Noteworthy

- A single homework page was posted-it's due on Tues-2/17-5pm. It deals with dropping an ice cube into water.
- The next major assignment will be given on Tues (2/17)
- The second exam is in two weeks (2/26)

Yet more on the second law

- Processes are spontaneous when $\triangle G<0$; are static when $\triangle G=0$ and nonspontaneous(or spontaneous in the opposite direction when $\triangle G>0$.

- Given $\triangle G= \triangle H- T\triangle S$, the conditions wherein a process is spontaneous can be readily identified
  - $\triangle H<0$ and $\triangle S>0$
  - $\triangle H>0$ and $\triangle S>0$ with $|T\triangle S|>\Delta H$
  - $\triangle H<0$ and $\triangle S<0$ with $|T\triangle S|<|\Delta H|$

- Note that the last two conditions above will have temperature dependence. Which is spontaneous at higher temperatures and which at lower temperatures (given that $\triangle H$ and $\triangle S$ are largely temperature independent).

- The third condition involves spontaneity wherein the entropy of the system is decreasing-how is this consistent with our understanding of the second law?

- "The energy of the universe is constant, the entropy increases toward a maximum." R.J.E. Clausius

Some dipole moments

- Acetone-$(CH_3)_2CO$ 2.7
- NH_3 1.5
- Benzene   0.0
- Carbon dioxide   0.0
- butyl amine $C_4H_9NH_2$ 1.40
- HCl 1.03 HBr 0.78 HI 0.38
- SO_2 1.6
- H_2O 1.84 H_2S 1.10

Why things dissolve

- The dissolution process occurs when the solvent-solute interactions(the solvation energy) are sufficient to overcome the solute-solute and solvent-solvent interactions.
- **Some thoughts**
  - In the cases where the interactions are particularly weak(van der Waals only) for both materials, it is somewhat of a misnomer to use the word "overcome"
  - In most solutions (exc those of miscible materials), the solvent greatly overnumbers the solute.
  - Perspective on the process can vary.
    - The solvent "surrounds" the solute
    - The solute "forces" its way between solvent molecules
- The dissolution of an ionic material in water can be viewed to a first approximation as the hydration energies of the ions being greater than the lattice energy of the salt. This is another application of Hess' Law.
- $Na^+(g) \Rightarrow Na^+(aq)$ hydration energy of Na+
- $Cl^-(g) \Rightarrow Cl^-(aq)$ hydration energy of Cl-
- $NaCl(s) \Rightarrow Na^+(g) + Cl^-(g)$ Uo Lattice energy
- Summing these yields
- $NaCl(s) \Rightarrow Na^+(aq) + Cl^-(aq)$ heat of solution

Some data

Heats of solution(KJ/mole))

- NaCl +4.94
- BaO -148
- NaOH –41.6
- $BaSO_4$ +23.3
- AgCl +15.75
- $PbBr_2$ +41.8

Entropies of solution are generally positive (text Table 11.2 p 432) and often sufficient for a material with a positive heat of solution to dissolve.

Aqueous Solubilities

- Only materials capable of ionization and/or hydrogen bonding exhibit significant aqueous solubility
- **The rule of four**: A hydrogen bonding group will lead to the dissolving of compounds with up to 4 carbons
    - methanol(CH_3OH),ethanol (C_2H_5OH) ,propanol (C_3H_7OH) ,butanol (C_4H_9OH) are all miscible with water
    - pentanol ($C_5H_{11}OH$) is slightly soluble
- Another example:
    - butanol (C_4H_9OH) is miscible
    - diethyl ether ($C_2H_5OC_2H_5$) is insoluble

The properties of solutions

- In what ways does a solution of water differ in its physical properties from the "neat" liquid.
  - vapor pressures are depressed
  - freezing points are depressed
  - boiling points are elevated
  - there's this thing called osmosis
- An extremely critical issue is to recall that ionic materials dissociate upon dissolution in water
- We are going to address these areas by first presenting the issues and equations and then returning (next week) to work thru exemplary problems

Vapor Pressure Depression

- There are two types of solutes:
  - nonvolatile-negligible vapor pressure (NaCl)
  - volatile-significant vapor pressure C_2H_5OH
- How could you demonstrate, at least in principle, that the vapor pressure of solution is less than that of the pure solvent?
- The vapor pressure depression follows is described in a manner that considers only the proportions in the mixture, not the identity of the solute. A property dependent only on proportions is termed "colligative."
- Why does this happen?

