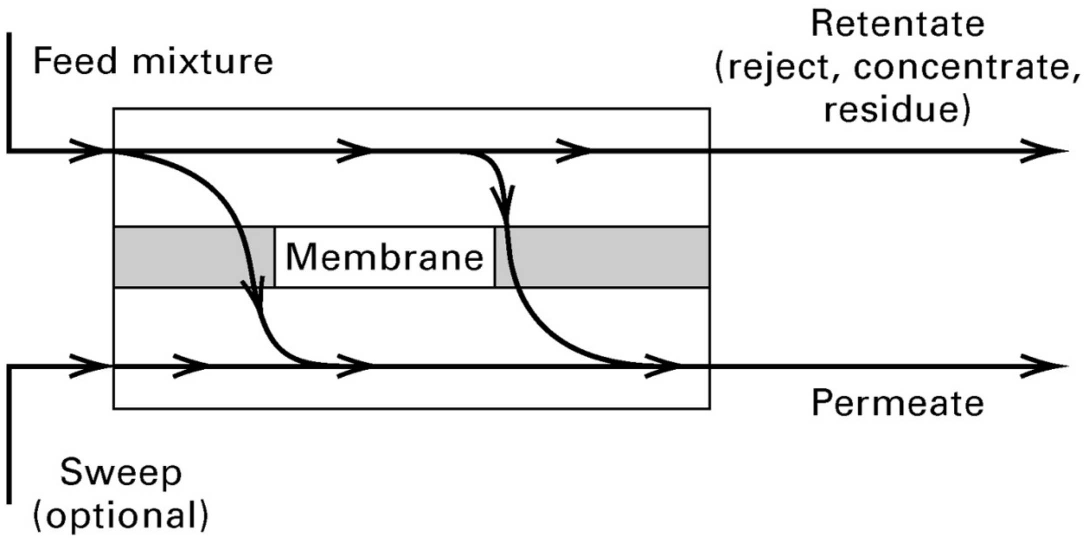
Lecture 17.
Membrane Separations
[Ch. 14]

- Membrane Separation
- Membrane Materials
- Membrane Modules
- Transport in Membranes
  - Bulk flow
  - Liquid diffusion in pores
  - Gas diffusion
  - Nonporous membranes

Membrane Separation

- Separation by means of a semipermeable barrier (membrane) through which one or more species move faster than another or other species



- Characteristics
  - The two products are usually miscible
  - The separating agent is a semipermeable barrier
  - A sharp separation is often difficult to achieve

History of Membrane Separation

- Large-scale applications have only appeared in the past 60 years
  - 1940s: separation of $^{235}UF_6$ from $^{238}UF_6$ (porous fluorocarbons)
  - 1960s: reverse osmosis for seawater desalinization (cellulose acetate), commercial ultrafiltration membranes
  - 1979: hollow-fiber membrane for gas separation (polysulfone)
  - 1980s: commercialization of alcohol dehydration by pervaporation

- Replacement of more-common separations with membrane
  - Potential: save large amounts of energy
  - Requirements
    - production of high-mass-transfer-flux, defect-free, long-life membranes on a large scale
    - fabrication of the membrane into compact, economical modules of high surface area

Characteristics of Membrane Separation

- Distillation *vs*. gas permeation

  : energy of separation for distillation is usually heat, but for gas permeation is the shaft work of gas compression

- Emerging (new) unit operation

  : important progress is still being made for efficient membrane materials and packaging

- Membrane separator *vs*. other separation equipment
  - more compact, less capital intensive, and more easily operated, controlled, and maintained
  - usually modular in construction: many parallel units required for large-scale applications

- Desirable characteristics of membrane

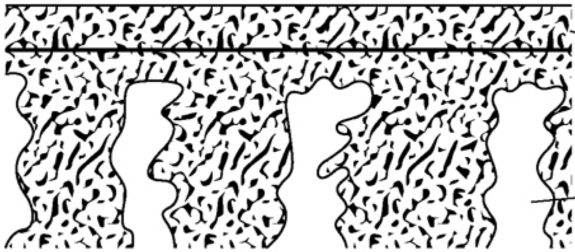
  (1) good permeability, (2) high selectivity, (3) chemical and mechanical compatibility, (4) stability, freedom from fouling, and useful life, (5) amenability, (6) ability to withstand large pressure differences

