# Lecture 11.
# Transport in Membranes (1)

- Mass Transfer in Membranes
- Bulk Flow
- Liquid Diffusion through Pores
- Gas Diffusion through Porous Membranes
- Transport through Nonporous Membranes
  - Solution-diffusion for liquid mixtures
  - Solution-diffusion for gas mixtures

# Transport in Membranes

- Molar transmembrane flux

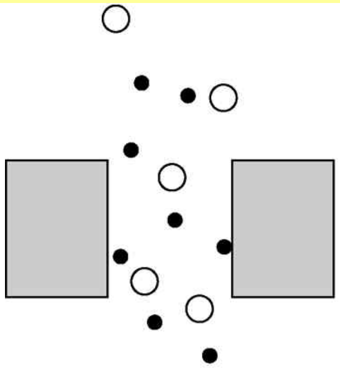
$$N_i = \left(\frac{P_{M_i}}{l_M}\right)(\text{driving force}) = \bar{P}_{M_i}(\text{driving force})$$

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

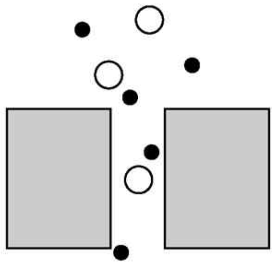
- Types of membrane: macroporous, microporous, dense
- Mechanisms of transport in membranes

Bulk flow through pores

No separation

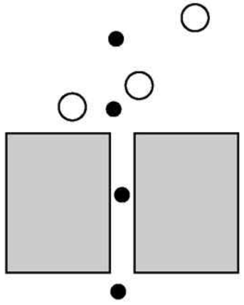


Diffusion through pores

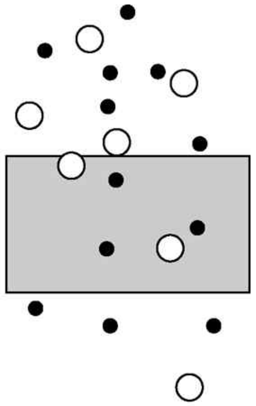


Restricted diffusion through pores

Size exclusion, sieving



Solution diffusion through dense membranes



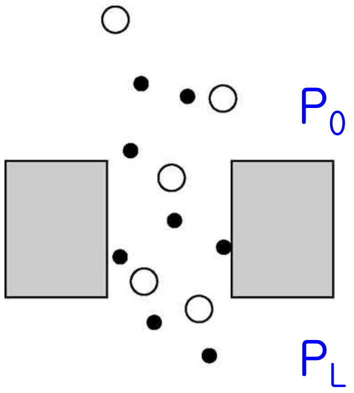
# Bulk Flow (1)

- 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 sectional area)

- 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)

# Bulk Flow (2)

- Pores may not be cylindrical and straight in real porous membrane
- Hydraulic diameter

$$d_H = 4\left(\frac{\text{Volume available for flow}}{\text{Total pore surface area}}\right) = \frac{4\left(\dfrac{\text{Total pore volume}}{\text{Membrane volume}}\right)}{\left(\dfrac{\text{Total pore surface area}}{\text{Membrane volume}}\right)} = \frac{4\varepsilon}{a}$$

- Total pore surface area per unit volume of just the membrane material (not including the pores)

$$a_v = a/(1-\varepsilon)$$

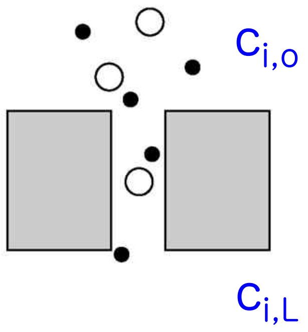
- Tortuosity factor, $\tau$

  If pore length is longer than the membrane thickness, $l_M \to l_M\tau$

$$N = \frac{\rho\varepsilon^2(P_0 - P_L)}{2(1-\varepsilon)^2\tau a_v^2\mu l_M} \quad \to \quad N = \frac{P_M}{l_M}(P_0 - P_L) \qquad P_M = \frac{\rho\varepsilon^3}{2(1-\varepsilon)^2\tau a_v^2\mu}$$

# Liquid Diffusion through Pores

- When identical total pressures but different component concentrations exist: no bulk flow, but different diffusion rates can achieve 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

