

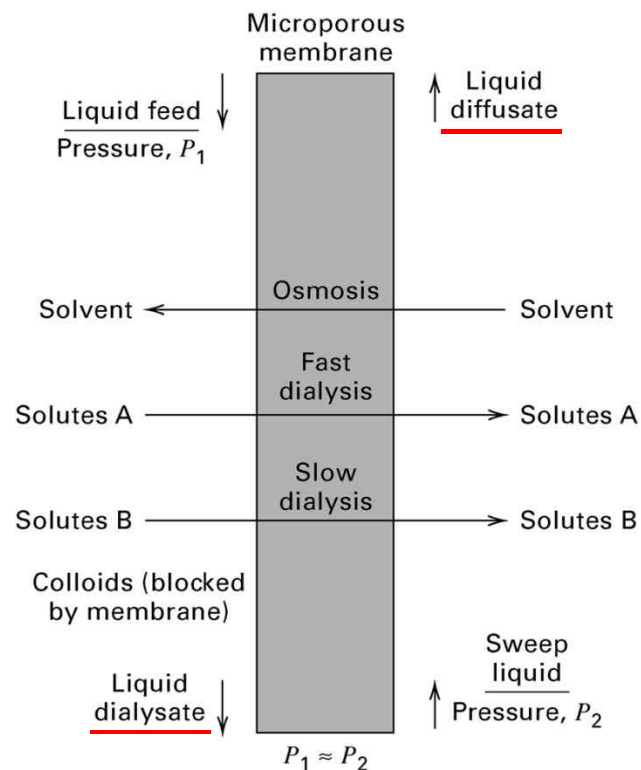
Lecture 13.

Membrane Separation Processes (1)

- Dialysis
 - Hemodialysis
- Electrodialysis
- Reverse Osmosis
 - Membranes for RO
 - Uses of RO
 - Osmotic pressure
 - Concentration polarization

Dialysis (1)

- The **dialysis** membrane is thin, with micropores of a size such that solutes of type A can pass through by a concentration-driving force
- Solutes of type B are larger in molecular size than those of type A and pass through the membrane only with difficulty or not at all
- Colloids do not pass through the membrane



