280.371 Process Engineering Operations

Membrane Separation Processes
Lecture 3

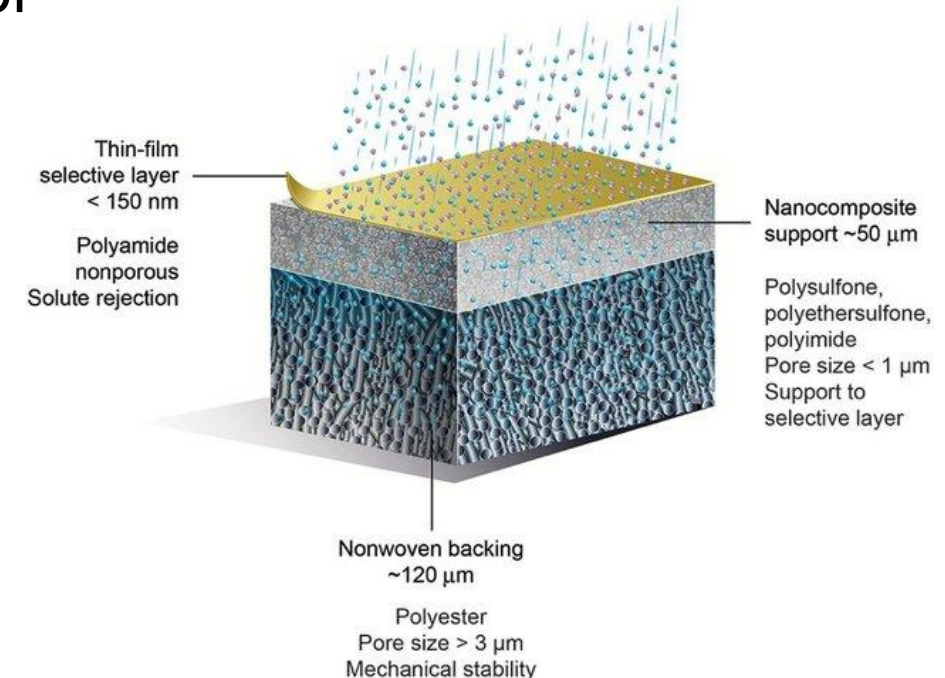## Professor Marie Wong

Relevant texts

- Geankoplis, C.J. 2003. Transport Processes and Separation Processes. 4th Edition