- Selectivity ratio for solute molecules not subject to size exclusion:

$$S_{ij} = \frac{D_i K_{r_i}}{D_j K_{rj}}$$

# Gas Diffusion through Pores (1)

- If total pressure and temperature on either side are equal

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

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

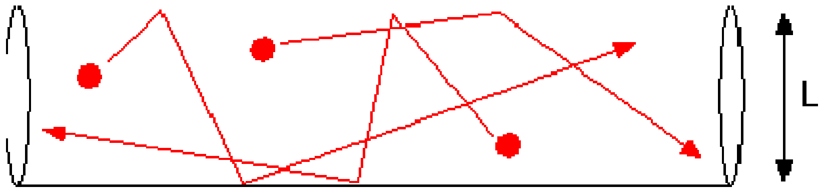
Partial–pressure driving force

$c_M$, 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

# Gas Diffusion through Pores (2)

- Knudsen diffusivity

$$D_{K_i} = \frac{d_p \bar{v}_i}{3}$$

From the kinetic theory of gases as applied to a straight, cylindrical pore of diameter $d_p$

$$\bar{v}_i = \left( \frac{8RT}{\pi M_i} \right)^{1/2}$$

Average molecule velocity of molecular weight M

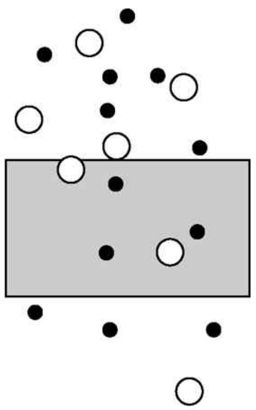
$$\Rightarrow \quad D_{K_i} = 4,850 d_p \left( \frac{T}{M_i} \right)^{1/2}$$

- When Knudsen flow predominates (as it often does for micropores)

$$\frac{P_{M_A}}{P_{M_B}} = \left( \frac{M_B}{M_A} \right)^{1/2}$$

# 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 : $1.2\times10^{-5}$
  - Water in cellulose acetate solid : $1\times10^{-8}$

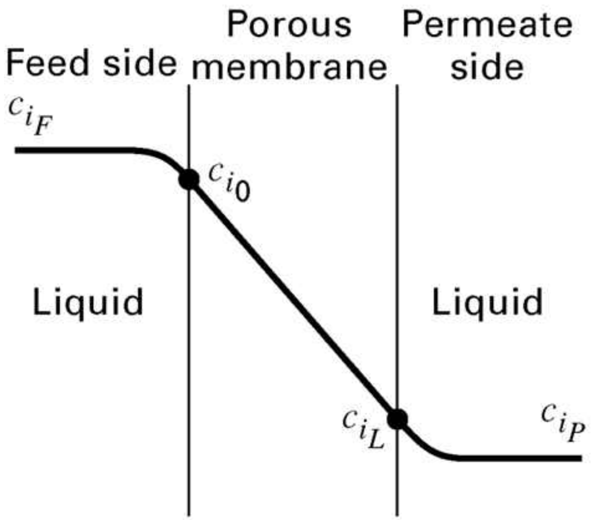
- Solution-diffusion model

: 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

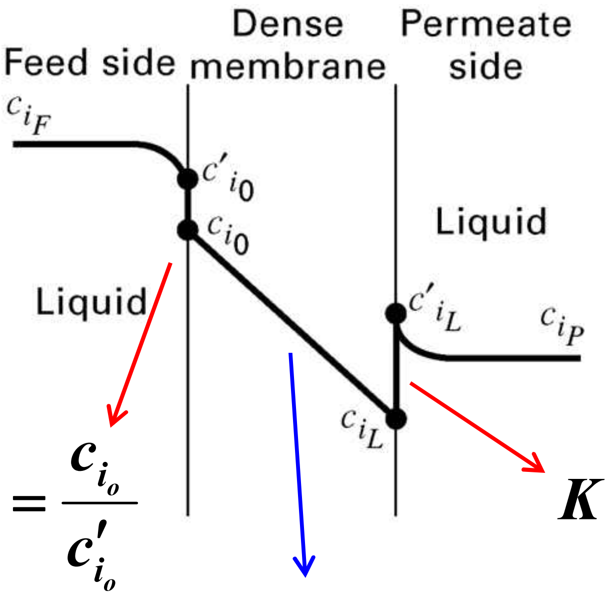
# Solution–Diffusion for Liquid Mixtures

