Things possibly worth noting

- Two corrections to last Thursday's notes:
  - $P_A = X_A * P_A^o$ and $P_B = X_B * P_b^o$
  - 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
- Homework and quiz scores should be posted by tomorrow afternoon, Thurs at the latest.
- If you need a formula or can't find something on your periodic chart during a quiz -please ask-such information is cheerfully provided.
- New homework assignment posted-due 3/2
- I may not be on campus tomorrow-which I'm sure pretty much ruins everyone's plans. Will be reachable via email.
- Who says science isn't relevant-packing M&Ms

  http://www.sciencenews.org/20040214/fob7.asp

Calculating Entropy

- Recall that $\Delta S = q_{rev}/T$
- If one has a reversible process for which the enthalpy and temperature are known then $\Delta S = \Delta H/T$
- Phase changes fit that requirement. Thus, the entropy of melting is simply $\Delta H_f/T_f$
- Web Page 66 presents this (and other) problems involving the second law.

Colligative Properties-General Properties

- How` solutions differ from pure materials is quite predictable and within your experience. Thus, an incorrectly addressed problem will lead to a result which you should recognize as **unreasonable and unacceptable**.
- What is known:
  - **Like dissolves like** (and a few terms like **ebullition**)
  - Vapor pressures go down: $P_A = X_A * P_A^o$
  - Mixtures of two volatile: the components can be treated independently and Dalton's Law applied to the vapor
    - There are two different mole fractions: solution and vapor
  - Boiling points increase: freezing points decrease
    - $\Delta T_b = K_b * m$
    - $\Delta T_f = K_f * m$
  - What about the sublimation point?
  - Phase diagram is readily redrawn to illustrate the differences
  - Osmosis: Π(this is cap pi)=MRT
  - The dissociation of ionic compounds must be considered when solving these problems.
  - There are two types of solution:
    - **Ideal-**follow Raoult's Law precisely
    - **Real**=deviate from Raoult's Law (more about these later)

A note about concentrations

- Proper analysis of colligative properties problems requires the identification and calculation of the appropriate concentration term ($\underline{\mathrm{M}}$,X, m). This may require consideration of solute dissociation.
- An error in the above will lead to a result which is computationally correct but **totally invalid**
- Appropriate points will always be awarded for totally invalid answers.

Raoult’s Law-nonvolatile solute

- Issues:
  - $P^o_{solvent}$,$X_{solvent}$,$P_{solution;}$
  - $P_{solution} = P^o_{solvent} * X_{solvent}$
  - How many different ways can the composition of such solution be described?
  - Dissociating solutes have an effect based upon the number of “particles” resulting from the ionization. You are expected to recognize ionic materials and treat them appropriately.

Raoult's Law-nonvolatile solute

- Basic Problem:
  - A solvent has P^{o} =312torr. A solution contains 12.0moles of solvent and 2.5 moles of a nonvolatile solute. What is the vapor pressure?
- Variations
  - Give P, P^{o} and one of the moles
  - Give both ns and P
  - Give masses and formulas (names) instead of moles
  - Regardless of the data, everything runs through the following
    - $P_{solution} = P^{o}_{solvent} * X_{solvent}$
    - $X = n/n_T$
    - n=mass/gfw
  - It is a very useful mental exercise to see how many paths there are.There was yet another article that thinking minimizes and may prevent Alzheimer's. Thinking is a good idea.
  - If the solute dissociates, its n must be multiplied by the total number of ions produced :NaCl(x2), calcium nitrate (x3). Significant increases in colligative effects when compared to a nondissociating model are strong evidence for the dissociation of a solute.

Raoult’s Law-two volatile

The real difference is that you now have to calculate the total pressure and the vapor mole fractions using Dalton’s Law

Total data set of a mixture A and B

For A: n_A, X_A(sol),$P^o{}_A$,P_A,X_A(vap),(m_A?)

For B: n_B, X_B(sol),$P^o{}_B$,P_B,X_B(vap),(m_B?)

Basic Problem, given both ns and both P^os-solve for everything else.

Provide a complete analysis given the following:

n_A=0.250, $P^o{}_A$=210torr, n_B=0.310, $P^o{}_B$=0.500torr

Variations-too numerous to list

Is ion dissociation an issue in this area?