- Kirk-Othmer Encyclopedia of Chemical Technology, 2000.
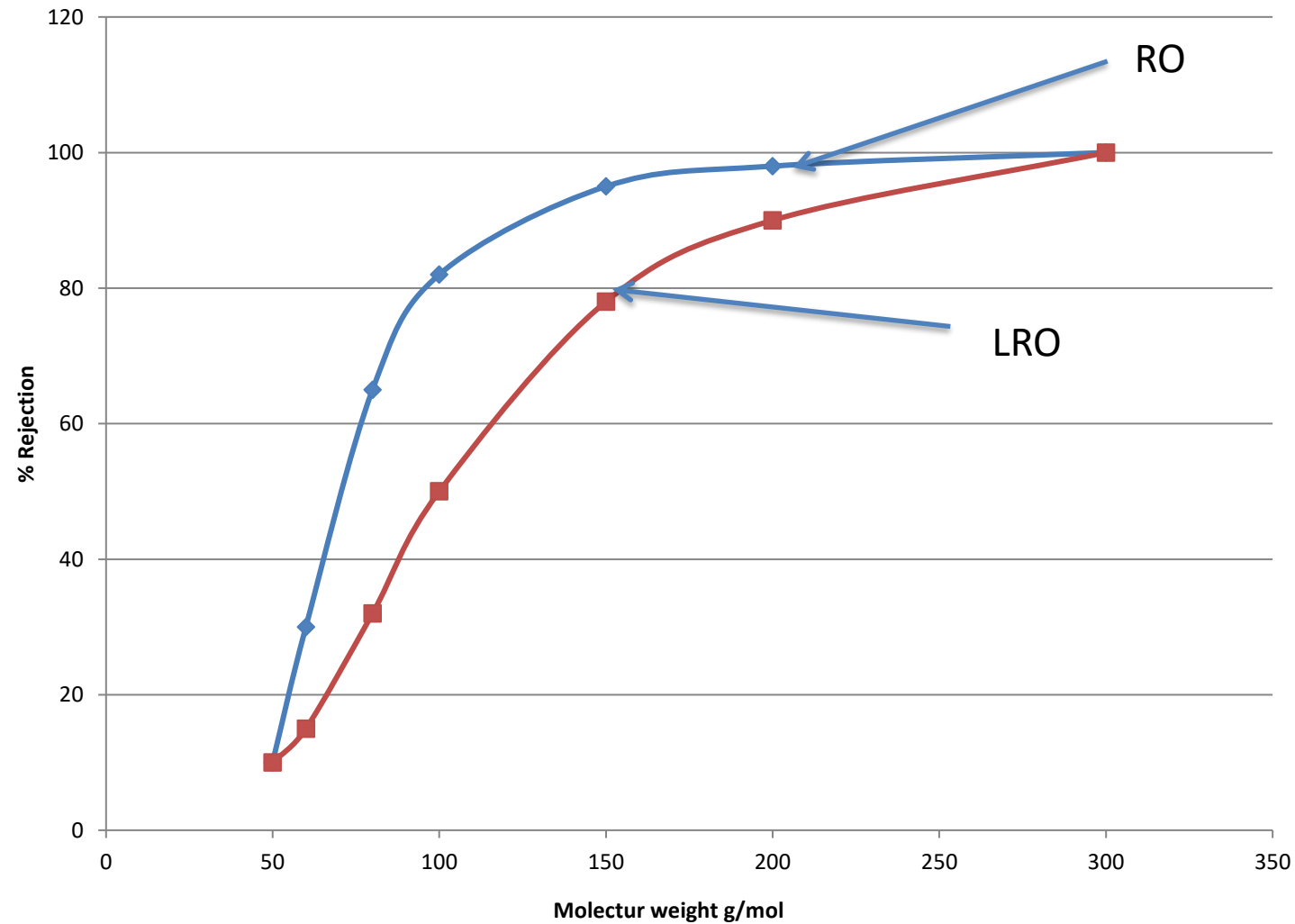
Reverse osmosis (RO)

- Concentration, demineralisation, desalting, purification

- Membranes are non-porous or porous

- Separation by molecular solubility and diffusivity

- Separation of low MW solutes and solvent

- Transfer of <u>solvent</u> across a semi-permeable membrane, against the osmotic gradient

- Hydraulic pressures applied > 2 MPa (20 bar)

Reverse Osmosis Membranes

- **Cellulose Acetate (CA)**
  - Asymmetric, formed by phase inversion, not resistant to chlorine

- **Polyamide Thin Film Composite**
  - Layered membrane (structural support, microporous interlayer and ultra thin barrier layer
  - Resistant to chlorine
  - Higher fluxes
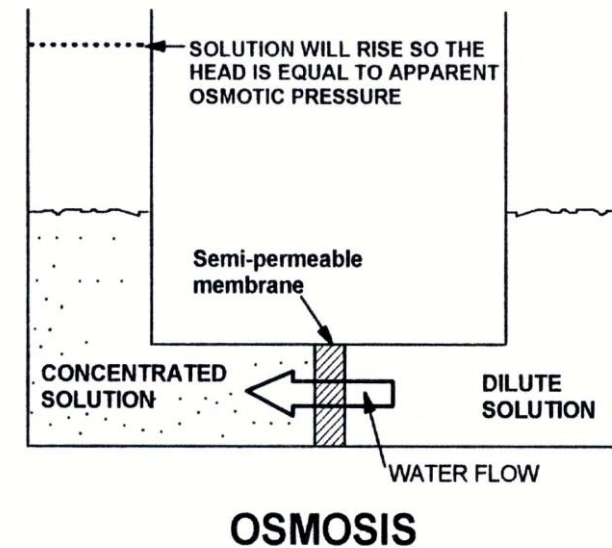 - Salt rejections up to 99%
  - Extended pH & temperature range