Porous membrane



Concentration profile is continuous

Nonporous membrane



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

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

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

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

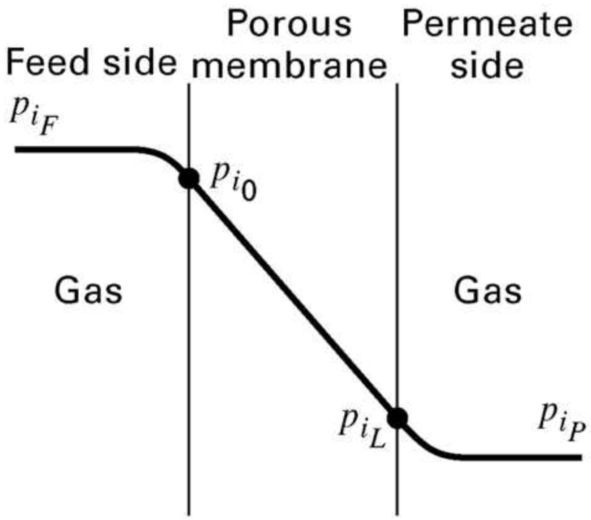
If the mass-transfer resistances in the boundary layers are negligible

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

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

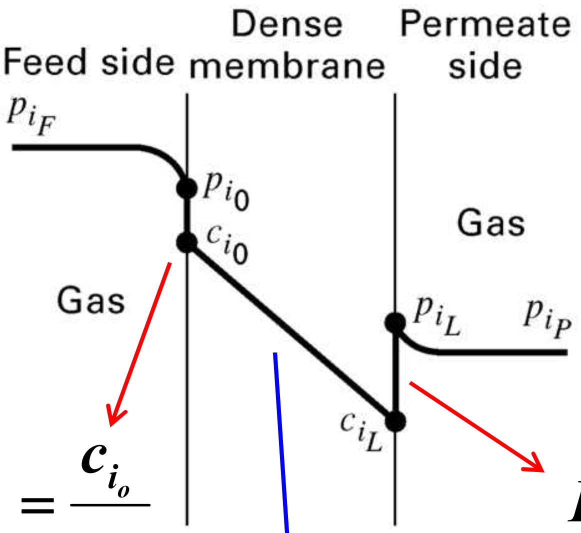
# Solution–Diffusion for Gas Mixtures (1)

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

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

$$P_{M_i} = H_i D_i$$

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

# Solution–Diffusion for Gas Mixtures (2)

- Separation factor

$$\alpha_{A,B} = \frac{(y_A / x_A)}{(y_B / x_B)}$$

$y_i$ : mole fraction in the permeate leaving the membrane
$x_i$ : mole fraction in the retentate on the feed side of the membrane

Unlike distillation, $y_i$ and $x_i$ are not in equilibrium

- For the separation of a binary gas mixture of A and B

$$N_A = \frac{H_A D_A}{l_M}(p_{A_F} - p_{A_P}) = \frac{H_A D_A}{l_M}(x_A P_F - y_A P_P)$$

$$N_B = \frac{H_B D_B}{l_M}(p_{B_F} - p_{B_P}) = \frac{H_B D_B}{l_M}(x_B P_F - y_B P_P)$$

- When no sweep gas is used

$$\frac{N_A}{N_B} = \frac{y_A}{y_B} = \frac{H_A D_A (x_A P_F - y_A P_P)}{H_B D_B (x_B P_F - y_B P_P)}$$

# Solution–Diffusion for Gas Mixtures (3)

- If the downstream (permeate) pressure, $P_P$, is negligible compared to the upstream pressure, $P_F$ $\quad y_A P_P \ll x_A P_F$ and $y_B P_P \ll x_B P_F$

  Ideal separation factor

$$\alpha^*_{A,B} = \frac{H_A D_A}{H_B D_B} = \frac{P_{M_A}}{P_{M_B}}$$

The factor depends on both transport phenomena and thermodynamic equilibria

- When the downstream pressure is not negligible

$$\alpha_{A,B} = \alpha^*_{A,B}\left[\frac{(x_B/y_B) - r\alpha_{A,B}}{(x_B/y_B) - r}\right]$$

$r$ : pressure ratio $\quad r = P_P/P_F$

$$\alpha_{A,B} = \alpha^*_{A,B}\left[\frac{x_B\left(\dfrac{y_A}{y_B}+1\right) - r\alpha_{A,B}}{x_B\left(\dfrac{y_A}{y_B}+1\right) - r}\right]$$

⇨

$$\alpha_{A,B} = \alpha^*_{A,B}\left[\frac{x_A\left(\alpha_{A,B}-1\right)+1-r\alpha_{A,B}}{x_A\left(\alpha_{A,B}-1\right)+1-r}\right]$$