Chap 5.5 Dilute Solutions

Solution - 1 component of mixture (solvent) is primary and the other components (solutes) is secondary

Mainly: solutes don't interact with each other, only interacts with solvent

To get properties need to get G : N_a = # solvent atoms/mol
N_b = # of solute atoms/mol

pure Solvent $G = N_A \mu_0(T,P)$

$$G = U - TS + PV = N_a \mu_0(T,P) + G_{add}$$

If you add N_b atoms to N_a, the mixing increase of entropy

$$-TS = -Tk_B \ln\binom{N_a+N_b}{N_a} = -Tk_B \ln\left[\frac{(N_a+N_b)!}{N_a!\,N_b!}\right]$$
$$= -Tk_B\left[(N_a+N_b)\ln(N_a+N_b) - (N_a+N_b) - N_a \ln N_a - N_b \ln N_b + N_a + N_b\right]$$
$$= -Tk_B\left[(N_a+N_b)\left(\ln N_a + \frac{N_b}{N_a}\right) - N_a \ln N_a - N_b \ln N_b\right]$$
$$= -Tk_B\left[N_b \ln N_a + N_b - N_b \ln N_b\right]$$

The $(U+PV)_{add}$ is proportional to N_b and depends on T and P

$$\Rightarrow (U+PV)_{add} = N_b f(T,P)$$

$$\Rightarrow G = N_a \mu_0(T,P) + N_b f(T,P) - N_b k_B T \ln N_a + N_b k_B T \ln N_b - N_b k_B T$$

To get the chemical potentials $\mu_a = \left(\frac{\partial G}{\partial N_a}\right)_{T,P,N_b} = \mu_0(T,P) - \frac{N_b k_B T}{N_a}$

$$\mu_b = \left(\frac{\partial G}{\partial N_b}\right)_{T,P,N_a} = f(T,P) + k_B T \ln\left(\frac{N_b}{N_a}\right)$$

Prob 5.74 pg 202

Eq 5.37 $G = N_a \mu_a + N_b \mu_b$ does this work for us?

$$= N_a\left(\mu_0(T,P) - \frac{N_b}{N_a} k_B T\right) + N_b\left[f(T,P) + k_B T \ln N_b - k_B T \ln N_a\right]$$
$$= \text{above}$$

Technical detail

$$G = N_a \mu_0(T,P) + N_b f(T,P) + N_b k_B T \ln\left(\frac{N_b}{N_a}\right) - N_b k_B T$$
$$= N_a \mu_0(T,P) + N_b \tilde{f}(T,P) + N_b k_B T \ln(m_b) - N_b k_B T$$

m = molality $= \frac{\text{moles of solute}}{\text{kgs of solvent}} = \frac{N_b \text{ lks}}{N_A M_a}$

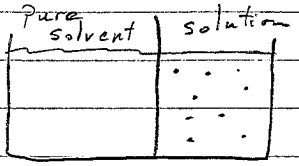
Another way to write the chemical potential is in terms of the chemical potential at $m = 1$

$$\mu_b = \mu_{0,b}(T, P) + k_B T \ln m$$

This allows you to relate the chemical potential at any molality to a "standard" value that can be measured/tabulated

Osmosis

From $\mu_a = \mu_0(T, P) - \frac{N_b}{N_a} k_B T$



Because chemical potential decreases μ_a decreases you get a flow if pressure is same on both sides

No flow if chemical potential same

left

$$\mu_0(T, P_1) = \mu_0(T, P_2) - \frac{N_b}{N_a} k_B T$$

If pressure change is small $\mu_0(T, P_2) \cong \mu_0(T, P_1) + (P_2 - P_1)\left(\frac{\partial \mu_0}{\partial P}\right)_T$

$$\Rightarrow (P_2 - P_1)\left(\frac{\partial \mu_0}{\partial P}\right)_T = \frac{N_b}{N_a} k_B T$$

