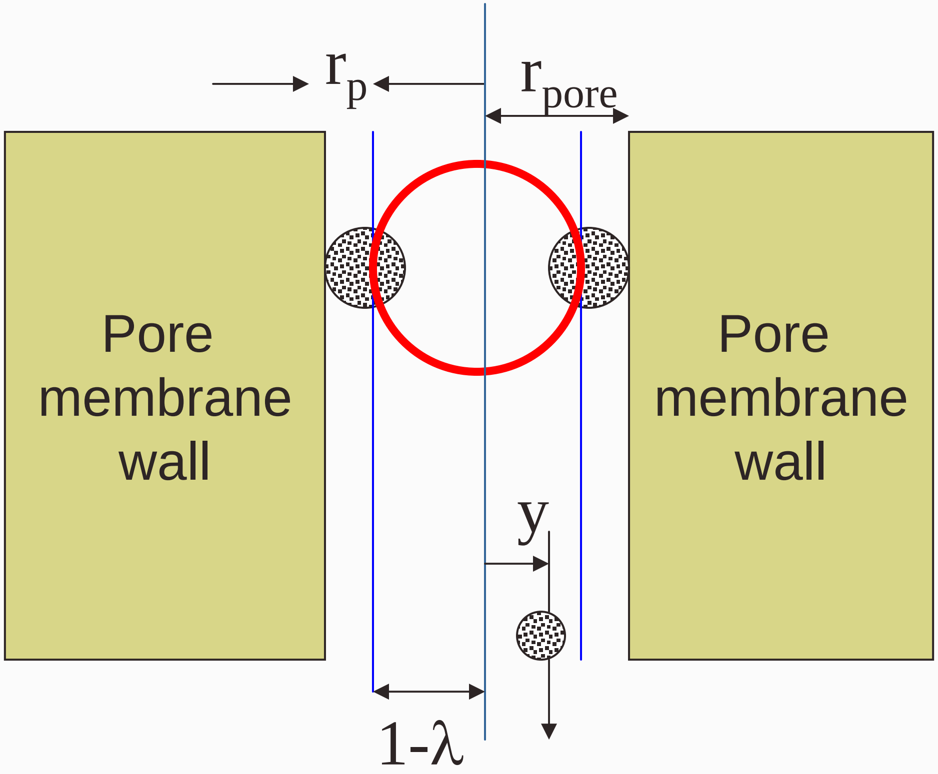
Mechanical sieving at membrane surface

- Particulate is removed by membrane via physical sieving
- Chemical factors play virtually no role, including for RO
- Other factors for UF and MF:

  - *Electrostatic interactions*
  - *Dispersion factors*
  - *Hydrophobic bonding*

Particle separation

Mechanical sieving at membrane surface



Particle Separation

Mechanical sieving at membrane surface

Rejection of particles by a membrane (1-p) can be estimated (as a function of $\lambda = r_p/r_{pore}$):

$$p = \begin{cases} (1-\lambda)^2\left[2-(1-\lambda)^2\right] & \lambda \le 1 \\ 1 & \lambda > 1 \end{cases}$$

G = lag coefficient empirically estimated by:
$G = \exp(-0.7146\,\lambda^2)$ (Zeman & Wales) or
$G = 1 - 2.104\lambda + 2.09\lambda^3 - 0.95\,\lambda^5$ (Lakshminarayanaiah)