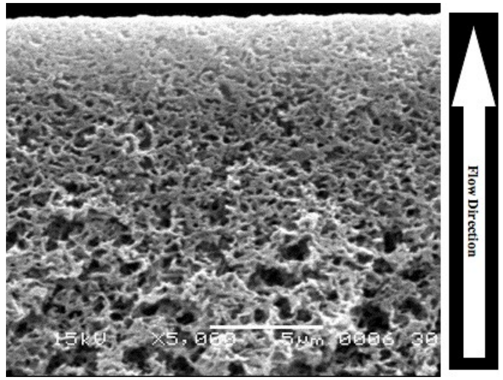
Membrane Materials

- Typical membrane materials
  - Natural polymers: wool, rubber, and cellulose
  - Synthetic polymers
  - Inorganic materials: microporous ceramics, metals, and carbons
- Almost all industrial membrane materials are made from polymers
  : limited to temperatures below 200℃ and chemically inert mixture
- Types of polymer membrane
  - Dense amorphous membrane
    - pores, if any, less than a few Angstroms in diameter
    - diffusing species must dissolve into the polymer and then diffuse through the polymer
  - Microporous membrane (microfiltration, ultrafiltration, nanofiltration)
    - contains interconnected pores of 0.001-10 μm in diameter
    - for small molecules, permeability for microporous membranes is high but selectivity is low

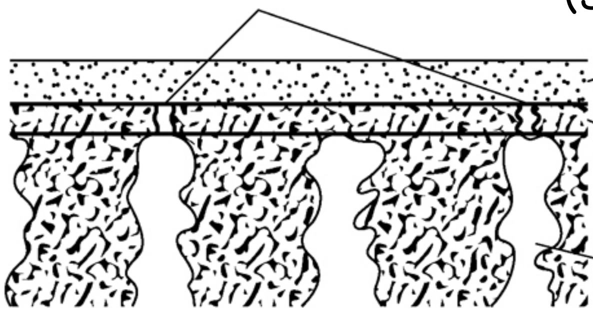
Asymmetric Polymer Membrane

- Asymmetric membrane
  - thin dense skin (permselective layer) about 0.1–1.0 μm in thick formed over a much thicker microporous layer (support)

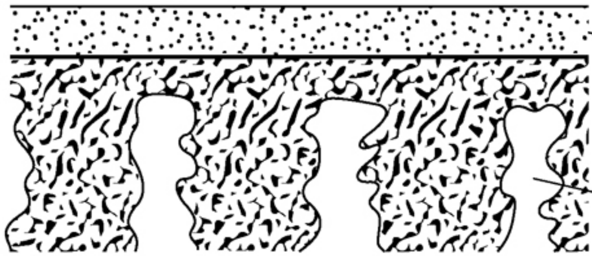




- Caulked membrane

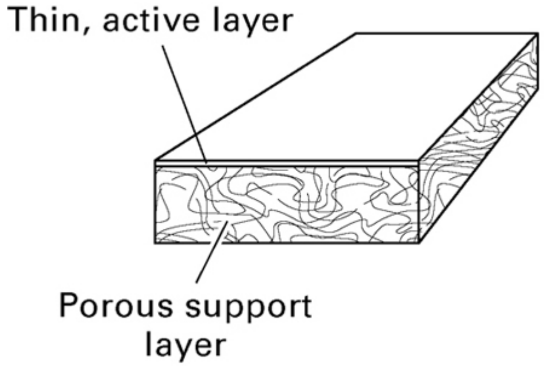


- Thin-film composite

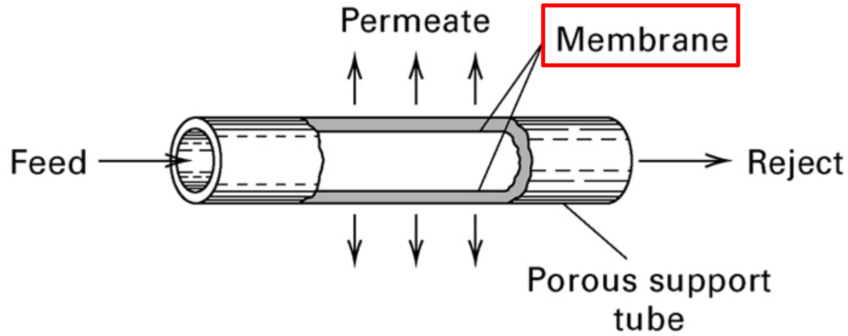


Membrane Modules (1)