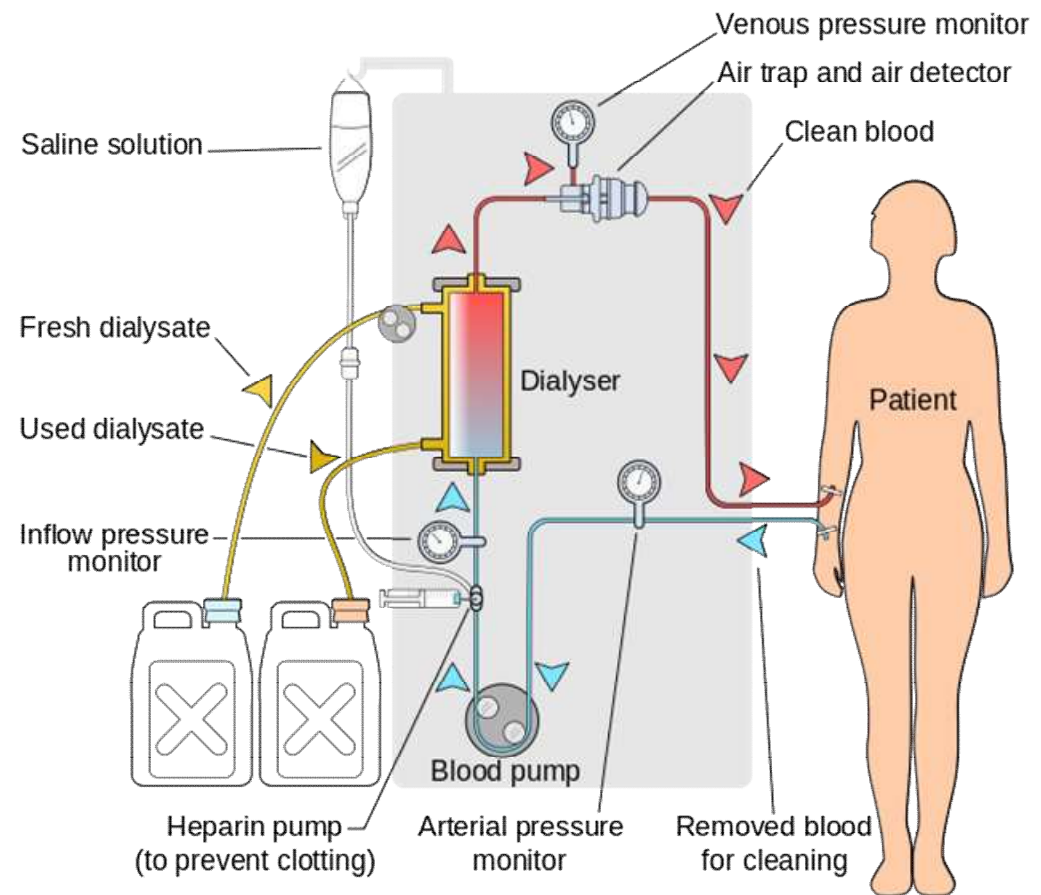
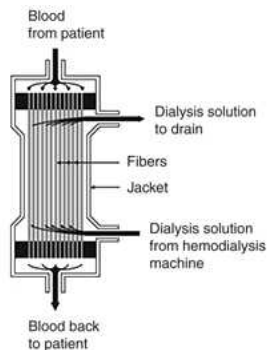
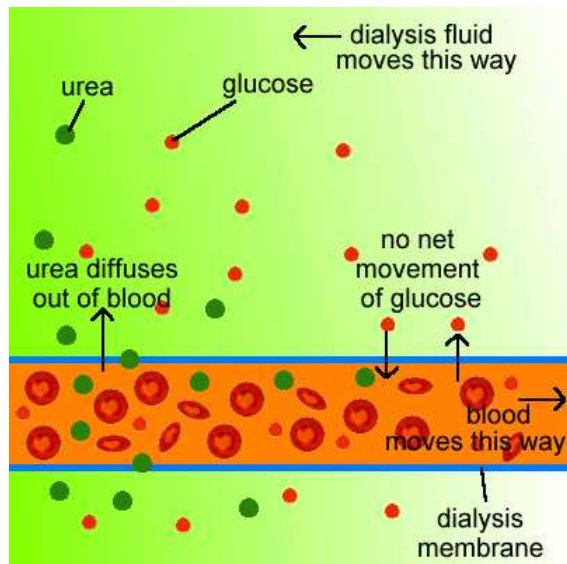
- When $P_1 = P_2$, the solvent may also pass through the membrane, but by a concentration-driving force acting in the opposite direction: osmosis
- When $P_1 > P_2$, solvent osmosis can be reduced or eliminated if the difference is higher than the osmotic pressure
- **Diffusate**: solvent, solutes of type A, and little or none of type B solutes
- **Dialysate**: solvent, type B solutes, remaining type A solutes, and colloidal matter

Dialysis (2)

- Dialysis is attractive when concentration differences for the main diffusing solutes are large and permeability differences between those solutes and the other solute(s) and/or colloids are large
- Application of dialysis
 - (1) Recovery of NaOH from a 17–20 wt% caustic viscose liquor contaminated with hemicellulose to produce a diffusate of 9–10 wt% caustic
 - (2) Recovery of chromic, hydrochloric, and hydrofluoric acids from contaminating metal ions
 - (3) Recovery of sulfuric acid from aqueous solutions containing nickel sulfate
 - (4) Removal of alcohol from beer to produce a low-alcohol beer
 - (5) Recovery of nitric and hydrofluoric acids from spent stainless steel pickle liquor
 - (6) Removal of mineral acids from organic compounds
 - (7) Removal of mineral low-molecular-weight contaminants from polymers
 - (8) Purification of pharmaceuticals

Dialysis (3)

- **Hemodialysis:** urea, creatine, uric acid, phosphates, and chlorides are removed from blood without removing essential higher-molecular-weight compounds and blood cells in a device called an artificial kidney