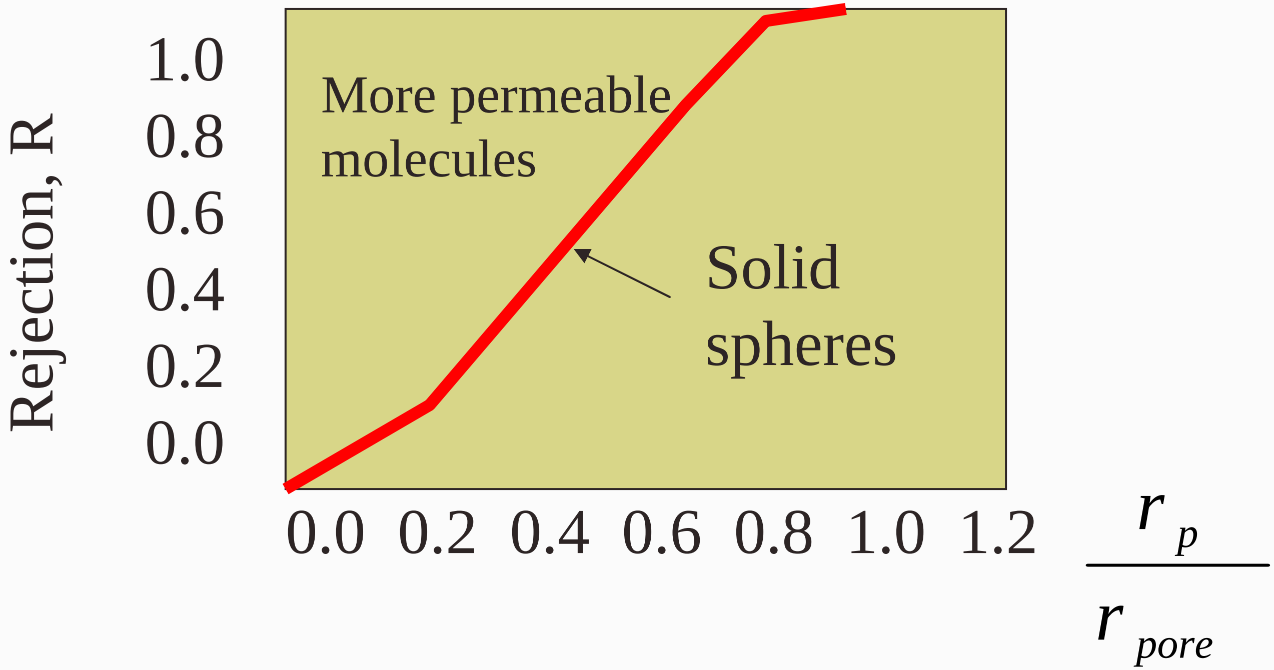
Particle Separation

Mechanical sieving at membrane surface

- ***G*** value by Lakshminarayanaih is much lower in estimating particle rejection compared to ***G*** value by Zeman and Wales, as the particle radius approaches the pore radius.
- (***1-p***) corresponds to local rejection of the membrane, $\boldsymbol{R_{local}}$
- Measurements of apparent rejection can be used to calculate value ***p**** which theoretically corresponds to the product of PF and particle passage, ***p***.
- Removal of materials in deposited cake or gel layers may further alter the apparent rejection of the membrane

Particle Separation

Rejection of particles and macromolecules as a function of the equivalent solid sphere radius of the molecule



Particle Separation

Extending physical sieving model for particle removal to describe rejection of macromolecular compounds e.g. humic materials, involves substituting the molecule's hydrodynamic radius for particle radius:

$$a_p = Z_1\left(\bar{M}\right)^{Z_2}$$

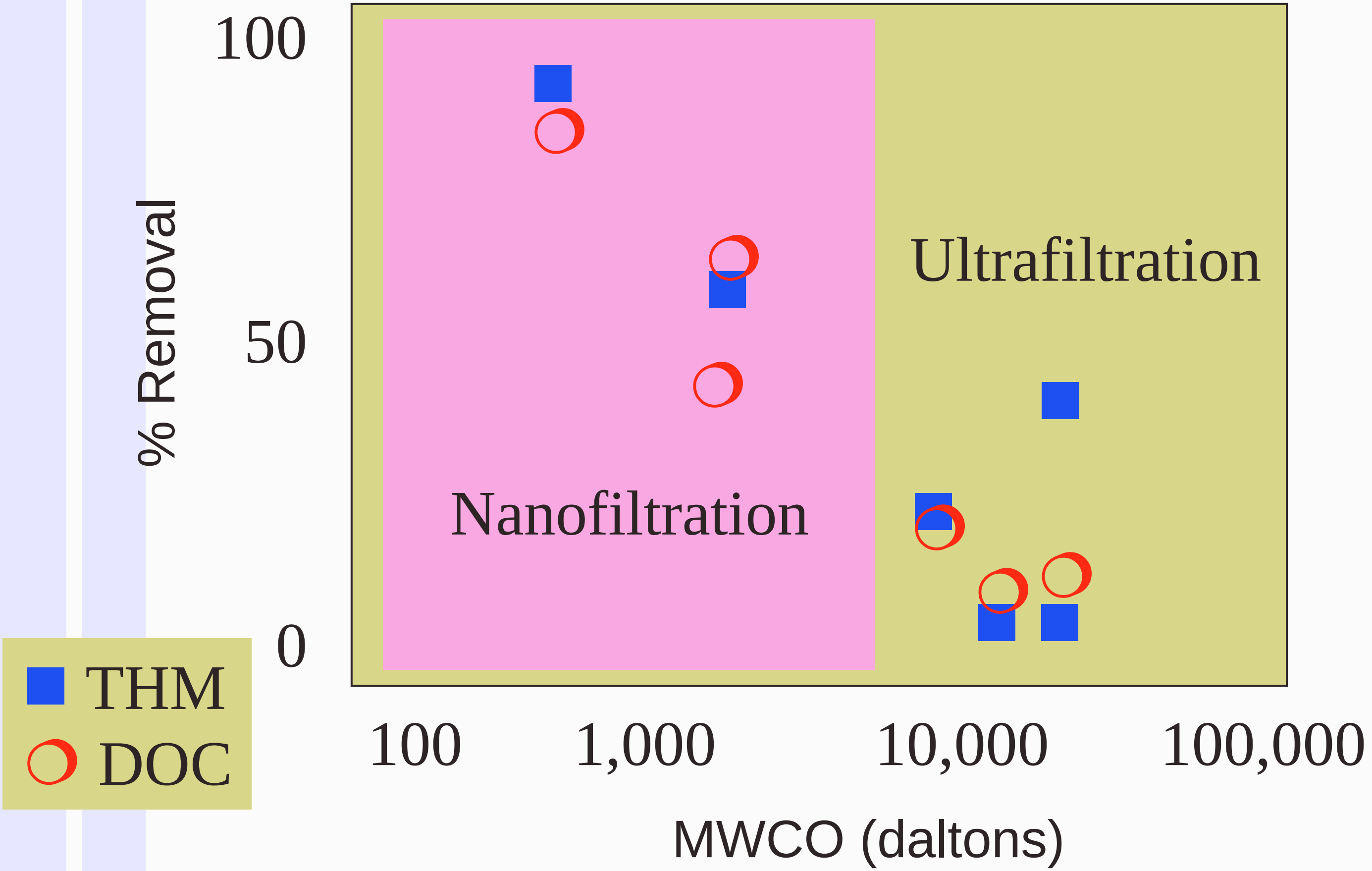
M = molecular weight of the compounds
Z_1, Z_2 = empirical constants
Z_2 ➔ maximum 1; sphere = 1/3