Raoult's Law-nonvolatile solute

- P^o=vapor pressure of the pure solvent
- P_{mix}=observed vapor pressure for the mixture
- X_{solv}=mole fraction of the solvent in the mixture
- $P_{mix}= X_{solv} * P^o$

- Note that the identity of the solute is not an issue, just the amount which is present. This is typical of a colligative property

Raoult's Law Plot-a plot of P vs mole fraction is linear
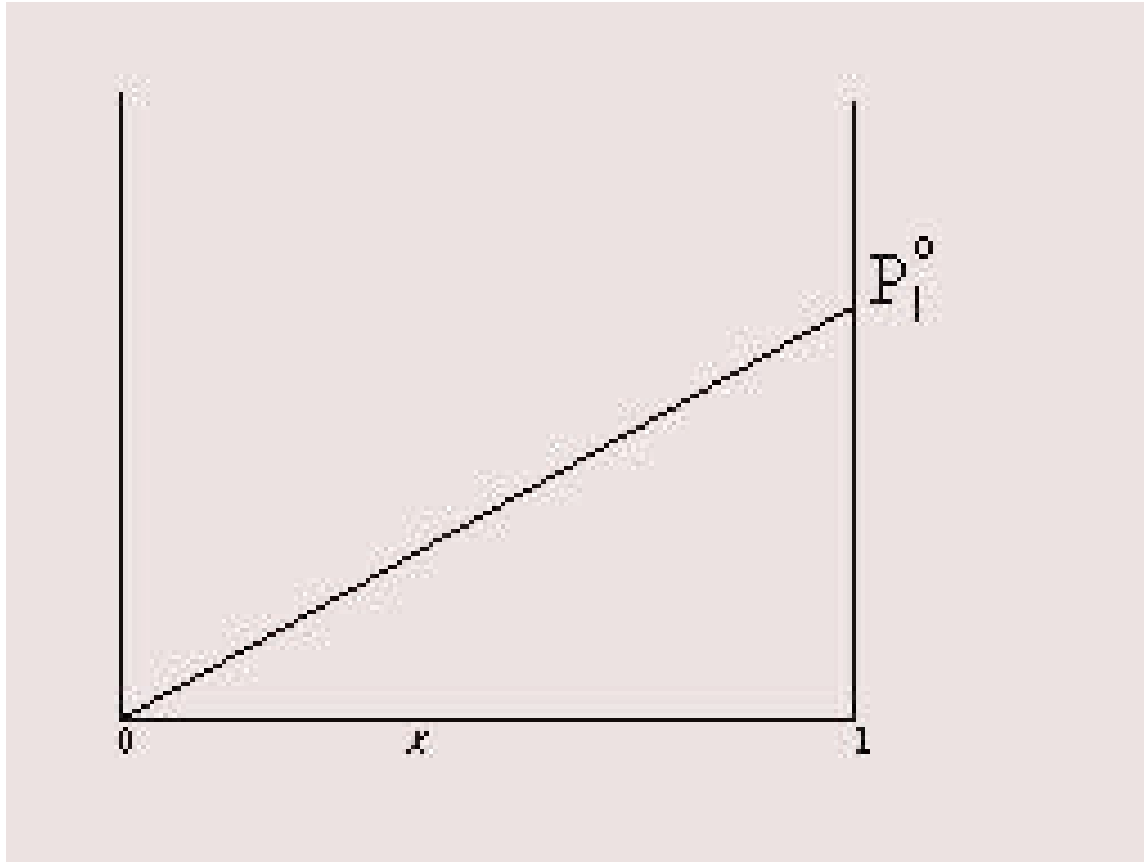
Raoult's Law=two volatile compoents

- A mixture containing two volatile components, A and B can be described by the following equations

- $P_A = X_A * P_A^o$ and $P_B = X_B * P_B^o$

- $P_T = P_A + P_B$

- These systems are made much more interesting by the fact that the vapor contains both A and B, unlike the previous one, which contained only solvent in the vapor phase. This results in a second set of mole fractions (remember your favorite gas law-Dalton's Law of Partial Pressures)-$X_{(vap)}$-for the vapor phase

- $X_{A(vap)} = P_A / P_T$ and $X_{B(vap)} = P_B / P_T$

- In comparing the solution and gas mole fractions, what changes would you expect to see?

- Is it possible for the mole fraction in the solution to equal the mole fraction in the vapor?