Dialysis (4)

- Dialysis membranes can be thin because pressures on either side of the membrane are essentially equal
- Differential rate of solute mass transfer across the membrane

$$dn_i = K_i (c_{i_F} - c_{i_P}) dA_M \quad K_i : \text{overall mass-transfer coefficient}$$

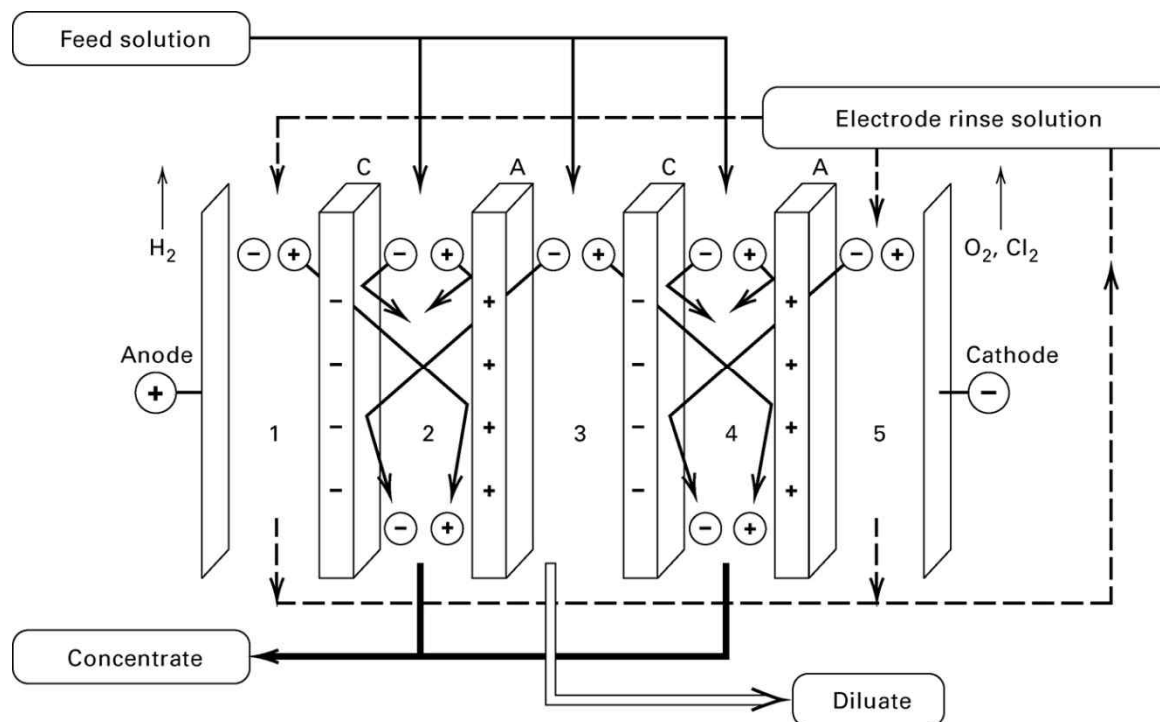
$$\frac{1}{K_i} = \frac{1}{k_{i_F}} + \frac{l_M}{P_{M_i}} + \frac{1}{k_{i_P}}$$

- **Water-transport number**: ratio of the water flux to the solute flux, with a negative value indicating transport of solvent in the solute direction
 - Ideally, the water-transport number should be a small value, $< +1.0$
- The most common dialysis membrane modules are plate-and-frame and hollow-fiber
- In a plate-and-frame dialyzer, the flow pattern is nearly countercurrent. When total flow rates change little and solute concentrations are small,

$$n_i = K_i A_M (\Delta c_i)_{LM} \quad (\Delta c_i)_{LM} : \text{log-mean concentration-driving force}$$

Electrodialysis (1)

- **Electrodialysis**: electrolytic process for separating an aqueous, electrolyte feed into concentrate and dilute or desalted water diluate by an electric field and ion-selective membranes
- Cation-selective membranes carry a negative charge, and thus attract and pass positively charged ions (cations), while retarding negative ions (anions)

