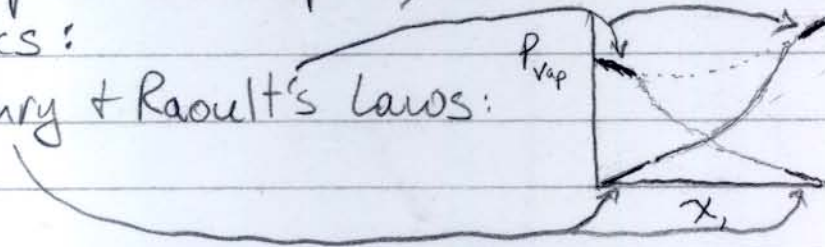


Solutions: Henry, Raoult, etc. 8.1

For this part of Chp 8, we'll look at 3 main topics:

① Henry + Raoult's laws:



② Colligative properties: $\Delta T = K_{\text{b (or "f")}} m$, $\Pi V = NRT$
 boil pt / Freeze pt change osmotic pressure, Π

③ Solubility + Ionic Strength: $K_{\text{sp}} \approx m_{\text{A}} + m_{\text{B}^-}$, $I = \frac{1}{2} \sum_k z_k^2 m_k$
 solubility equilibrium constant
 sp = solubility product

There are lots of tricky derivations, so it's important to remember the big conclusions summarized above.

Now for the details:

for a "perfect" solution:

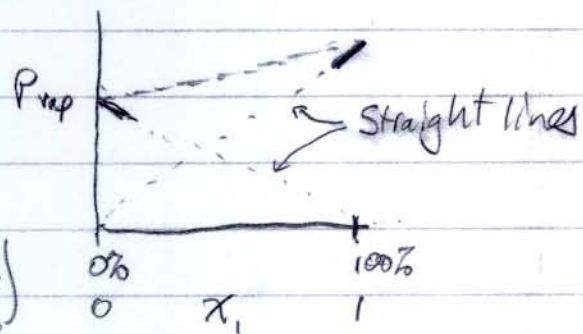
Since:

$$\mu_{1,l}^0 + RT \ln x_1 = \mu_{1,g}^0 + RT \ln \left(\frac{P_1}{P_0} \right)$$

and:

$$e^{\frac{\mu_{1,l}^0 - \mu_{1,g}^0}{RT}} = e^{\ln \left(\frac{P_1}{P_0} \right) - \ln x_1} \Rightarrow e^{\Phi} = \frac{P_1}{P_0} x_1 \therefore P_1 = \underbrace{P_0}_{K_1} e^{\Phi} \cdot x_1$$

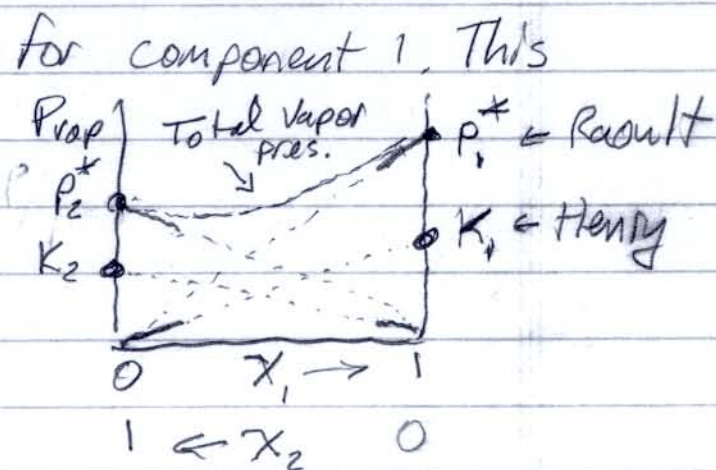
but for "perfect" solutions $K_1 = P_1^*$ so $P_1 = P_1^* x_1$



But the chance that a solution is "perfect" is very low. K_1 only = p_1^* for $X_1 \approx 1$ (Raoult's law)