- Mixtures of two volatile materials can be described as shown below
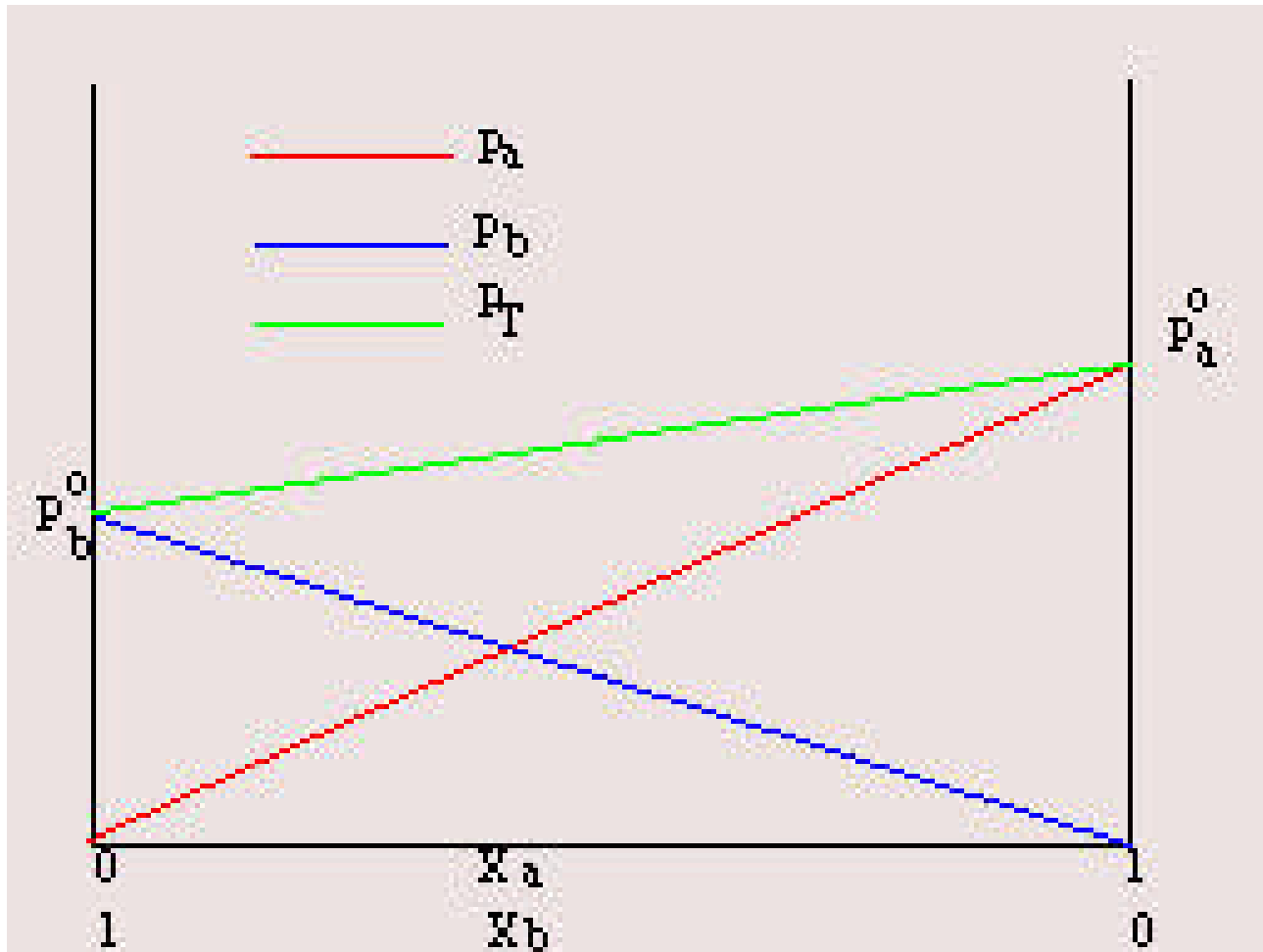
Boiling point elevation

- If the vapor pressure is depressed, the boiling temperature should increase. Why?

- Why should the freezing temperature decrease?

- Although a colligative property should use X as the measure, in this area molality(m)=moles solute/kg solvent is the dimension of choice. Why is this valid?

- It can be seen that since $X_A = n_A/n_T$, if the solution is sufficiently dilute, n_T is roughly equal to $n_{solvent}$.

- Further, since n is directly proportional to mass, molality is directly proportional to X_A.

- Molality is only a useful quantity for relatively dilute solutions. For example, a kg of water contains 55 moles. a 2m solution(kind of at the limit) in water has 2 moles of solute per 55moles of water. The "molal" X= 2/55=0.0364 and the true X is 2/57=.0351. The difference is .0013 or roughly 4%. For a 1 m solution, the difference would be about .6%

- For solvents other than water, with higher gmws, the difference is greater. However, since the constants used are experimentally determined, there is a built-in correction and no real errors are introduced.