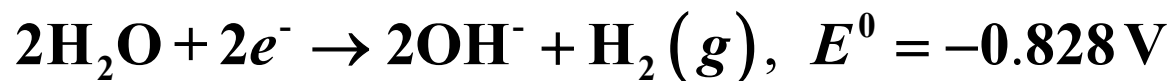


- Anion-selective membranes carry a positive charge that attracts and permits passage of anions
- Both types of membranes are impervious to water
- Compartment pressures are essentially equal

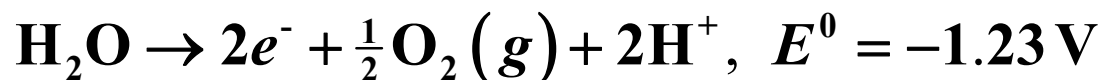
Electrodialysis (2)

- Both electrodes are chemically neutral metals, with the anode being typically stainless steel and the cathode platinum-coated tantalum, niobium, or titanium
- The most easily oxidized species is oxidized at the anode and the most easily reduced species is reduced at the cathode

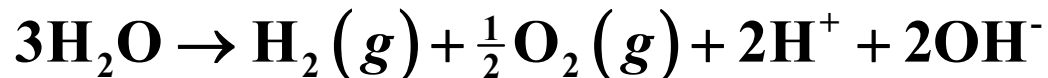
Reduction half reaction at the cathode



Oxidation half reaction at the anode



Corresponding overall cell reactions

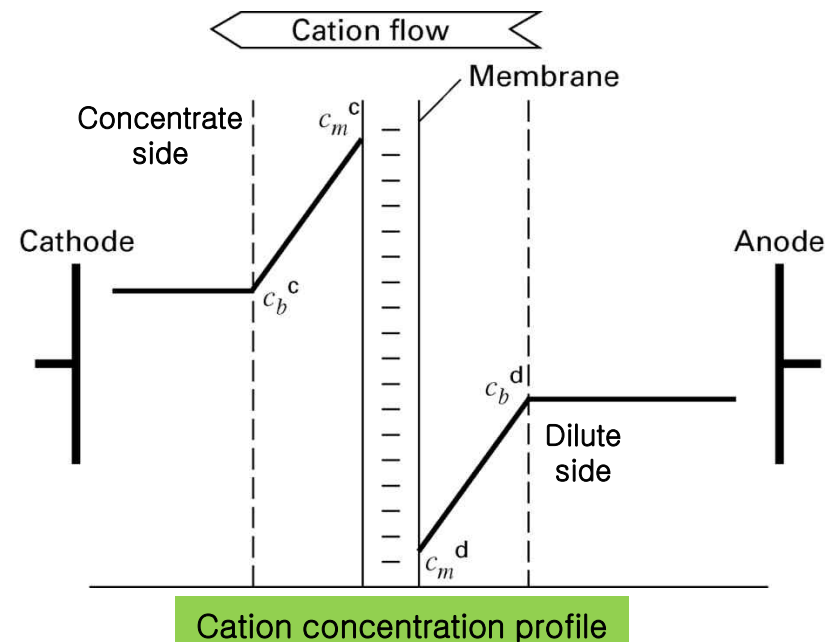


Net reaction



Electrodialysis (3)

- A cell pair or unit cell contains one cation-selective membrane and one anion-selective membrane
- A commercial electrodialysis system consists of a large stack of membranes in a plate-and-frame configuration, containing 100 to 600 cell pairs
- In a stack, membranes of 0.4 to 1.5 m² surface area are separated by 0.5 to 2 mm with spacer gaskets
- As the current density (amps flowing through the stack per unit surface area of membranes) is increased for a given membrane surface area, the concentration-polarization effect increases
- The maximum or limiting current density occurs when c_m^d reaches zero



Electrodialysis (4)

- The membrane area is estimated from the current density by applying Faraday's law

$$A_M = \frac{FQ\Delta c}{i\xi}$$

F : Faraday's constant
 Q : volumetric flow rate of the diluate (potable water)
 Δc : difference between feed and diluate ion concentration in equivalents
 i : current density of a cell pair
 ξ : current efficiency