As X_1 goes from $1 \rightarrow 0$, K_1 decreases or increases

When $X_1 \approx 0$, $K_1 = K_{\text{Henry}}$ leads to the graph:



Take home message: Raoult tells us the partial pressure of gas that's due to evaporating solvent as a function of solute. Henry tells us the partial pressure of gas that's due to a (volatile) solute as a function of that same solute. $K_{\text{Henry}} = \frac{P_{\text{vap}}}{X_{\text{solute}}}$ or $= \frac{P_{\text{vap}}}{[\text{solute}]} = \frac{\text{Product}}{\text{Reactant}}$

What about in between Raoult + Henry?

→ use activity, a , or activity coeff., γ , or osmotic coeff., ϕ , → all these are "corrections"

$$\mu_i = \mu_i^{\circ} + RT \ln a_i = \mu_i^{\circ} + RT \ln \gamma_i x_i = \mu_i^{\circ} + \phi_i RT \ln x_i$$

$$a_i = \gamma_i x_i \quad \phi_i - 1 = \frac{\ln \gamma_i}{\ln x_i}$$

Colligative Properties

Consider the "reaction": $(\text{liq}_A + \text{non-volatile solute}_B) \rightleftharpoons (\text{gas}_A)$

Normally $\mu_{gA} = \mu_{gA}^\circ + RT \ln\left(\frac{P_A}{P^\circ}\right)$ but for Raoult: $P_A = P^\circ x = P^\circ x_A$

so: $\mu_{gA} = \mu_{gA}^\circ + RT \ln x_A$ which must = μ_l at equilibrium

but for a pure liquid A: $\mu_{lA}^* = \mu_{gA}^*$ (note: as soon as solute B is added, this is not true; instead we have: $\mu_{lA} = \mu_{gA}^*$ since gas is still pure)

substituting: $\mu_{gA} = \mu_{lA}^* + RT \ln x_A$

this should hold true even for the chemical pot. of pure gas:

$$\mu_{gA}^* = \mu_{lA}^* + RT \ln x_A \quad \text{or} \quad \mu_{gA}^* - \mu_{lA}^* = RT \ln x_A = RT \ln(1-x_B)$$

The left side is products - reactants, i.e. $\bar{G}_g - \bar{G}_l = \Delta \bar{G}_{\text{vap}}$

$$\text{Using } \Delta \bar{G}_{\text{vap}} = \Delta \bar{H}_{\text{vap}} - T \Delta \bar{S}_{\text{vap}}: \ln(1-x_B) = \frac{\Delta \bar{H}_{\text{vap}} - T \Delta \bar{S}_{\text{vap}}}{RT} \quad \Delta \bar{S}_{\text{vap}} = \frac{\Delta \bar{H}_{\text{vap}}}{T_{\text{boil}}}$$

$$\text{So: } \ln(1-x_B) = \frac{\Delta \bar{H}_{\text{vap}}}{RT} - \frac{\Delta \bar{H}_{\text{vap}}}{RT_{\text{boil}}} = \frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{boil}}} \right)$$

$$\text{When } T \approx T_{\text{boil}} \quad \frac{1}{T} - \frac{1}{T_{\text{boil}}} = \frac{T_{\text{boil}}}{T_{\text{boil}} \cdot T} - \frac{T}{T_{\text{boil}} \cdot T} \approx \frac{T_{\text{boil}} - T}{T^2} = \frac{-\Delta T}{T_{\text{boil}}^2}$$

then, using the $\ln(1-x) = -x$ for x small trick, $-x_B = \frac{-\Delta \bar{H}_{\text{vap}} \Delta T}{R T_{\text{boil}}^2}$

$$\text{or. } \Delta T = \frac{RT_{\text{boil}}^2}{\Delta \bar{H}_{\text{vap}}} \cdot x_B$$