Critical thought #1-Given P_T,X_A and P_B, can the system be fully defined? If so, what is the path. If not, what else would be needed.

Critical thought #2: Given $P_A{}^o$, n_B and $P_{T,}$, can the system be fully defined? If so, what is the path. If not, what else would be needed.

Freezing and boiling point changes

- Here the concentration term is molality,*m*, moles solute/kg solvent
- The constants K_b and K_f as well as the normal melting and boiling points are needed.
- You are calculating the change. Be certain to add that to the BP and subtract it from the FP.
- Ion dissociation is important.
- What are the boiling and freezing point of a solution prepared by dissolving 26.1 g of potassium nitrate in 100mL of water?

Molecular weights from FP depression

- An important practical application of FP depression is the determination of molecular weights:
  - $\Delta T_f = K_f * \boldsymbol{m}$
  - $\boldsymbol{m}$=moles/kg
  - moles=mass/gmw
- In a typical experiment, the solute and solvent are weighed and the FP depression determined. The path then goes $\Delta T_f \Rightarrow m \Rightarrow$moles=>gmw
- A solution of 9.54 grams of solute in 90.0 grams of a solvent(**K_f=8.57;T_f=55.9°C**) is found to have a freezing point of 50.6°C. What is the solute's MW?

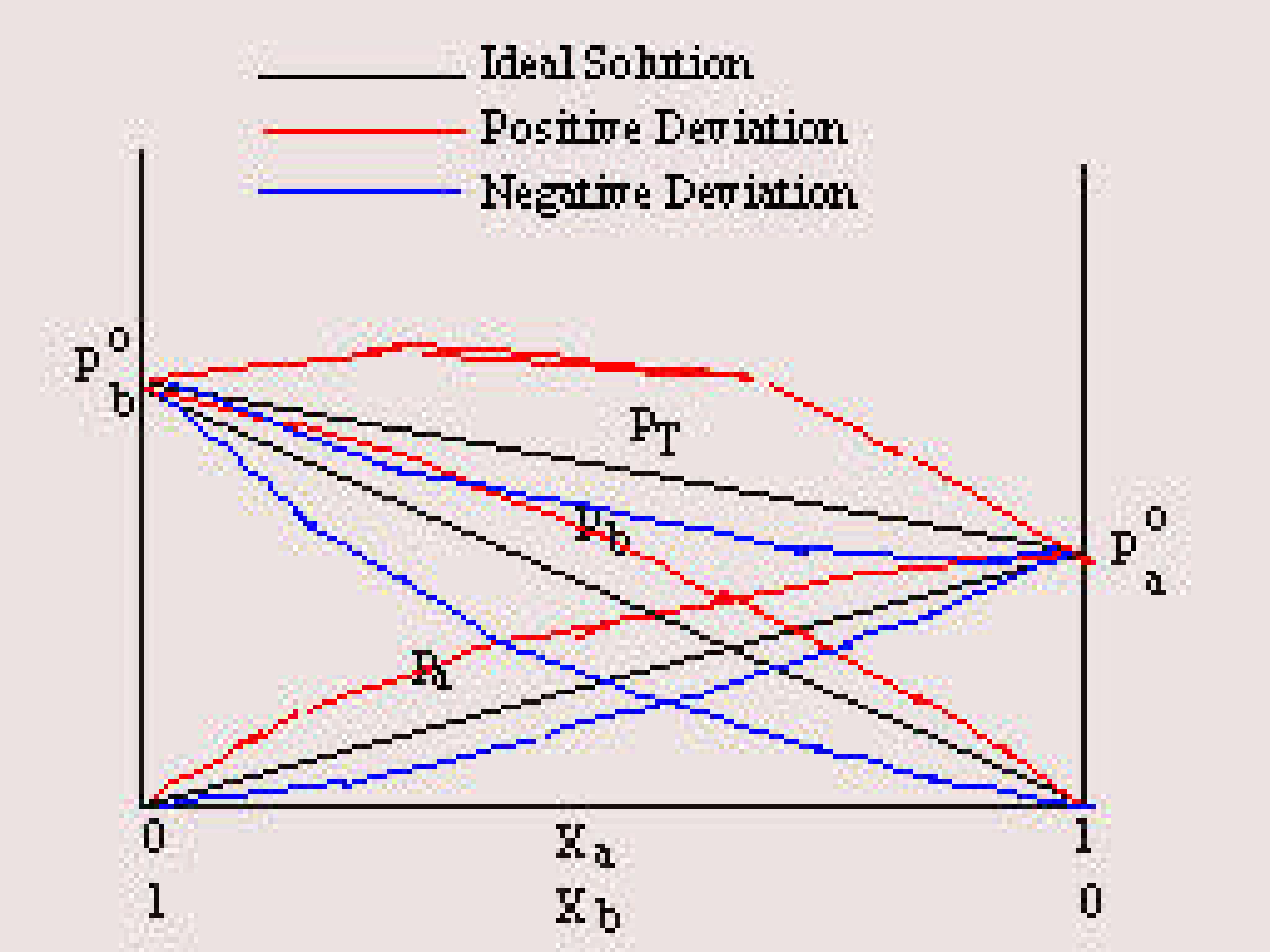
Osmosis

- Concentration measure is molarity of solute
- T must be in K
- R is the gas constant
- Dissociation is very important
- If there is solute on both sides of the membrane, the difference in the concentrations is used.
- What is the osmotic pressure for a solution prepared by dissolving 15.3g of methanol (CH_3OH) to a total volume of 200mL?

Real Solutions-Raoult’s Law

- There are positive and negative deviations from Raoult’s Law
- Strict adherence to Raoult’s Law assumes that the presence of the solute does not alter the energy needed to escape from the surface. The effect is purely statistical. In reality, two other scenarios are likely:
  - The presence of the solute makes escape easier leading to an observed vapor pressure greater than Raoult’s Law. This is termed a positive deviation
  - The presence of the solute makes escape more difficult leading to a vapor pressure less than Raoult’s Law. This is a negative deviation
  - What general type of solvent/solute pairs (based upon type of interactions) do you think are most likely to be ideal?

Deviations from Raoult’s Law



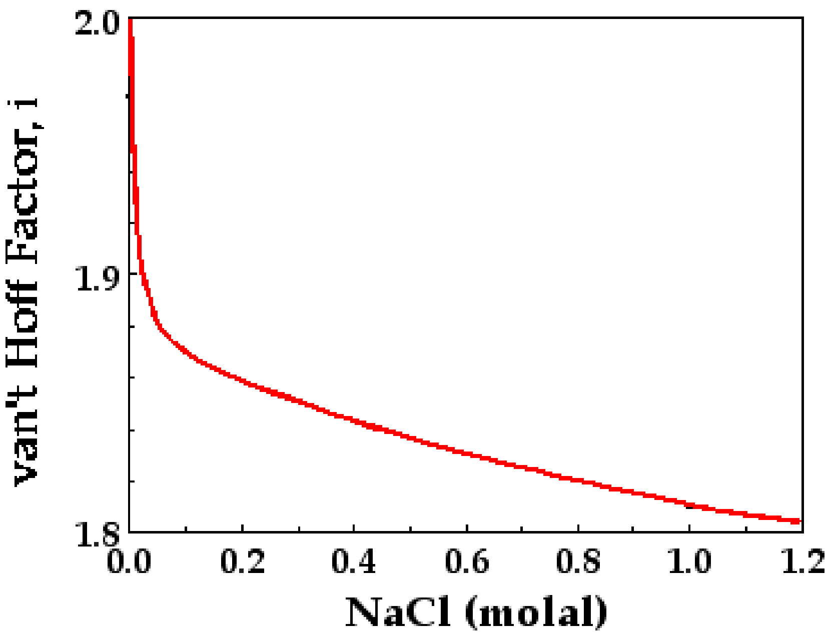
Real Solutions-van’t Hoff Factors

- The basic treatment of dissociating solutes treats the resultant ions as if they do not interact. This is true of dilute solutions.
- However, as the ion concentrations increase, the ions interact with each other. This has the effect of lowering the effective concentration of the solute. One way to look at is to consider the transient formation of ion pairs. That is, a sodium ion temporary pairs with a chloride ion to make “NaCl”.
- Evidence for this can be seen in the fact that at sufficiently high concentrations, the ion concentration as shown by colligative property measurements is less than that predicted by complete dissociation. There is an adjustment “constant” called the van’t Hoff factor(*i*) that can be used to account for this. To get the effective concentration, you multiply the initial concentration ($n,\underline{M},m$) by the van’t Hoff factor.
- Actually using van’t Hoff factors in calculations is a bit awkward as they are both solute and concentration dependent. That is, a factor that is valid for NaCl at 1.00M will not be valid for KCl at 1.00M or for NaCl at 0.20M.

i vs [NaCl]

At "infinite dilution"

$$i_{\mathrm{NaCl}} = 2$$



i **is a measure of the amount of dissociation**

… so why does it vary with concentration?