- Power consumption

$$P = IE$$

P : Power, [W]
 I : electric current flow through the stack
 E : voltage across the stack

- Electric current

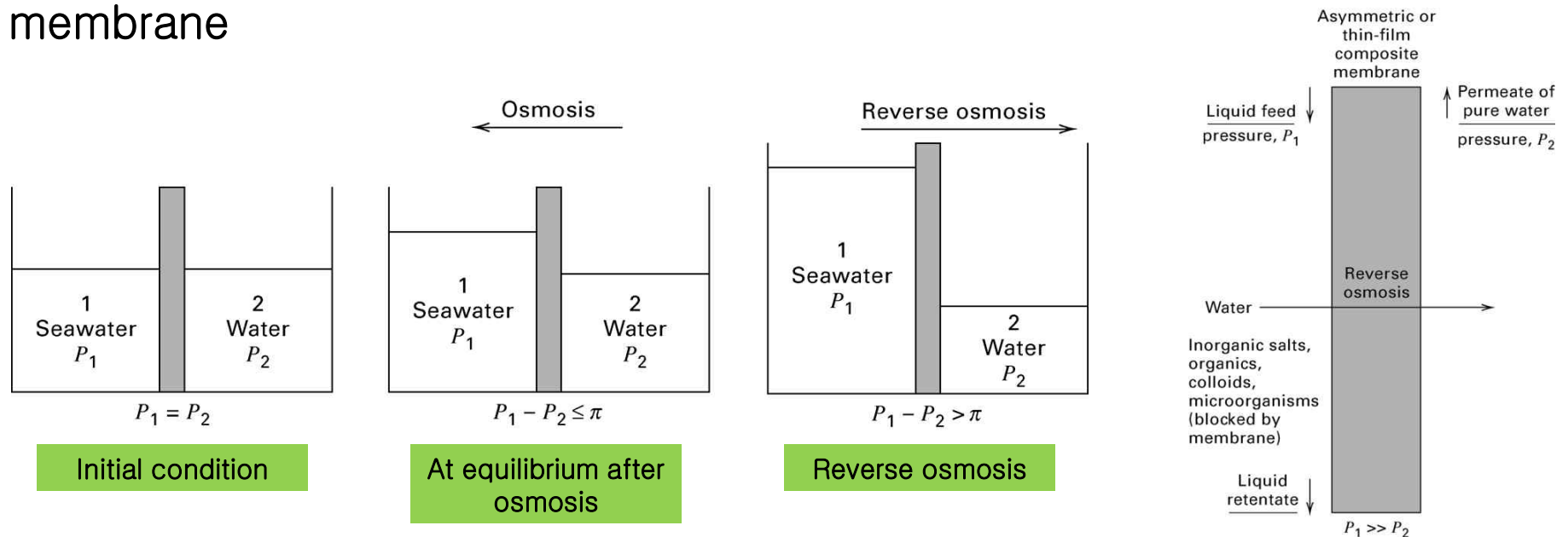
$$I = \frac{FQ\Delta c}{n\xi}$$

n : number of cell pairs

- The main application of electrodialysis is to the desalinization of brackish water in the salt-concentration range of 500 to 5,000 ppm (mg/L)

Reverse Osmosis (1)

- Osmosis: passage of a solvent, such as water, through a membrane that is much more permeable to solvent than to solute(s)
- **Osmotic pressure** (π): pressure which needs to be applied to a solution to prevent the inward flow of water across a semipermeable membrane; proportional to the solute concentration
- **Reverse osmosis**: a membrane-technology filtration method that removes many types of large molecules and ions from solutions by applying pressure to the solution when it is on one side of a selective membrane



Reverse Osmosis (2)