similarly

$$\Delta T = \frac{RT_{\text{melt}}^2}{\Delta \bar{H}_{\text{fusion}}} x_B$$

8.4

A note about mole fraction, molal and molar :

$$x_B = \frac{m_B}{M_A} = [B] \bar{V}_A \quad \text{where } M_A \text{ is kg/mol of A (solvent)}$$

mole fract.
molal
molar
and \bar{V}_A is l/mol of A

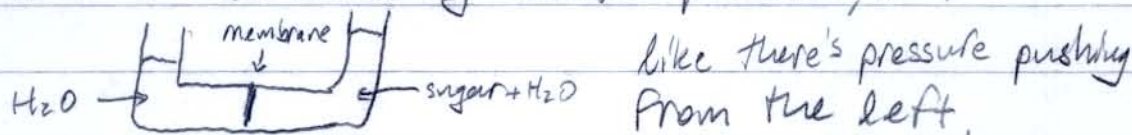
So the two previous eq can be written in terms of molal:

$$\Delta T = \underbrace{\frac{RT_{\text{boil}}^2}{\Delta H_{\text{vap}}}}_{K_b} \cdot M_A \cdot m_B \quad \text{and} \quad \Delta T = \underbrace{\frac{RT_{\text{melt}}^2}{\Delta H_{\text{fusion}}}}_{K_f} \cdot M_A \cdot m_B$$

$K_b \leftarrow 0.512 \frac{\text{K} \cdot \text{kg}}{\text{mol}}$ for H_2O
 $K_f \leftarrow 1.858 \frac{\text{K} \cdot \text{kg}}{\text{mol}}$ for H_2O

Osmosis: How do we get that ideal gas eq: $\pi V = nRT$?

First, what do we mean by "osmotic pressure", π ?



We know G changes w/ pressure: $dG = \bar{V} dP - S dT$ (closed)

and via partial derivatives: $dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$

$$\rightarrow \bar{V} = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{and since } \bar{G} = \mu_{\text{pure}} \quad \bar{V} = \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_T$$

but again by partial derivatives $d\mu = \left(\frac{\partial \mu}{\partial P}\right)_T dP + \left(\frac{\partial \mu}{\partial T}\right)_P dT$

so, at constant T , $d\mu = \left(\frac{\partial \mu}{\partial P}\right)_T dP = \bar{V} dP$

This means we can write the change in μ as:

$$\mu(P + \pi) = \mu(P) + \int_0^\pi \bar{V} dP = \mu(P) + \bar{V} \Big|_0^\pi \quad \text{for } \bar{V} \text{ const.}$$

So, we have an equation for the chemical pot. of, for example, the sugar + H₂O solution that is at a higher pressure (P+ π) than the H₂O (just P).

We can use this equation to get the "ideal gas" form

First, we remember that $\mu_{\text{sugar+H}_2\text{O}}^{\text{soln}}(P+\pi, x_{\text{sugar}}) = \mu_{\text{pure}}(P+\pi) + RT \ln x_A$

but we found that $\mu(P+\pi) = \mu(P) + \bar{V}\pi$ so we can write:

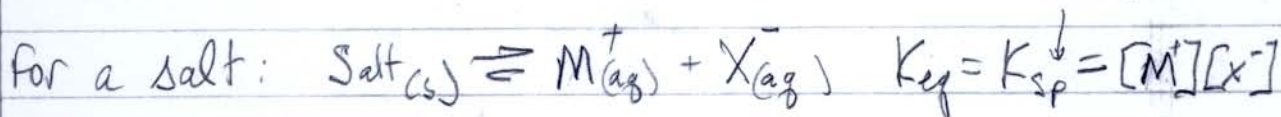
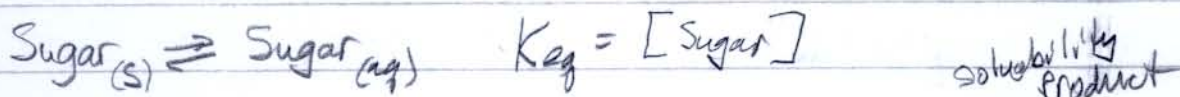
$$\mu_{\text{soln}}(P+\pi, x_B) = \mu_{\text{pure}}(P) + \bar{V}\pi + RT \ln x_A$$