Of Things to Come

- In evaluating the true “impact” of any change, there are two universal factors-how large is it and how fast does it occur. This is true whether one is speaking of global warming, changes in interest rates or chemical reactions.
- How the issues of degree and speed are applied to chemical change are the central issues for much of the remainder of the year.
- The study of the extent to which a chemical reaction occurs is called equilibrium.
- The study of how quickly (or slowly) a reaction occurs is called kinetics
- Not surprisingly, the two areas are closely related.

Kinetics

- You are well aware that not all chemical changes occur at the same rate.
- Kinetics is an experimental area. Little if any information about the kinetics of a reaction can be gleaned from the balanced equation.
- Some parameters
  - Recall that many reactions can occur in either direction. In kinetics, reactant and products are strictly defined: the reaction is always written in the direction in which it is occurring.
  - reaction rates are defined as $\Delta[\ ]/\Delta t$ (should actually be a derivative) with dimensions $\underline{M}\text{sec}^{-1}$ but pressures are sometimes used
  - reaction rates are always positive by convention
  - For the reaction 2A + B => 3C
    - if we define the rate as: rate = $\Delta[C]/\Delta t$
    - then rate= $-3*\Delta[B]/\Delta t$ or
    - rate= $-2\Delta[A]/\Delta t$
  - the – sign is needed to produce a positive number since the concentrations of A and B will be decreasing with time, the coefficient is required due to the stoichiometry. Everytime a B reacts, 3 Cs are produced, thus the rate for C is 3x that of B.

The key to everything-the rate law

- The defining kinetic property of a chemical reaction is the rate law: a statement of what chemical species affect the reaction rate and how fast the reaction is.
- For reasons that will be presented later, not all reactants necessarily affect the rate of a reaction. This is a major reason why experiments are critical in kinetics.
- For a reaction 2A + B =>3C, one begins by writing the "general rate law" $\text{rate}=k[A]^a[B]^b$ where k is the rate constant(more on that later) and a,b are the reaction orders which show how the rate is affected by the chemical species. The most common values for orders are 0 and 1, but other values, including fractions and negatives are known.
- The process of determining whether a reactant affects the rate is very straightforward. If the concentration of the species is changed, does the rate change?

Experimental Design-initial rates and integral changes

- It seems logical (with one very rare exception) that a reaction will slow down as the reagents are consumed and that the rate is certainly not likely to be linear.
- Given the above, how is a rate actually measured?
  - The tangent to the line of [] vs t will give d[]/dt
  - If the reaction is studied at the start and over a period of time when [] vs t is relatively linear, the rate can be approximated with fairly good precision as $([\ ]_o - [\ ]_t)/t$. This is called an initial rate study and is a common approach. There are a number of variations on it.
- Regardless of the method chosen, measuring rates is relatively simple
- Likewise getting a reaction order is straightforward. You do two rate measurements where the reaction systems vary only due to a change in a single concentration. If the experiment is designed for easy interpretation, then the data analysis requires little math.
- Assume you wanted the order in A, You do first rate measurement. The you double the concentration of A while leaving everything ealse the same.
  - no change in the rate (Run 1 vs Run 2)-rate doesn’t depend on A=>zero order
  - rate doubles-first order
  - rate quadruples-second order

- This operation is repeated until orders for all of the reactants have been obtained.
- rate=k[A][B]^2
- the rate constant can now be determined by taking any one of the runs => k=rate/([A][B]^2)
- k
  - the value of k gives you the actual reaction rate.
  - k has variable dimensions-remember that the rate is always M sec^{-1}, but the concentration terms will vary with the reaction system. The dimensions of k are set by the overall reaction order or the sum of the individual orders. For the example above, that’s 3.
  - What would the dimensions of k be in that case?