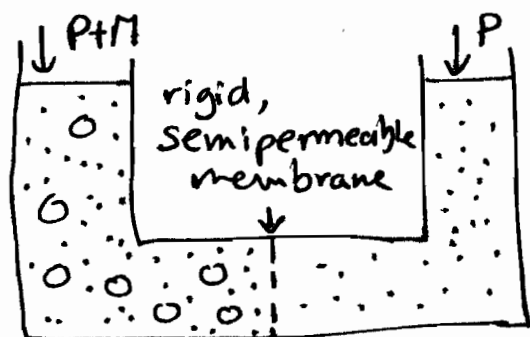


## Osmotic Equilibria



- : Species 2, solute - cannot cross the membrane
- : Species 1, solvent - can pass through

$\Pi \equiv$  "osmotic pressure"

@ equilibrium,  $\mu_1(\tau, P + \Pi, x_1) = \mu_1(\tau, P, \text{pure}) \Rightarrow$

$$\Rightarrow \gamma_1 x_1 f_1(\tau, P + \Pi) = f_1(\tau, P)$$

$$\left. \frac{\partial \ln f_1}{\partial P} \right|_{\tau} = \frac{v_1}{RT} \Rightarrow f_1(\tau, P + \Pi) = f_1(\tau, P) \exp\left(\frac{\Pi v_1}{RT}\right)$$

$$\therefore \gamma_1 x_1 \exp\left(\frac{\Pi v_1}{RT}\right) = 1 \Rightarrow \Pi = -\frac{RT}{v_1} \ln(\gamma_1 x_1)$$

For dilute solutions,  $\gamma_1 \approx 1$ ,  $\ln(1 - x_2) \approx -x_2 \Rightarrow$

$$\Pi = \frac{RT}{v_1} x_2 = \frac{RT N_2}{v_1 N} \Rightarrow \Pi v_1 = RT N_2 \text{ or}$$

$$\Pi = RT c_2$$

↓  
[mol/m<sup>3</sup>]

Numerical estimate (Ex. 9.7)

Seawater, 3.5% w/w NaCl,  $\rho = 1030 \text{ kg/m}^3$

$$X_{\text{NaCl}} = \frac{3.5 \text{ g} / 58.4 \text{ g/mol}}{3.5 / 58.4 + 96.5 / 18.0} = 0.011$$

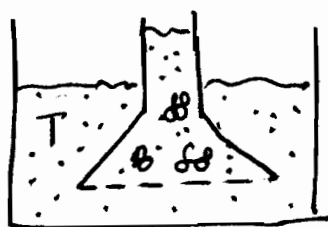
However, NaCl dissociates into  $\text{Na}^+$  and  $\text{Cl}^-$ ,

$$\text{So } X_{\text{H}_2\text{O}} = 1 - 2 \cdot 0.011 = 0.978 \text{ ; assume } \gamma_{\text{H}_2\text{O}} = 1$$

$$\Pi = -RT/\underline{V}_1 \ln x_1 \Rightarrow \Pi = 32 \text{ bar}$$

Application: desalination of sea water by "reverse osmosis" - applying  $P > 32 \text{ bar}$  on salty water to push water to the right and make it drinkable

### Membrane Osmometry (Ex. 9.8)



$$\delta h = 3.2 \text{ cm}$$

0.2 g / kg of  $\text{H}_2\text{O}$

MW = ?

$$\Pi = \rho_1 g \delta h = \frac{RT}{\underline{V}_1} x_2 \Rightarrow x_2 = 2.3 \cdot 10^{-6}$$

$$x_2 = \frac{w_2 / M_2}{\underbrace{w_2 / M_2 + w_1 / M_1}_{\text{small}}} \Rightarrow M_2 \approx \frac{w_2 M_1}{w_1 x_2} = \frac{0.2 \text{ g} \cdot 18 \frac{\text{g}}{\text{mol}}}{100 \text{ g} \cdot 2.3 \cdot 10^{-6}} = 15,400 \frac{\text{g}}{\text{mol}}$$

Small mole fractions give measurable  $\delta h$

### Virial Expansion of $\Pi$

Osmotic pressure measurements at moderate concentrations can be used to obtain solute-solute interactions:

By analogy to }  
 virial equation }  
 of state } 
$$\frac{\Pi \underline{V}}{RT} = 1 + B(\tau) \rho_2 + \dots$$

$\underline{V}$ : volume of solution

$\rho_2$ : molar conc. of solute

$B > 0$ : repulsions  
 between solute molecules

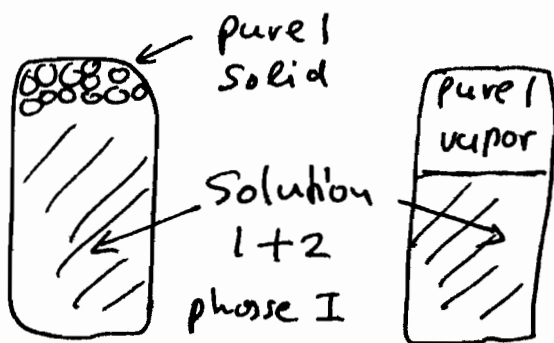
$B < 0$ : attractions

CBE 246 Osmotic Eq., Colligative Props. (3)

Colligative properties: properties that depend on the mole fractions (but not the nature) of a solute.

Osmotic pressure is a colligative property. Also:

Boiling Point Elevation / Freezing Point Depression



e.g.  $H_2O$  with a little dissolved solute (comp. 2), present only in solution.  
 $\Rightarrow T_{boil}, T_{melt}$  different from  $T_{pure}$

$$\mu_{i,I}(T, P, x_i) = \mu_{i,II}(T, P) \Rightarrow RT \ln(\gamma_i x_i) + \mu_{i,I}(T, P) = \mu_{i,II}(T, P)$$

$$\Rightarrow RT \ln(\gamma_i x_i) = -\Delta\mu(T, P) \quad (i)$$

$\Delta\mu(T_{pure}, P) = \mu_I - \mu_{II} = 0$  at  $T_{boil}$  or  $T_{melt}$

$$\left. \frac{\partial(\mu/T)}{\partial T} \right|_P = \left. \frac{\partial(G/T)}{\partial T} \right|_P = -\frac{G}{T^2} + \frac{1}{T} \left. \frac{\partial G}{\partial T} \right|_P = \frac{-G + TS}{T^2} = -\frac{H}{T^2}$$

$$\Rightarrow \left. \frac{\partial \Delta\mu/T}{\partial T} \right|_P = -\frac{\Delta H}{T^2}$$

If  $\Delta H = H_I - H_{II}$  is independent of  $T$ ,

$$\frac{\Delta\mu(T)}{T} - \frac{\Delta\mu(T_{pure})}{T_{pure}} = \Delta H \left( \frac{1}{T} - \frac{1}{T_{pure}} \right) \stackrel{(i)}{\Rightarrow} R \ln(\gamma_i x_i) = -\frac{\Delta H (T_{pure} - T)}{R T_{pure} T}$$

For dilute solutions,  $\gamma_1 \approx 1$ ,  $\ln x_1 \approx \ln(1-x_2) \approx -x_2$

$$T \approx T_{\text{pure}} \quad \therefore \quad -x_2 = -\frac{\Delta H (T_{\text{pure}} - T)}{R T_{\text{pure}}^2} \Rightarrow$$

$$\Rightarrow T = T_{\text{pure}} - \frac{x_2 R T_{\text{pure}}^2}{\Delta H}$$

For melting,  $\Delta H = H_{\text{I}} - H_{\text{II}} = H(\text{liq.}) - H(\text{solid}) > 0$

$T < T_{\text{pure}}$  : freezing point depression

For boiling,  $\Delta H = H_{\text{I}} - H_{\text{II}} = H(\text{liq.}) - H(\text{vapor}) < 0$

$T > T_{\text{pure}}$  : boiling point elevation

Example: freezing point depression for solution of polymer in example 9.8

$$x_2 = 2.3 \cdot 10^{-6}$$

$$\Delta H = 601 \text{ kJ/mol} \quad T_{\text{pure}} = 273 \text{ K}$$

$$T - T_{\text{pure}} = -\frac{2.3 \cdot 10^{-6} \cdot 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 273^2 \text{ K}^2}{6011 \frac{\text{J}}{\text{mol}}} = 2.4 \cdot 10^{-4} \text{ K}$$

(too small to measure accurately)