- A dense membrane such as an acetate or aromatic polyamide, permselective for the solvent, is used
- To withstand the large ΔP , the membrane must be thick
 - Asymmetric or thin-wall composite membranes, having a thin, dense skin or layer on a thick, porous support, are needed
- Use of RO to desalinate water is accomplished mainly with spiral-wound and hollow-fiber membrane modules utilizing cellulose triacetate, cellulose diacetate, and aromatic polyamide membrane materials
 - Cellulose acetates are susceptible to biological attack, and to acidic or basic hydrolysis back to cellulose, making it necessary to chlorinate the feed water and control the pH to within 4.5–7.5
 - Polyamides are not susceptible to biological attack, and resist hydrolysis in the pH range of 4–11, but are attacked by chlorine
- Products of reverse osmosis: a permeate of almost pure solvent and a retentate of solvent-depleted feed
- A perfect separation between solvent and solute is not achieved, since only a fraction of the solvent is transferred to the permeate

Reverse Osmosis (3)

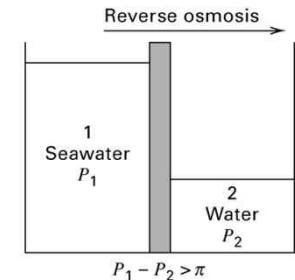
- RO is used to desalinate and purify seawater, brackish water, and wastewater
- Shift from a thermally-driven processes to a more economical, pressure-driven process for desalination
 - : Prior to 1980, multistage, flash distillation was the primary process → by 1990 RO became the dominant process for new construction
- The preferred membrane for the desalination of seawater, which contains about 3.5 wt% dissolved salts and has an osmotic pressure of 350 psia
 - : spiral-wound, multileaf module of polyamide, thin-film composite operating at a feed pressure of 800 to 1,000 psia
- For desalinizing of brackish water containing less than 0.5 wt% dissolved salts
 - : hollow-fiber modules of high packing density, containing fibers of cellulose acetates or aromatic polyamides, are used if fouling is not serious; because the osmotic pressure is much lower (<50 psi), feed pressures can be <250 psia

Reverse Osmosis (4)

- Other uses of RO
 - (1) Treatment of industrial wastewater to remove heavy-metal ions, nonbiodegradable substances, and other components of possible commercial value
 - (2) Treatment of rinse water from electroplating processes to obtain a metal-ion concentrate and a permeate that can be reused as a rinse
 - (3) Separation of sulfites and bisulfites from effluents in pulp and paper processes
 - (4) Treatment of wastewater in dyeing processes
 - (5) Recovery of constituents having food value from wastewaters in food-processing plants
 - (6) Treatment of municipal water to remove inorganic salts, low-molecular-weight organic compounds, viruses, and bacteria
 - (7) Dewatering of certain food products such as coffee, soups, tea, milk, orange juice, and tomato juice
 - (8) Concentration of amino acids and alkaloids

Reverse Osmosis (5)

- Driving force for water transport in RO
: concentration or activity difference, osmotic pressure
- At thermodynamic equilibrium, solvent chemical potentials or fugacities on the two sides of the membrane must be equal



$$f_A^{(1)} = f_A^{(2)}$$

$$a_A^{(1)} f_A^0 \{T, P_1\} = a_A^{(2)} f_A^0 \{T, P_2\}$$

$$f_A^0 \{T, P_2\} = x_A^{(1)} \gamma_A^{(1)} f_A^0 \{T, P_1\}$$

For pure solvent, $a_A^{(2)} = 1$

For seawater, $a_A^{(1)} = x_A^{(1)} \gamma_A^{(1)}$

For an incompressible liquid of specific volume, v_A

$$f_A^0 \{T, P_2\} = f_A^0 \{T, P_1\} \exp \left[\frac{v_{A_L} (P_2 - P_1)}{RT} \right]$$

Poynting correction

$$\pi = P_1 - P_2 = -\frac{RT}{v_{A_L}} \ln \left(x_A^{(1)} \gamma_A^{(1)} \right)$$

Reverse Osmosis (6)

- For a dilute mixture in the solute, $\gamma_A^{(1)} = 1$

$$x_A^{(1)} = 1 - x_B^{(1)} \quad \ln(1 - x_B^{(1)}) \approx -x_B^{(1)}$$

$$\pi = P_1 - P_2 = RT x_B^{(1)} / v_{A_L}$$

$$\pi \approx RTc_B$$



$$x_B^{(1)} \approx n_B / n_A \quad n_A v_{A_L} = V \quad n_B / V = c_B$$

- Approximation expression for osmotic pressure

$$\pi = 1.12T \sum \bar{m}_i$$

π in psia

T in K

$\sum \bar{m}_i$: summation of molarities of dissolved ions and nonionic species in the solution in mol/L