Sieving Mechanisms

- Rejection of organic compounds, e.g. NOM is predicted to increase with molecular weight (assume: molecular size also increase) in UF and NF

- NF can remove DOC and THM precursors

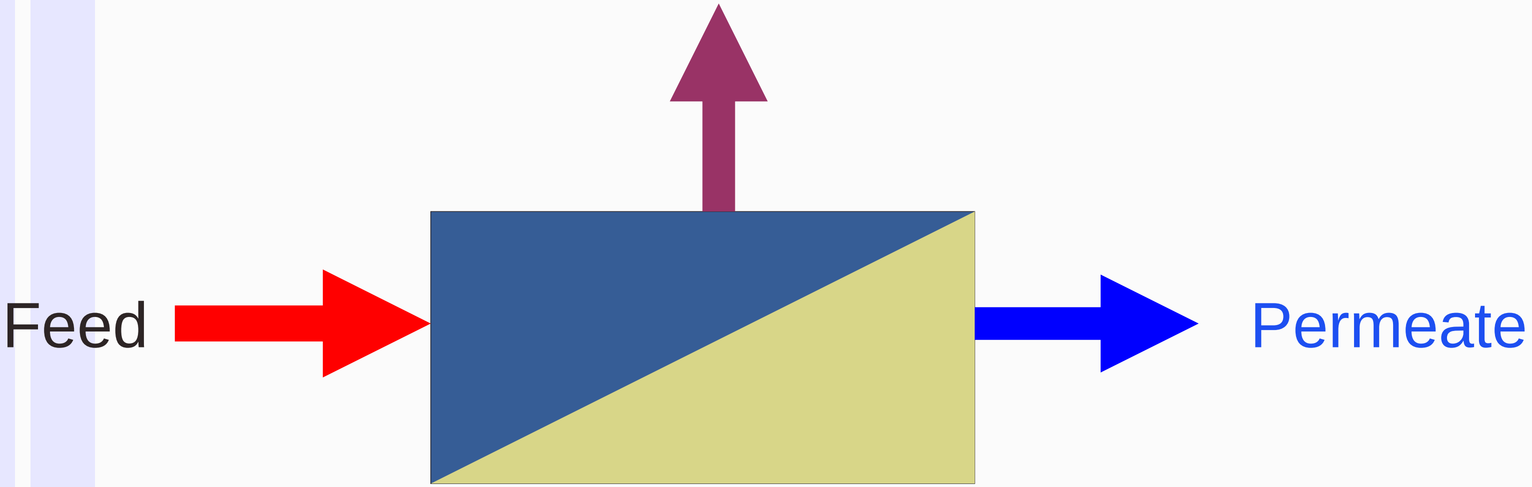
Sieving Mechanisms



Principles of Membrane Operations

- Ability of membrane to differentiate amongst entities ➔ SELECTIVITY.
- Differentiation based on:
  - ❶ size
  - ❷ solubility
  - ❸ charge etc.

Membrane Operations



Membrane Driving Force

Driving force for transport across the membrane:

- dependent on type of membrane process
- dependent on:
    1. Pressure difference
    2. Concentration gradient
    3. Electrical potential gradient
    4. Temperature

Classification of membrane operations

- Driving forces
- Mechanisms of separation
- Membrane structures
- Phases in contact

Driving forces of membrane operation

Pressure-driven	RO, NF, UF, MF
Activity across the membrane	- Gas permeation - Gas diffusion - Pervaporation - Membrane stripping - Membrane distillation
Concentration gradient	- Dialysis
Electrical potential	- Electrodialysis

Pressure-driven membrane processes

Process	Separation potential	Driving force
Reverse osmosis	Aqueous molar mass solution; aqueous organic solution	△P (2-10 MPA)
Nanofiltration	Low and medium mass solutions	△P (0.5 – 6 MPA)
Ultrafiltration	Macromolecule solutions, emulsions	△P (0.1 - 1 MPA)
Microfiltration	Suspension, emulsions	△P (0.01 – 0.5 MPA)