- Common membrane shapes

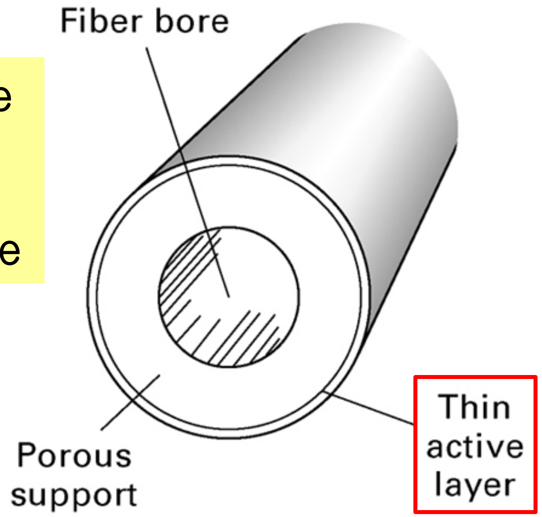


Flat asymmetric or thin-film composite

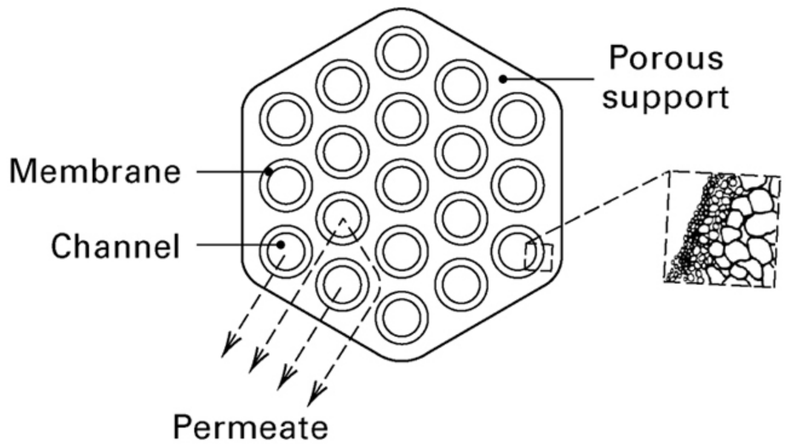


Tubular

Provide a large membrane surface area per unit volume



Hollow fiber

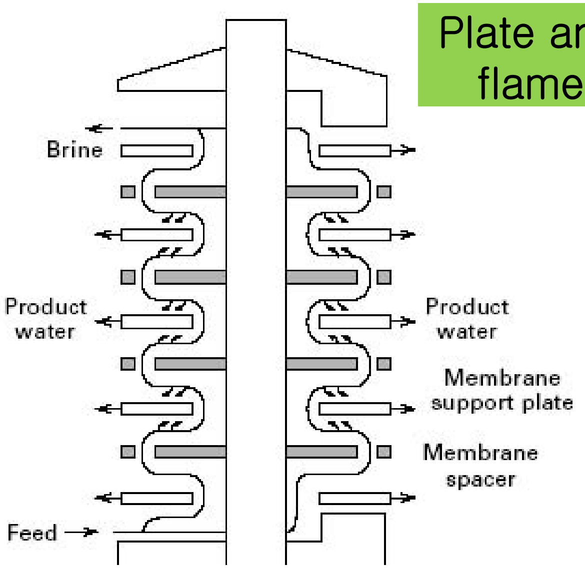


Monolithic

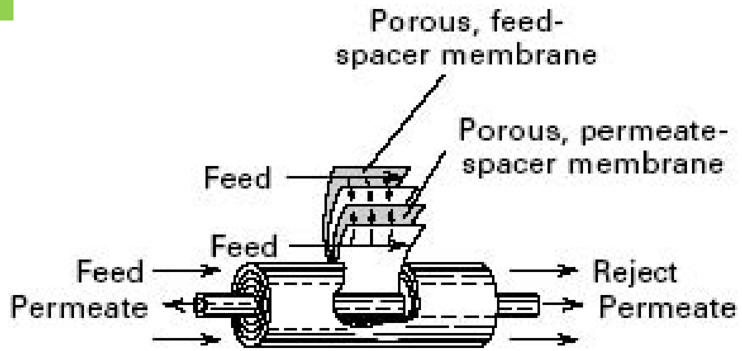
Membrane Modules (2)