But for pure substance $\mu_0 = \frac{G}{N_a} \Rightarrow \left(\frac{\partial \mu_0}{\partial P}\right)_T = \frac{1}{N_a}\left(\frac{\partial G}{\partial P}\right)\Big|_{N,T} = \frac{V}{N_a}$

$$\Rightarrow (P_2 - P_1) = \frac{N_b}{V} k_B T = \frac{n_b}{V} RT$$

$\frac{n_b}{V}$ = # of moles per volume of solute

$P_2 - P_1$ = osmotic pressure

Prob 5.77

The pressure difference is $\rho g \Delta h = 1000 \frac{kg}{m^3} 9.8 \frac{m}{s^2} \Delta h$

$n_b/V = \frac{m_{sol}}{V}\frac{1}{M}$ where M is atomic mass

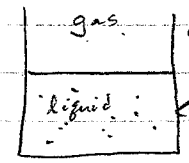
$$\Rightarrow M = \frac{m_{sol}}{V} RT / \Delta P = 5.6 \times 10^{-3} \frac{kg}{10^{-3} m^3}\ 8.31 \frac{J}{mol K}\ 276 K / (1000 \frac{kg}{m^3}\ 9.8 \frac{m}{s^2}\ 2 \times 10^{-2} m)$$

$$= 66 \text{ kg/mol} = 66{,}000 \text{ g/mol}$$

Impurity shift of boiling/freezing points

Having impurity in liquid will shift the vaporization pressure at a given T; see the book for derivation

Shift of PT boundary between different phases occurs because concentration of solute in diff. phases can be wildly diff.



At fixed P, how does T of boiling change?

No solute: $\mu_{a,liq}(T_0, P) = \mu_{a,gas}(T_0, P)$

The reason for equality is no cost for molecule to go liq ↔ gas

With solute $\mu_{a,liq}(T_0, P) - \frac{N_b k_B T}{N_a} = \mu_{a,gas}(T, P)$ T_0 = temp of phase change at press. P

Do expansion $T = T_0 + \overbrace{T - T_0}^{\text{small}}$

$$\mu_{a,liq}(T_0, P) + (T - T_0)\left(\frac{\partial \mu_{a,liq}}{\partial T}\right)_P - \frac{N_b k_B T}{N_a} = \mu_{a,gas}(T_0, P) + (T - T_0)\frac{\partial \mu_{a,gas}}{\partial T}$$

$$\left(\frac{\partial \mu_{a,liq}}{\partial T}\right)_P - \left(\frac{\partial \mu_{a,gas}}{\partial T}\right)_P = \frac{1}{N_{liq}}\left(\frac{\partial G_{liq}}{\partial T}\right) - \frac{1}{N_{gas}}\left(\frac{\partial G_{gas}}{\partial T}\right) = \frac{S_{gas}}{N_{gas}} - \frac{S_{liq}}{N_{liq}}$$

The difference in entropy per particle between gas and liquid is $L \cdot m_a / T$ where L is latent heat (unit J/kg), m_a is the mass of 1 solvent particle and T

$$\Rightarrow (T - T_0) = \frac{N_b k_B T}{N_a L m_a / T} \simeq \frac{n_b R T_0^2}{\underbrace{M_a}_{\text{mass of liquid solvent}} L} = m \frac{R T_0^2}{L}$$

molality (aha!)

Prob 5.79 Add 1 tsp of salt to pot of water, what is ΔT?

1 tsp salt ~ 6 g

Avg mass Na, Cl ~ 29 g/mol $\Rightarrow$ $n_b \sim \frac{6\text{ g}}{29\text{ g/mol}} \sim 0.2$ mol

If pot holds 1 liter H_2O $M_a = 1$ kg

$L = 2.26 \times 10^6$ J/kg

$T_0 = 373$ K

$$\Delta T = \frac{0.2\text{ mol} \quad 8.3 \frac{\text{J}}{\text{mol K}} \quad (373\text{K})^2}{1\text{ kg} \quad 2.26 \times 10^6\text{ J/kg}} \simeq 0.1\text{ K} \quad \text{(not much)}$$