Transmembrane pressure

(for side stream membrane)

$$P_{tm} = [P_{feed} - P_{con}] / P_p$$

P_{tm} = transmembrane pressure
P_{feed} = pressure at the inlet of the module
P_{con} = pressure at the outlet
P_p = pressure at permeate stream

Transmembrane pressure

(for submerged membrane)

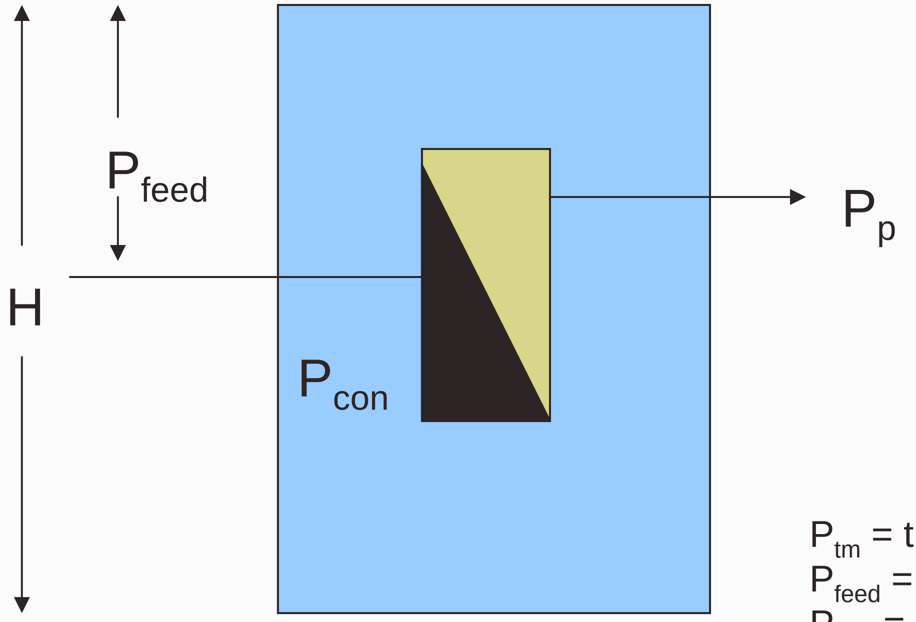
$$P_{tm} = \{[P_{feed} - P_{con}] / 2\} - P_p$$

P_{tm} = transmembrane pressure
P_{feed} = pressure at the inlet of the module
P_{con} = pressure at the outlet
P_p = pressure at permeate stream

Transmembrane pressure

(for submerged membrane)

$$P_{tm} = \{[P_{feed} – P_{con}] / 2\} - P_p$$



$$P_f = H / 2$$

P_{tm} = transmembrane pressure
P_{feed} = pressure at the inlet of the module
P_{con} = pressure at the outlet
P_p = pressure at permeate stream

Preparation of membranes

Techniques

- Sintering
- Stretching
- Tract etching
- Coating
- Phase inversion

Preparation of membranes

Techniques

- Coating – composite dense membranes
- Sintering, stretching & track etching only for MF
- Phase inversion is for general purposes

Preparation of membranes

Phase inversion for asymmetric membrane

- Asymmetric membrane – the most important commercial membrane
- Preparation: Phase inversion
- A polymer is dissolved in an appropriate solvent and cast as a 0.1 to 1 mm-thick film. Non solvent is added to this liquid film, causing phase separation and precipitation.
- At the inter-phase between the polymer solution and non solvent, diffusion will occur.