Thin-film selective layer < 150 nm

Polyamide nonporous Solute rejection

Nanocomposite support ~50 µm

Polysulfone, polyethersulfone, polyimide Pore size < 1 µm Support to selective layer

Nonwoven backing ~120 µm

Polyester Pore size > 3 µm Mechanical stability

Example of Rejection properties of RO + Loose RO membranes
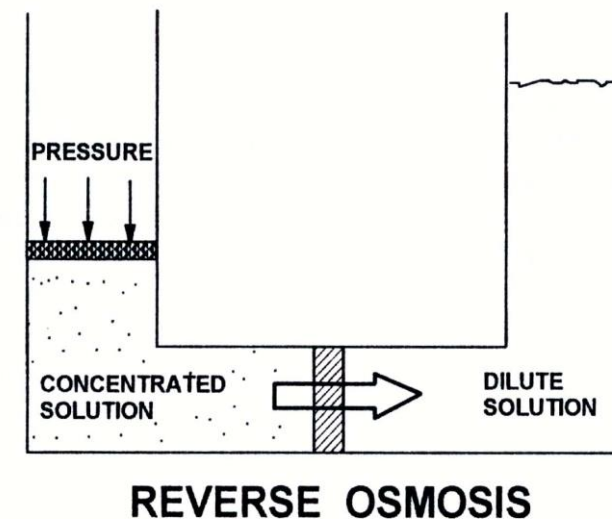
Osmosis & Reverse Osmosis (RO)

Osmosis

- the spontaneous transport of solvent from a dilute solution to a concentrated solution across a <u>semi-permeable</u> membrane.

Reverse Osmosis

- Apply a hydraulic pressure greater than the osmotic pressure difference between the two solutions to the more concentrated solution then solvent flows in the reverse direction against the osmotic gradient

Osmosis & Reverse Osmosis (RO)