at equilibrium $\mu_{\text{pure}}(P) = \mu_{\text{soln}}(P+\pi, x_B)$ so $\bar{V}\pi = -RT \ln x_A$

but $x_A = 1 - x_B$ and x_B is small, so $\ln x_A \approx -x_B \approx \frac{-N_B}{N_A}$, also $\bar{V} = \frac{V}{N_A}$

so we get: $\pi \frac{V}{N_A} = \frac{N_B}{N_A} RT$ or $\boxed{\pi V = N_B RT}$
↳ moles of solute

Solubility: how many moles of sugar can we dissolve?



to be more accurate, we should use activities not []

$$K_{sp} = a_m^+ a_x^- = \frac{\gamma_m^+ m_m^+ \gamma_x^- m_x^-}{m^{\circ+} m^{\circ-}} \quad \text{where } \gamma_{\pm} = \sqrt{\gamma_m^+ \gamma_x^-} \quad \text{and } m^{\circ} = 1 \text{ molal}$$

clearly, the moles of solute we can dissolve depends on what other things we have already dissolved. for ions:

$$\text{Ionic Strength} = I = \frac{1}{2} \sum_k z_k^2 m_k \quad \text{in which } z \text{ is charge}$$

↑
molar

Now γ_{M^+} and γ_{X^-} depend on I , e.g.:

$$\log_{10} \gamma_{M^+} = -A z_{M^+}^2 \sqrt{I}$$

= 1 for M^+

$$\text{and } A = \frac{N_A^2}{2.3026} \left(\frac{2\pi P_{\text{sol}}}{R^3 T^3} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0 \epsilon_{\text{rel}}} \right)^{3/2}$$

↑
correction for \log_{10}

where P_{sol} is the density of solvent, $\epsilon_0 + \epsilon_{\text{rel}}$ are the permittivity of vacuum and solvent (relative), respectively, and e is the electron's charge

It's not important to remember the expression for A , just note that all terms are constants, except T

recall that for $MX_{(s)} \rightleftharpoons M_{(aq)}^+ + X_{(aq)}^- \quad K_{eq} = K_{sp} = (m_{M^+})(m_{X^-})\gamma_{\pm}^2$

set $S = m_{M^+} = m_{X^-}$ so: $K_{sp} = S^2 \gamma_{\pm}^2$, but $\log_{10} \gamma_{\pm} = -A\sqrt{I}$

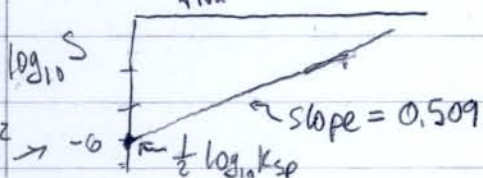
IF we had already dissolved NaCl, $\sqrt{I} = \sqrt{\frac{1}{2}(m_{Na^+} + m_{Cl^-} + 2S)}$

Now $\log_{10} K_{sp} = \log_{10} S^2 + \log_{10} \gamma_{\pm}^2 = 2 \log_{10} S + 2(-A\sqrt{I})$

or $\log_{10} S = \frac{1}{2} \log_{10} K_{sp} + A \sqrt{\frac{1}{2}(m_{Na^+} + m_{Cl^-} + 2S)}$ For $S \ll m_{Na^+}$

↑
 m_{Na^+}

we get: $\log_{10} S = \frac{1}{2} \log_{10} K_{sp} + A \sqrt{m_{Na^+}}$ $A = 0.509 \sqrt{\frac{kg}{mol}} @ 298K$
in H_2O for ions



Solubility actually increases!!