- Common membrane modules

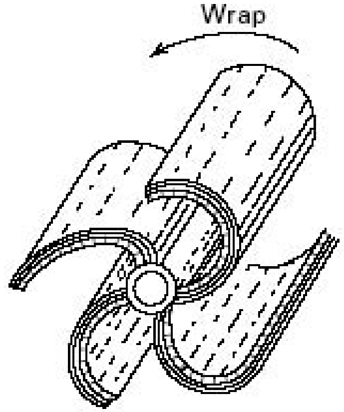
Plate and flame



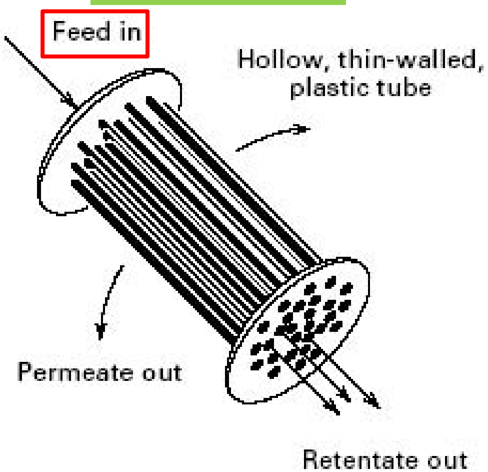
Spiral-wound



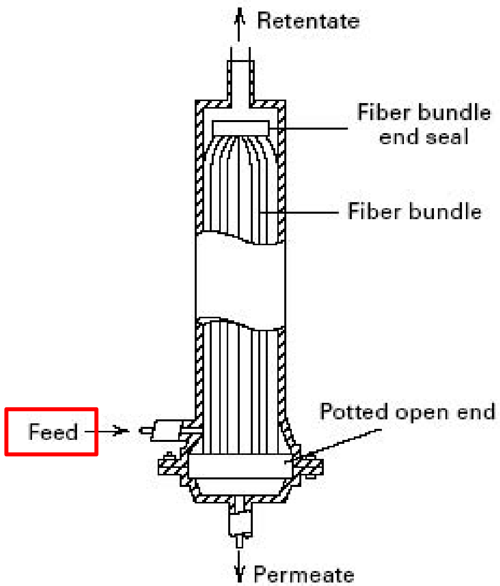
Four-leaf spiral-wound



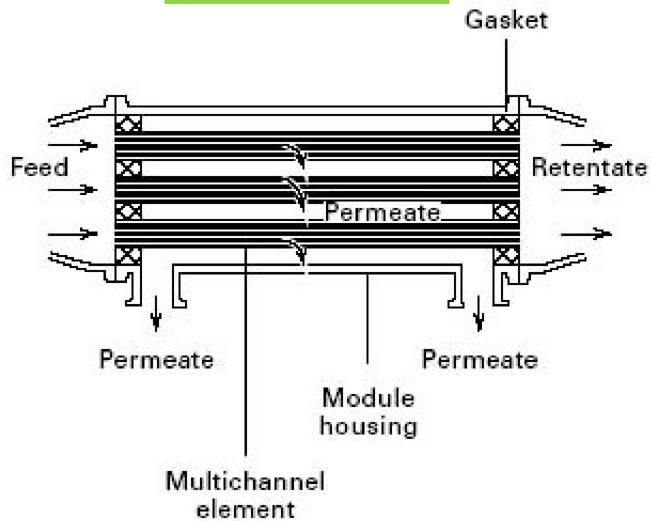
Tubular



Hollow-fiber



Monolithic



Membrane Modules (3)

- Typical characteristics of membrane modules

	Plate and frame	Spiral-wound	Tubular	Hollow-fiber
Packing density, m^2/m^3	30 – 500	200 – 800	30 – 200	500 – 9,000
Resistance to fouling	Good	Moderate	Very good	Poor
Ease of cleaning	Good	Fair	Excellent	Poor
Relative cost	High	Low	High	Low
Main application	D, RO, PV, UF, MF	D, RO, GP, UF, MF	RO, UF	D, RO, GP, UF