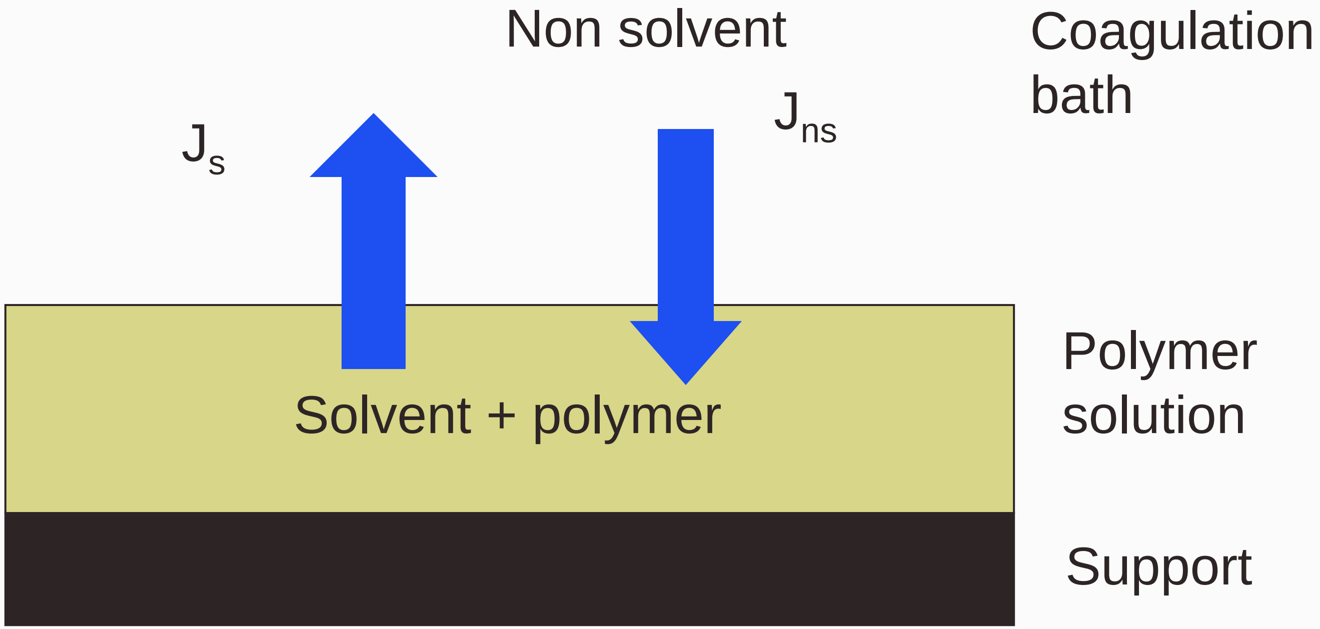
Preparation of membranes

Phase inversion for asymmetric membrane

- The solvent diffuses into the coagulation bath with a flux J_s whereas the non solvent will diffuse into the case film, J_{ns}
- $J_s > J_{ns}$
- The polymer composition in the cast film will increase, while the non solvent / solvent ratio increases

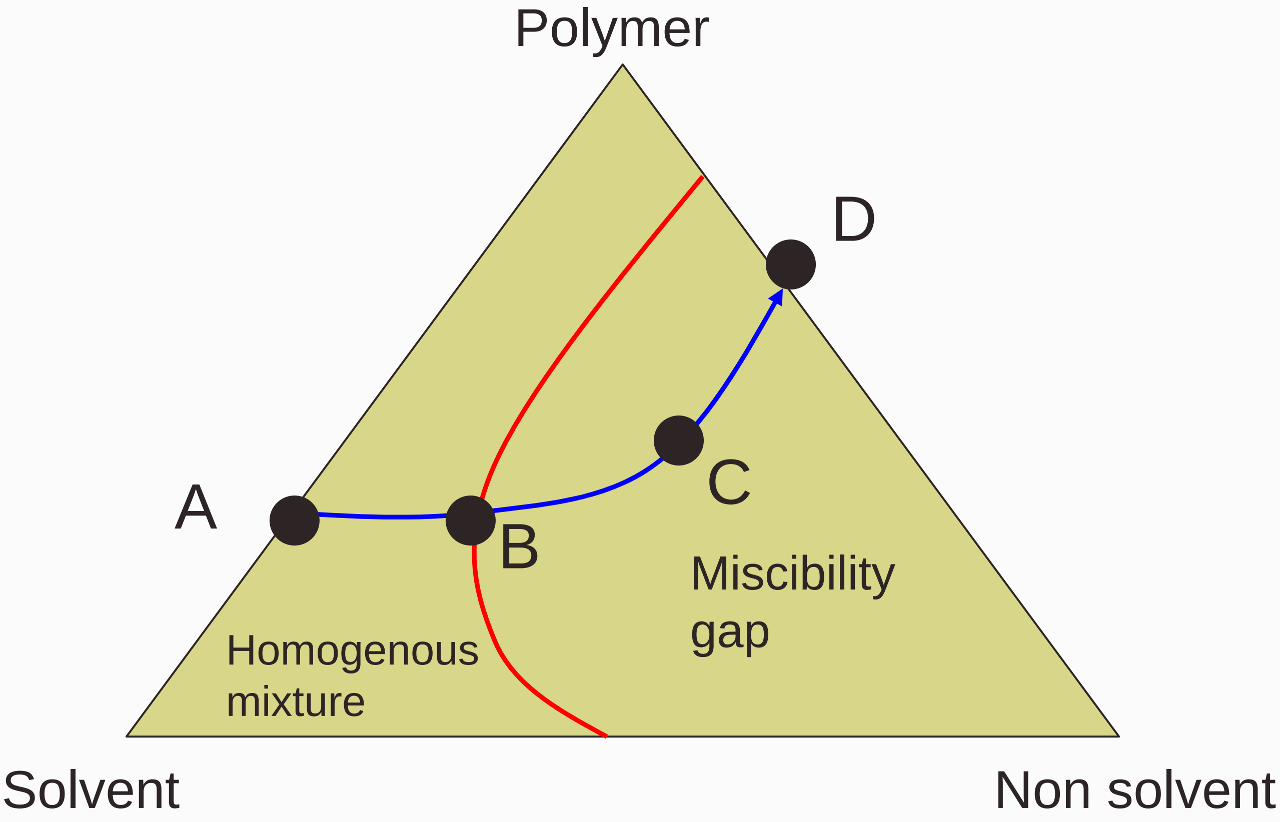
Preparation of Membranes

Phase inversion for asymmetric membrane



Preparation of membranes

Phase inversion for asymmetric membrane



A – composition of the casting solution; B – composition of ternary mixture where demising occurs; C – point of solidification; D – composition of the membrane after complete exchange between solvent and non solvent