Solution Phase Diagram

- The blue lines are for the pure material, the red are for a solution
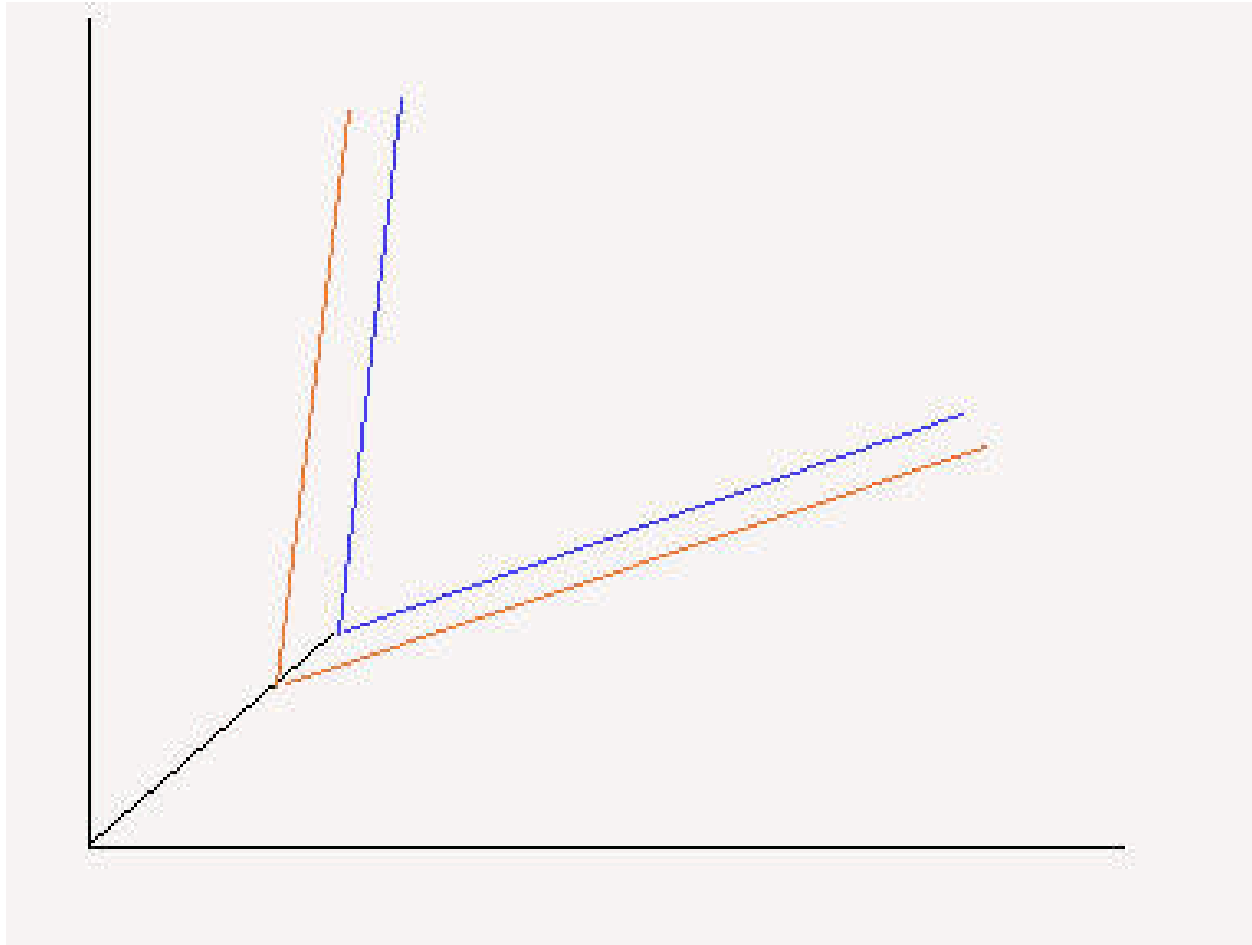
The Equations

- Unlike Raoult's Laws, in this area, we calculate the change in the freezing and boiling points.
- $\Delta T_b = K_b * m$
- $\Delta T_f = K_f * m$
- K_b and K_f are the molal boiling and freezing constants for a given solvent

Osmosis

- What is it?
- Flow of water through a semipermeable membrane from a region of lower to higher solute concentration or
- Flow of water through a semipermeable membrane from a region of higher to lower solvent concentration
- Why should this happen
- What is osmotic pressure and how is it measured?
- Π(this is cap pi)=MRT