Osmosis

- the spontaneous transport of solvent from a dilute solution to a concentrated solution across a <u>semi-permeable</u> membrane.
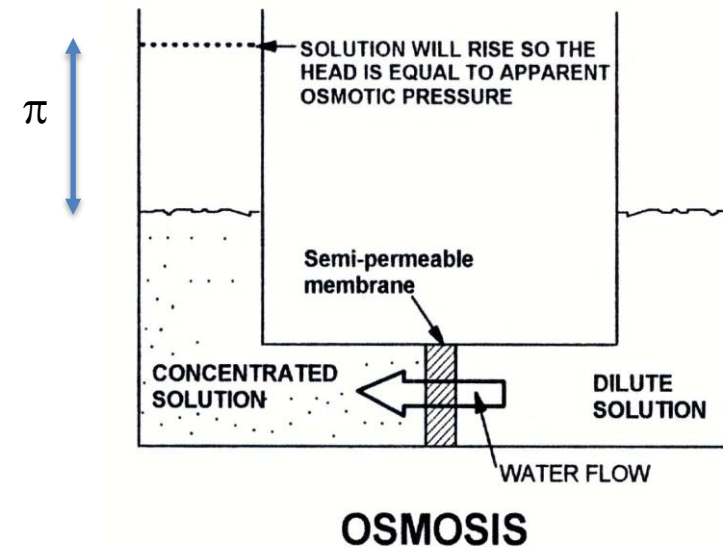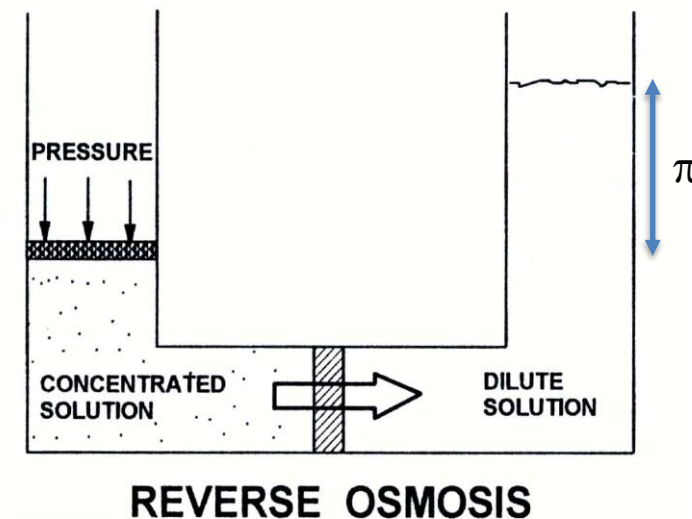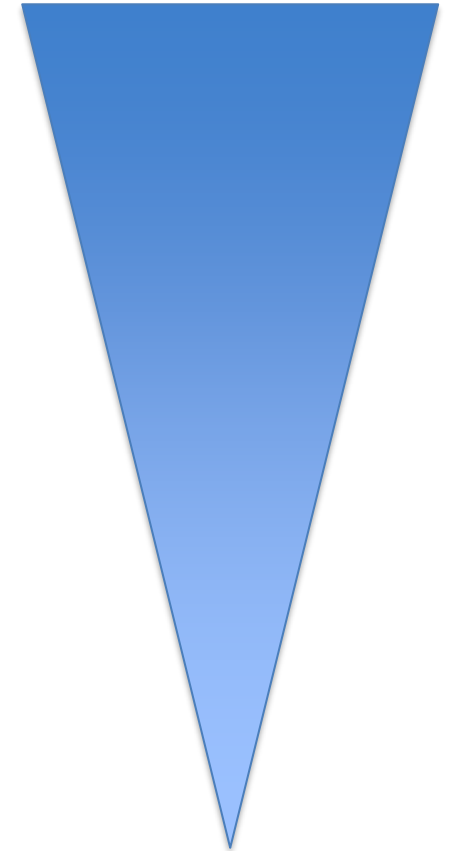
Reverse Osmosis

- Apply a hydraulic pressure greater than the osmotic pressure difference between the two solutions to the more concentrated solution then solvent flows in the reverse direction against the osmotic gradient