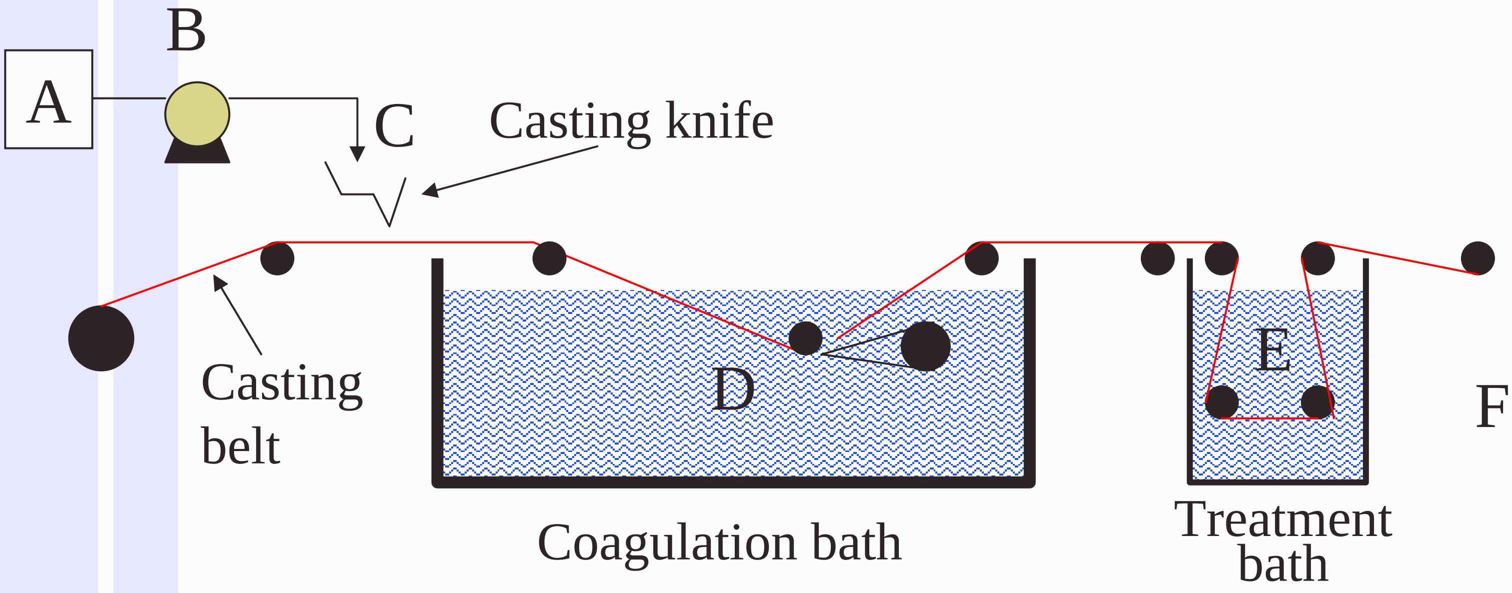
Preparation of membranes

Anisotropic structure of membrane depends on thermodynamic and kinetic factors:

- Nature of polymer
- Nature of solvent and non solvent
- Composition of casting solution
- Composition of coagulation bath
- Gelation and crystallization behavior of the polymer
- Location of the liquid-liquid demixing gap
- Temperature of the casting solution and the coagulation bath
- Evaporation time

Preparation of membranes

Principle of manufacturing flat-sheet membranes using casting machine



After filtration and degassing, the solution (A) is pumped (B) through a casting knife (C) andcast as a thin fluid film onto a non-woven fabric or directly on a metallic casting belt. After ashort residence in the air, the cast film enters into a coagulation bath (D). Following gelation,the membrane is washed free of solvent (E). Before collecting the membrane on a take-uproll (F), other treatments can also be applied e.g. heat treatment, conditioning & drying.