D: dialysis, RO: reverse osmosis, GP: gas permeation,
PV: pervaporation, UF: ultrafiltration, MF: microfiltration

Transport in Membranes

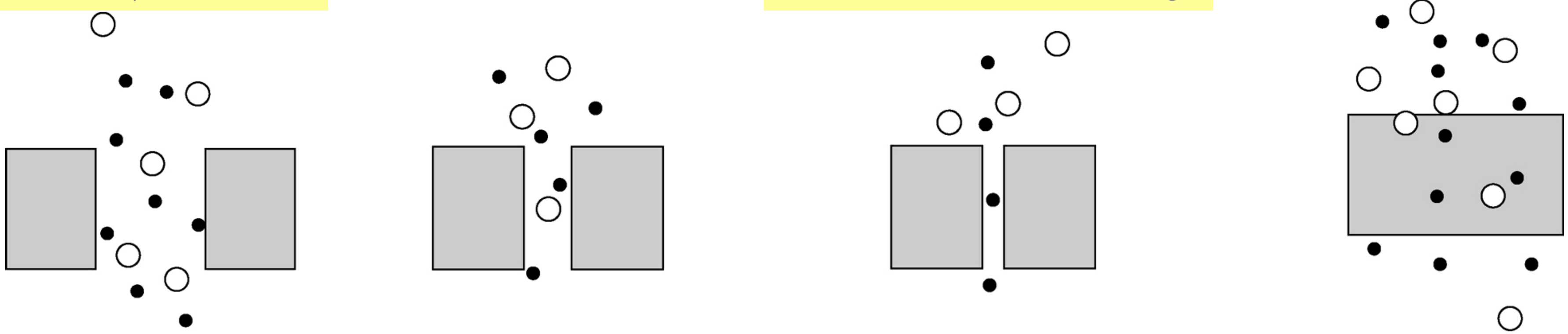
- Molar transmembrane flux

$$N_i = \left(\frac{P_{M_i}}{l_M} \right) (\text{driving force}) = \bar{P}_{M_i} (\text{driving force})$$

$$P_{M_i} : \textit{permeability} \ , \ \bar{P}_{M_i} : \textit{permeance}$$

- Types of membrane: macroporous, microporous, dense
- Mechanisms of transport in membranes

Bulk flow through pores	Diffusion through pores	Restricted diffusion through pores	Solution diffusion through dense membranes
No separation		Size exclusion, sieving	



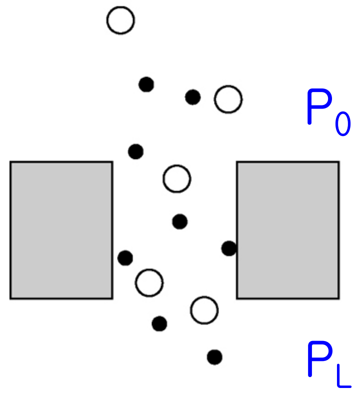
Bulk Flow

- Hagen-Poiseuille law (for laminar flow)

$$v = \frac{D^2}{32\mu L}(P_0 - P_L)$$

(D: pore diameter
L: length of the pore)

Pressure difference



- Porosity (void fraction)

$$\varepsilon = n\pi D^2/4$$

(n: pores per unit cross section)

- Superficial fluid bulk-flow flux (mass velocity)

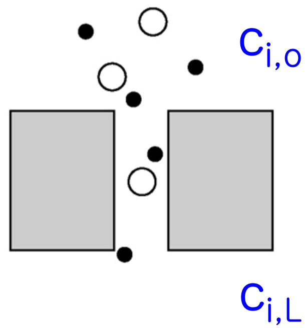
$$N = v\rho\varepsilon = \frac{\varepsilon\rho D^2}{32\mu l_M}(P_0 - P_L) = \frac{n\pi\rho D^4}{128\mu l_M}(P_0 - P_L)$$

(l_M: membrane thickness)

- Tortuosity factor, τ
  If pore length is longer than the membrane thickness, $l_M \rightarrow l_M\tau$

Liquid Diffusion in Pores

- When identical total pressures but different component concentrations exist
  → no bulk flow,
  but different diffusion rates → separation



