5.60 Thermodynamics & Kinetics
Spring 2008

Colligative Properties

These are properties of solutions in the **dilute** limit, where there is a solvent "A" and a solute "B" where $n_A \gg n_B$.

These properties are a direct result of $\mu_A^{mix}(\ell, T, p) < \mu_A^{pure}(\ell, T, p)$

Use two measures of concentration:

a.   Mole Fraction: $x_B = n_B/(n_A+n_B) \sim n_B/n_A$

b.   Molalility: m_B = (moles solute)/(kg solvent) = $n_B/(n_A M_A)$
     Where M_A is the mass in kg of one mole of solvent.

There are **FOUR Colligative Properties**:

1.   Vapor pressure lowering:
$$\Delta p_A = p_A - p_A^* = -x_B p_A^*$$

2.   Boiling point elevation:
$$\Delta T_b = T_b - T_b^* = K_b m_B$$

$$K_b = \frac{M_A R \left(T_b^*\right)^2}{\Delta H_{vap}}$$

3.   Freezing point depression:
$$\Delta T_f = T_f - T_f^* = -K_f m_B$$

$$K_f = \frac{M_A R \left(T_f^*\right)^2}{\Delta H_f}$$

4.   Osmotic pressure:
$$\pi = RT\tilde{c}$$

where $\tilde{c} = \dfrac{n_B}{V}$ is concentration of solute

Let's go through these one at a time:

1.   <u>Vapor pressure lowering</u>: This is just Raoult's Law.

$$p_A = x_A p_A^* = (1 - x_B)p_A^* \qquad \text{So} \qquad \Delta p_A = p_A - p_A^* = -x_B p_A^* \ (<0)$$

2.   <u>Boiling point elevation:</u>

Let's derive this. Start with $\qquad \mu_A(\ell, T, p) = \mu_A(g, T, p)$

So, $\qquad\qquad\qquad\qquad \mu_A^*(\ell, T, p) + RT \ln x_A = \mu_A(g, T, p)$

And $\qquad\qquad\qquad\qquad \ln x_A = \dfrac{1}{RT}[\mu_A(g, T, p) - \mu_A^*(\ell, T, p)] = \dfrac{\Delta \overline{G}_{vap}}{RT}$

But $\ln x_A = \ln(1 - x_B) \sim -x_B = -n_B/(n_A + n_B) \sim -n_B/n_A = -(Mn_B)/(Mn_A)$

Where M is the total mass of A,

So, $\ln x_A \sim m_B M_A,$ where M_A is the molar mass of A.

Putting it all together then, $\qquad\qquad\qquad m_B = \dfrac{-\Delta \overline{G}_{vap}}{M_A RT}$

But we need ΔT in there!

$$\ldots \quad \left(\frac{\partial m_B}{\partial T}\right)_p = \frac{-1}{M_A R}\left(\frac{\partial\left(\Delta \overline{G}_{vap}/T\right)}{\partial T}\right)_p = \frac{-\Delta \overline{H}_{vap}}{M_A RT^2}$$

which gives us $\delta T = \dfrac{M_A RT^2}{\Delta \overline{H}_{vap}} \delta m_B$

If $\delta m_B = m_B - 0$ (mixed – pure) and m_B is very small

Then
$$\boxed{\delta T = T_b - T_b^* = \frac{M_A R(T_b^*)^2}{\Delta \overline{H}_{vap}} m_B = K_b m_B}$$

3. Freezing point depression:

Same arguments as above, replacing

ΔG_{vap} with $-\Delta G_f$
ΔH_{vap} with $-\Delta H_f$
T_b with T_f
K_b with K_f

4. Osmotic Pressure:
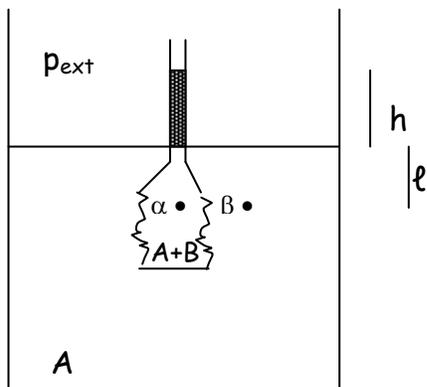
The pressures at points:

β: $p = p_{ext} + \ell \rho g$

α: $p + \pi = p_{ext} + \ell \rho g + h \rho g$

At equilibrium: $\mu_A(\ell, p + \pi, T) = \mu_A^*(\ell, p, T)$

Using Raoult's Law: $RT \ln x_A + \mu_A^*(\ell, p + \pi, T) - \mu_A^*(\ell, p, T) = 0$

At constant T: $dG = Vdp$, or $d\mu_A^* = \overline{V}_A^* dp$

Integrating...
$$\mu_A^*(\ell, p + \pi, T) - \mu_A^*(\ell, p, T) = \int_p^{p+\pi} \overline{V_A}^* dp = \overline{V_A}^* \pi$$

(this assumed an incompressible liquid, where volume does not depend on p)

So then $RT \ln x_A + \overline{V_A}^* \pi = 0$

Again using $\ln x_A \sim -n_B/n_A$

Then $RT(-n_B/n_A) + (V_A/n_A)\pi = 0$

But $V_A \sim V_A + V_B = V$ $\qquad (V_B \ll V_A)$

So finally, $\boxed{\pi V = RTn_B}$

This is the Van't Hoff Equation. It looks like the ideal gas law!

If we replace $\tilde{c} = n_B/V$ in the Van't Hoff Eq., then we get the osmotic pressure relation:

$$\boxed{\pi = RT\tilde{c}}$$