π

SOLUTION WILL RISE SO THE HEAD IS EQUAL TO APPARENT OSMOTIC PRESSURE

Semi-permeable membrane

CONCENTRATED SOLUTION

DILUTE SOLUTION

WATER FLOW

OSMOSIS

PRESSURE

π

CONCENTRATED SOLUTION

DILUTE SOLUTION

REVERSE OSMOSIS

Estimation of osmotic pressure

- Solutes in solution
- Type of solutes – Do they dissociate?
- Number of ionic species in solution
- Concentration of solutes
- Estimation based on
  - Stoichiometric formula
  - Theoretical and thermodynamic equations
  - Empirical equations
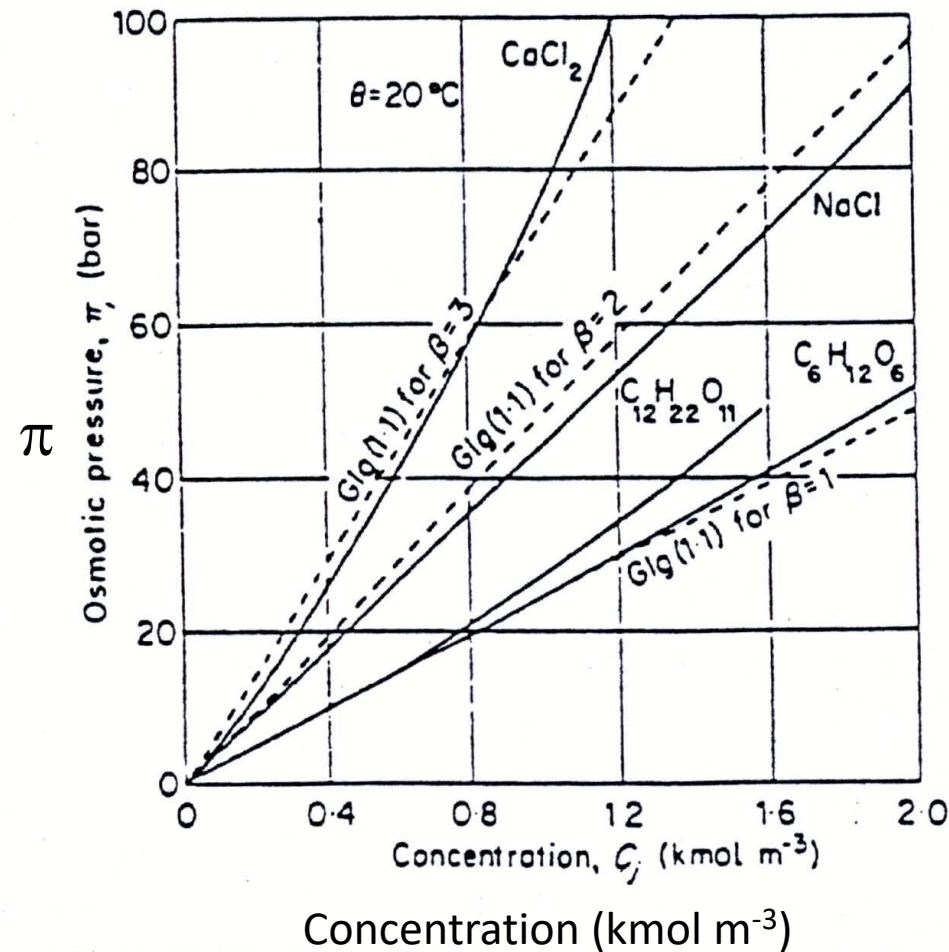 - Experimental measurements

Osmotic Pressure (π)

- Fundamental physical property determined by temperature, pressure and solute concentration

- For <u>dilute</u> solutions π can be estimated by Van't Hoff's law

$$\pi = \beta\,nRT$$

β - number of ionic species formed in solution

n - molar concentration of solute in solution (mol m^{-3})

R   - gas constant = 8.314 J mol^{-1} K^{-1}

T   - temperature (K)

Osmotic Pressure (π) –

Van't Hoff compared to measured data

Concentration (kmol m^{-3})

(Rautenbach & Albrecht, 1989)

Models for Mass Transfer in Reverse Osmosis

- Solution Diffusion Model
- Irreversible Thermodynamics Model
- Capillary Pore Model

Solution Diffusion Model for RO

- Membrane is a non-porous diffusion barrier

- Molecules dissolve into the membrane according to equilibrium relationships

- Diffusion through the membrane in response to concentration and pressure gradients

- Dissolution of molecules from the membrane matrix on the other side

Solution Diffusion Model for RO

Solvent flux

Mass flux (kg m^{-2} s^{-1})

$$J'_{solv} = \rho_{solv} A (\Delta P_{tm} - \Delta \pi)$$

Volumetric flux (m^3 m^{-2} s^{-1} or LMH)

$$J_{solv} = A (\Delta P_{tm} - \Delta \pi)$$

ρ_{solv} - density of solvent (kg m^{-3})

ΔP_{tm} - pressure difference across the membrane (Pa)

$\Delta \pi$ - osmotic pressure difference across the membrane (Pa)

A - membrane constant (m s^{-1} Pa^{-1}) *not membrane area*

Solvent membrane constant (A)

$$A = \frac{D_{solv}\, c_{solv}\, V_{solv}}{RT\, \Delta x\, MW_{solv}\, \rho_{solv}}$$