- Modified form of Fick's law

$$N_i = \frac{D_{e_i}}{l_M}(c_{i_0} - c_{i_L})$$

Concentration driving force

Effective diffusivity

$$D_{e_i} = \frac{\varepsilon D_i}{\tau} K_{r_i}$$

Restrictive factor

$$K_r = \left[1 - \frac{d_m}{d_p}\right]^4, \ (d_m / d_p) \le 1$$

effect of pore diameter, d_p, in causing interfering collisions of the diffusing solutes with the pore wall

Gas Diffusion

- If total pressure and temperature on either side are equal

$$N_i = \frac{D_{e_i} c_M}{P l_M}(p_{i_0} - p_{i_L})$$

$$N_i = \frac{D_{e_i}}{RT l_M}(p_{i_0} - p_{i_L})$$

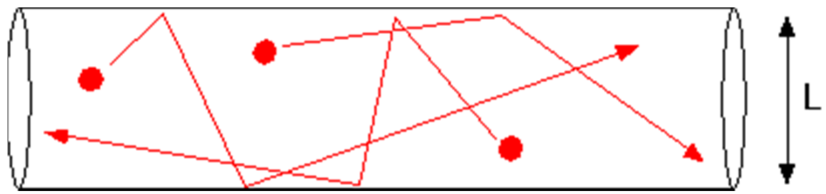
Partial-pressure driving force

c_M, total concentration of the gas mixture (=P/RT by the ideal-gas law)

$$D_{e_i} = \frac{\varepsilon}{\tau}\left[\frac{1}{(1/D_i)+(1/D_{K_i})}\right]$$

Ordinary diffusion

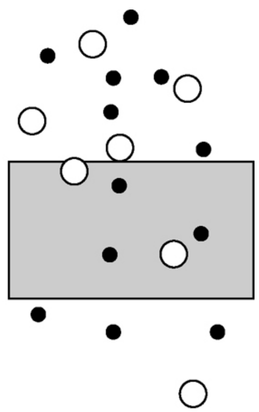
Knudsen diffusion



Collisions occur primarily between gas molecules and the pore wall

Nonporous Membranes

- Mechanism
  - Absorption of gas or liquid components into the membrane
  - Diffusion through the solid membrane
  - Desorption at the downstream face



- Diffusivities of water (cm^2/s at 1 atm, 25℃)
  - Water vapor in air : 0.25
  - Water in ethanol liquid : 1.2×10^{-5}
  - Water in cellulose acetate solid : 1×10^{-8}

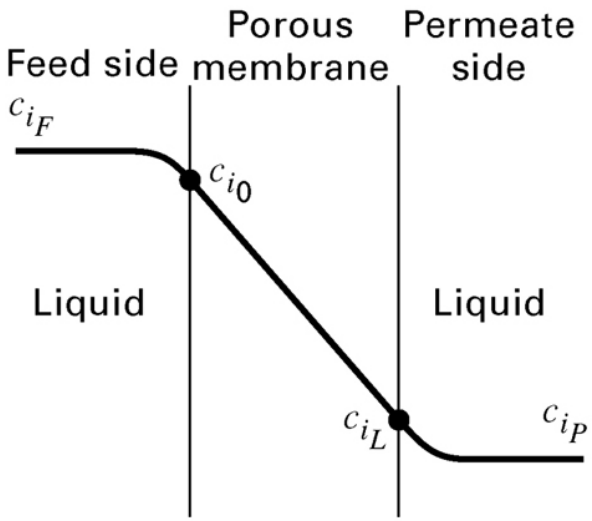
- Solution-diffusion model

  : The concentrations in the membrane are related to the concentrations or partial pressures in the fluid adjacent to the membrane faces

  → thermodynamic equilibrium for the solute between the fluid and membrane material at the interfaces