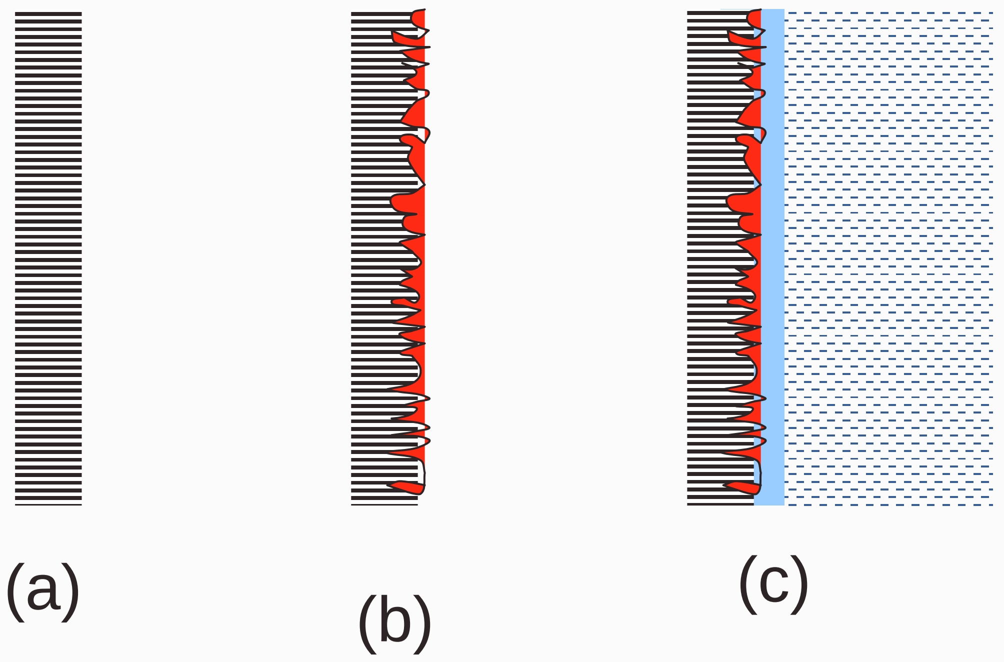
Preparation of Membranes

Composite membranes prepared by interfacial polymerization

- Mainly to produce RO membrane
- Polymerizing 2 reactive monomers or pre-polymers on the skin of a UF membrane
- Membrane is immersed in a second bath containing a reactive monomer 1, or pre-polymer. The film is then immersed in the second bath containing a water-immiscible solvent with monomer 2.
- Reaction occures at the interface to form a dense top layer
- Advantage – the first polymerized layers offer great resistance to the diffusion of the reactants, resulting in an extremely thin film of thickness within the 50 nm range

Preparation of Membranes

Composite membranes prepared by interfacial polymerization



Formation of composite membrane via interfacial polymerization: (a) support layer (UFasymmetric membrane); (b) immersion of the support in an aqueous solution of monomer 1;(c) immersion in a water-immiscible solution of monomer 2 and formation of very thin filmat the surface of the support

Preparation of Membranes

Preparation of hollow fiber by phase inversion

- HF can be prepared from the same materials used to cast flat-sheet membranes
- The fibers can be spun directly as a membrane as a substrate which is post-treated to get a composite HF
- The technology employed in the fabrication of synthetic fiber applies also to be spinning of HF membranes

Preparation of Membranes

Preparation of hollow fiber by phase inversion

- In melt spinning, a polymer melt is extruded into a cooler atmosphere, which induces phase transition: the controlled solidification of the nascent filament determines its characteristics.
- Result: Dense, isotrophic membrane
- Result: with addition of removable additives to the dope yields a porous membrane