D_{solv} - diffusivity of solvent in membrane

Δx - thickness of membrane

Solute flux

$$J_{solute} = B \Delta c$$

$$B = \frac{D_2 K}{\Delta x}$$

$$K = \frac{molar\ conc\ of\ solute\ in\ membrane}{molar\ conc\ of\ solute\ in\ solution}$$

$$\Delta c = c_R - c_P$$

D_2 - diffusivity of solute in membrane ($m^2\,s^{-1}$)

K   - distribution coefficient of membrane

B – membrane constant for solute ($m\,s^{-1}$)

Assumptions:

- D is independent of concentration

- membrane properties (A and B) are independent of pressure

Typical values for membrane constants

$A = 1 \text{ to } 10 \times 10^{-6} \text{ m s}^{-1} \text{ bar}^{-1}$

$B = 0.05 \text{ to } 1 \times 10^{-6} \text{ m s}^{-1}$

Remember

$$SRC = 1 - \frac{c_p}{c_b}$$

For dilute solutions, the total mass flux is approximately equal to the solvent flux

$$J_{tot} = J_{solv} + J_{solute} = J_{solv}$$

$$SRC = \frac{A(\Delta P_{tm} - \Delta\pi)}{A(\Delta P_{tm} - \Delta\pi) + B}$$

$$SRC = \frac{J_{solv}}{J_{solv} + B}$$

Solution Diffusion Model for RO

It is evident that:

1. The flows of solvent and solute are inversely proportional to the membrane thickness

2. Solute rejection is independent of membrane thickness

3. Solvent flux is dependent on the pressure difference but solute flux is not. Thus as ΔP_{TM} increases the solute rejection should also increase.

Concentration polarisation (CP) in RO

- Solvent flux decreases at a given ΔP due to the increased π at membrane surface

- Solute flux is increases as c_m increases

- CP increases likelihood of precipitation of sparingly soluble salts at membrane surface

- CP may accelerate membrane deterioration

Design of RO systems

- From volumetric flux

$$J_{solv} = A(\Delta P_{tm} - \Delta \pi)$$

$$SRC = \frac{A(\Delta P_{tm} - \Delta \pi)}{A(\Delta P_{tm} - \Delta \pi) + B} = \frac{J_{solv}}{J_{solv} + B}$$

5. Osmotic pressure / RO membrane performance

Estimate the osmotic pressure of a 3 wt % (w/v) solution of the following compounds at 30°C:

      (a)   NaCl (MW = 58.5)

      (b)   glucose (MW = 180)

      (c)   albumin protein (MW $\approx$ 65,000)

An RO membrane is characterised by :

$A = 5 \times 10^{-6}$ m s^{-1} bar^{-1}

$B = 5 \times 10^{-7}$ m s^{-1}

(d) Estimate the flux and SRC for a feed concentration of 5,000ppm NaCl, operating temperature of 35°C, and ΔP of 2.5 x 10^6 Pa.

6. Osmotic pressure and Reverse osmosis

An RO system is used to concentrate an electroplating waste stream available at 25°C.

Given:

- the retentate stream contains 2 kg m^{-3} ZnCl$_2$ (MW: Zn = 65.4, Cl = 35.5)
- the SRC is 0.95
- the feed pressure is 20 bar (with negligible permeate pressure)
- the flux is 25 LMH

Calculate the values of the membrane constants A and B.

7. Osmotic pressure and Reverse osmosis

It is proposed to concentrate a salt brine (NaCl, MW = 58.5) at 30°C using an RO membrane with membrane constants of A = 9×10^{-7} m.s^{-1}.bar^{-1} and B = 7×10^{-7} m.s^{-1}.
The retentate brine concentration is 10,000 mg.l^{-1} and the permeate salt concentration
is not to exceed 1,000 mg. l^{-1}.

Estimate the flux and minimum required operating pressure. The osmotic pressure is given by:

$$\pi = \beta n R T$$

where R = 8,314, for π in Pa and n in kg-mole.m^{-3}.