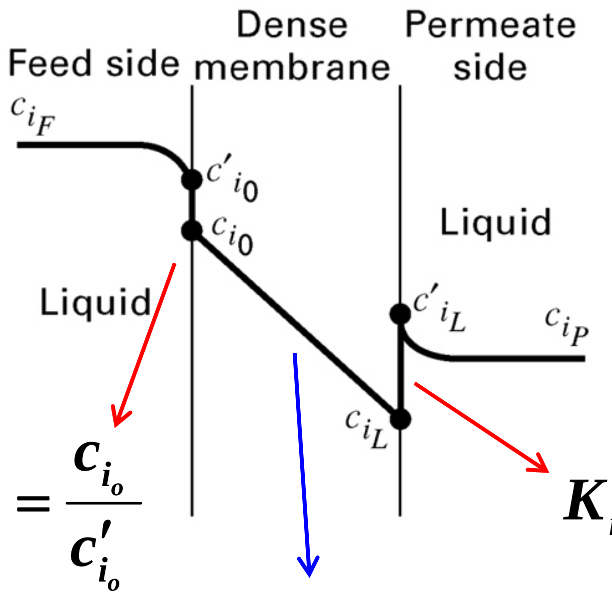
Solution–Diffusion for Liquid Mixtures

Porous membrane



Concentration profile is continuous

Nonporous membrane



$$K_{i_o} = \frac{c_{i_o}}{c'_{i_o}}$$

$$K_{i_L} = \frac{c_{i_L}}{c'_{i_L}}$$

$$N_i = \frac{D_i}{l_M}(c_{i_0} - c_{i_L})$$

$$N_i = \frac{K_i D_i}{l_M}(c'_{i_0} - c'_{i_L})$$

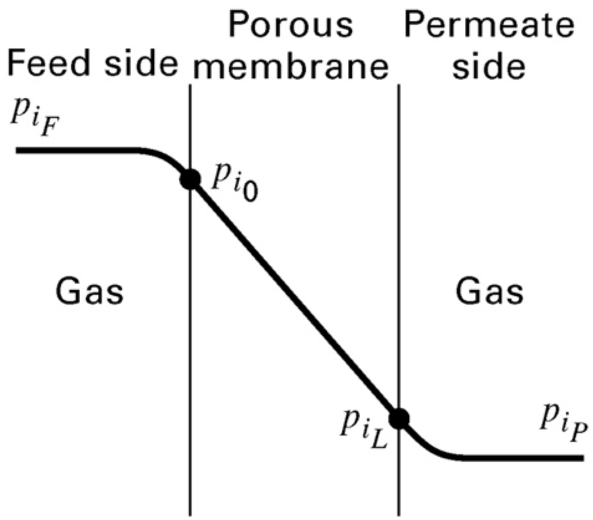
If the mass-transfer resistances in the boundary layers are negligible

$$N_i = \frac{K_i D_i}{l_M}(c_{i_F} - c_{i_P})$$

$K_i D_i$ is the permeability, P_{Mi}, for the solution-diffusion model

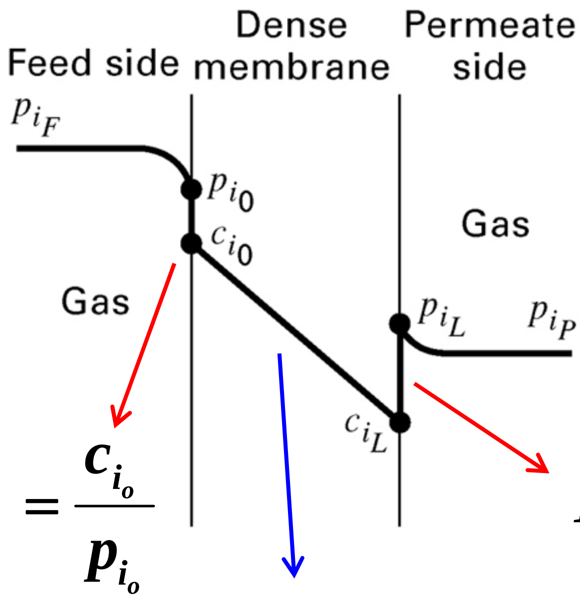
Solution–Diffusion for Gas Mixtures

Porous membrane



Continuous partial–pressure profile

Nonporous membrane



$$H_{i_o} = \frac{c_{i_o}}{p_{i_o}}$$

$$H_{i_L} = \frac{c_{i_L}}{p_{i_L}}$$

$$N_i = \frac{H_i D_i}{l_M}(p_{i_0} - p_{i_L})$$

If the external mass–transfer resistances are negligible

$$N_i = \frac{H_i D_i}{l_M}(p_{i_F} - p_{i_P})$$

$$P_{M_i} = H_i D_i$$

$$N_i = \frac{P_{M_i}}{l_M}(p_{i_F} - p_{i_P})$$