- When there are solutes on each side, at equilibrium $P_1 - \pi_1 = P_2 - \pi_2$

$$N_{H_2O} = \frac{P_{M_{H_2O}}}{l_M} (\Delta P - \Delta \pi)$$

ΔP : hydraulic pressure difference across the membrane (= $P_{\text{feed}} - P_{\text{permeate}}$)

$\Delta \pi$: osmotic pressure difference across the membrane (= $\pi_{\text{feed}} - \pi_{\text{permeate}}$)

Reverse Osmosis (7)

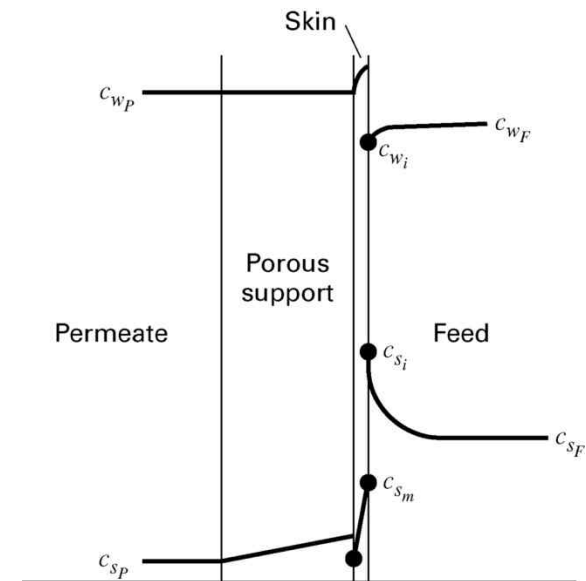
- Salt passage decreases with increasing ΔP

$$SP = (c_{\text{salt}})_{\text{permeate}} / (c_{\text{salt}})_{\text{feed}}$$

- Salt rejection $SR = 1 - SP$
- ΔP must be $> \Delta\pi$ for reverse osmosis to occur
 - For desalination of brackish water by RO, ΔP is typically 400–600 psi
 - For seawater, ΔP is 800–1,000 psi
- The feed water to an RO unit contains potential foulants, which must be removed prior to passage through the membrane unit
 - Suspended solids and particulate matter are removed by screening and filtration
 - Colloids are flocculated and filtered
 - Scale-forming salts require acidification or water softening
 - Biological materials require chlorination or ozonation
 - Other organic foulants are removed by adsorption or oxidation

Reverse Osmosis (8)

- Concentration polarization
 - Salt concentration adjacent to the surface of the membrane, $c_{Si} > c_{SF}$
 - This difference causes mass transfer of salt by diffusion from the membrane surface back to the bulk feed
 - The value of c_{Si} is important because it fixes the osmotic pressure, and influences the driving force for water transport
- Steady-state transport of water with back-diffusion of salt



$$N_{\text{H}_2\text{O}} c_{S_F} (SR) = k_S (c_{S_i} - c_{S_F})$$

$$c_{S_i} = c_{S_F} \left(1 + \frac{N_{\text{H}_2\text{O}} (SR)}{k_S} \right)$$

The concentration-polarization effect is most significant for high water fluxes and low mass-transfer coefficients

- If the permeate is pure solvent, then there is no film resistance on that side of the membrane

Reverse Osmosis (9)

- Concentration polarization factor, Γ

$$\Gamma \equiv \frac{c_{S_i} - c_{S_F}}{c_{S_F}} = \frac{N_{\text{H}_2\text{O}}(SR)}{k_S}$$

- Feed-side pressure drop is also important because it causes a reduction in the driving force for water transport
 - Spiral-wound modules
 - : 43–85 psi
 - Hollow-fiber modules
 - : 1.4–4.3 psi