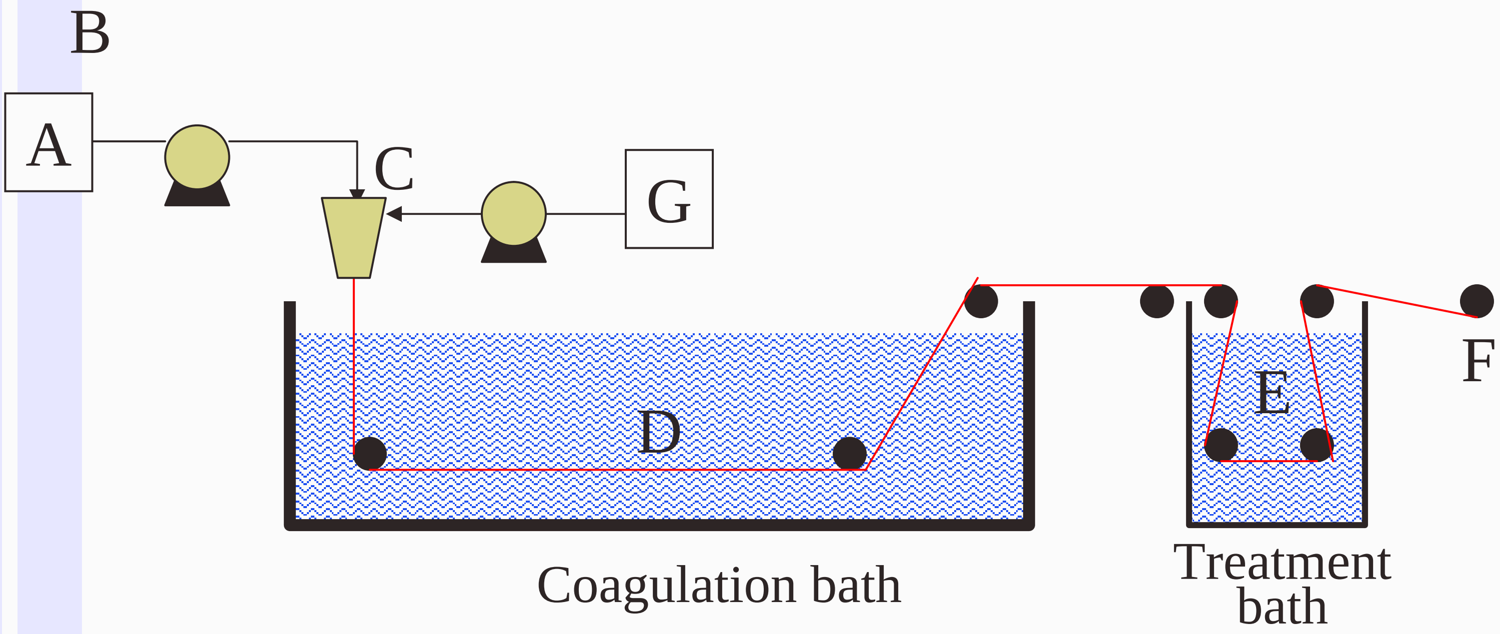
Preparation of Membranes

Preparation of hollow fiber by phase inversion

- In the dry process, the dope consists of the polymer dissolved in a volatile solvent.
- Evaporation of solvent induces phase transition and produces isotropic or anisotropic membrane
- In the wet process, the extruded mixture is coagulated in a non solvent in liquid or vapor phase
- In dry-wet spinning technique is a combination of both methods: the spinneret is positioned above a coagulation bath allowing evaporation or cooling to take place in the air gap

Preparation of Membranes

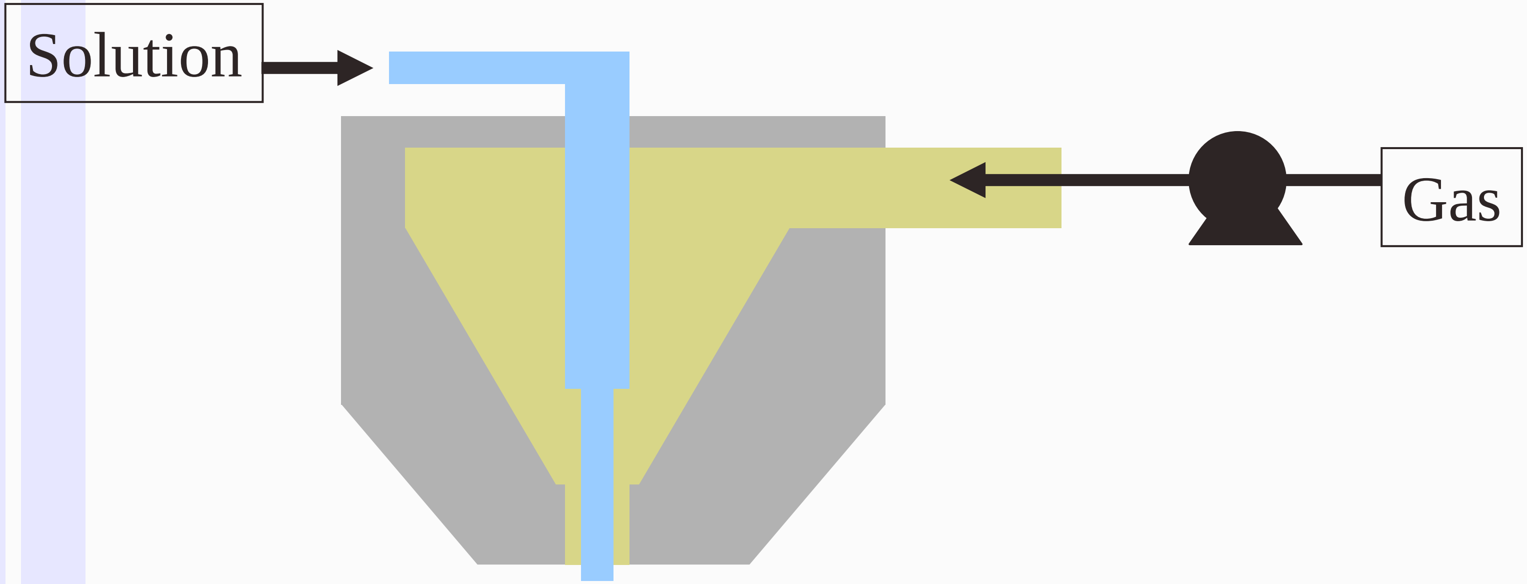
Preparation of hollow fiber by phase inversion



C - spinneret

Preparation of Membranes

Preparation of hollow fiber by phase inversion



Preparation of Membranes

Inorganic membrane

- Ceramic pastes derived from powders as alumina (Al_2O_3) and zirconia (ZrO_2) are extruded and then sintered at high temperature to give macroporous supports with pore diameters larger than 1 micron
- Flat, tubular or multichannel supports can be obtained
- Suspensions of submicronic powders are then laid on the support in successive layers to get MF with lower pore diameters
- Sol-gel process starting from suspensions of colloidal particles are used to form UF layers exhibiting pore down to 3 nm