Today's News

- Database reset and new homework posted
- Lab –things went very smoothly last week. That's much appreciated
- You should continue reviewing nomenclature as needed
- Tutoring is available now-times and place on course webpage
- The pace of this class is going to increase. You must stay on top of things
- Who says science isn't relevant-packing M&Ms
  - http://www.sciencenews.org/20040214/fob7.asp
- In covering this next set of topics, we will go thru the entire area, then review with problem examples.
- Exam 1 is Feb 21 and will cover material thru Feb 14.

Sample Calculations

- How many KJ of heat are required to melt 35.6g of ice if its molar heat of fusion is 6.01KJ/mol.
  - 35.6g/18g/mole=1.97moles
  - 1.97moles*6.01KJ/mole=11.9KJ
- How is the above different from the question: What is q for the melting of 35.6g of ice?
  - Prob 1 does not require sign considerations, Prob 2 does
- A cube of ice with a mass of 14.5g is dropped into 120g of water(l) at 87°. What is the resulting temperature?
  - 14.5g/18g/mole=.806moles ; .806moles*6.01KJ/mole=4.84KJ
    - Heat required to melt the ice
  - 120g*4.184J/(g*deg)*87deg=43.7KJ
    - Heat available in liquid as it cools to 0°
  - Ice will melt-requiring 4.84KJ and lowering the liq temp to ~77.4°
    - ΔT=-4840/(4.184*120)=-9.6°
  - Prob is now a mixture of 14.5g of water at 0° and 120g of water at 77.4°. You should know how to do this from Chem 112

Like dissolves like

- Any mixture which is homogeneous at the microscopic level is a solution. These are by no means limited to the traditional "dissolve a solid in a liquid" scenario. What is a colloid?
- How do you differentiate a colloidal suspension and a true solution?
- Several aspects of solutions are well known
  - not all combinations form solutions (water and gasoline don't mix)
  - some combinations mix in all proportions-such combinations are termed "miscible". Thus, two which don't mix are termed "immiscible"
  - some combinations have limits (sugar and water). When that limit is reached the solution is said to be **saturated**. How is it recognized?
  - temperature has an effect on the solubility (you can dissolve much more sugar in hot coffee than ice tea)
  - We use words like "solvent" and "solute(s)" to identify the components due to either
    - relative amounts, or
    - logic (can't accept the idea of a liquid dissolving in a solid)

The mixing process

- What's involved, qualitatively, in producing a homogeneous mixture from two pure substances?
- The enthalpy for the process is called the heat of solution $\Delta H_{solution}$ (KJ/mole)
- If you're dissolving a solute at fairly high concentration, the heat involved is not linear vs amount added. That is, the heat for the first gram dissolving will be different than that for the second-sounds like it violates the first law

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- Using the terms solute and solid-how does one explain the properties described earlier?
- Why wouldn't two substances mix?
- Why would there be limits?
- Why would temperature matter (and why would the behavior not be constant-some materials have decreasing solubility with increasing temperature)?
- Do the solubility rules seem to fit into this picture?You need to review these (p 143-144)

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 greate r 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 and often sufficient for a material with a positive heat of solution to dissolve.

Describing the mixture quantitatively-concentration

- There are numerous ways of describing a mixture. You are already familiar with the more common ones: molarity, mole fraction and % by mass. The fourth shown-molality will be discussed shortly.
- Molarity is the most common, but suffers from being temperature dependent. How critical is that issue?
- at 22^{o}C d_{H2O}=0.99780. At 50^{o}C d_{H2O}=.98807, a change of slightly less than 1%. If one realizes that the actual temperature difference you're likely to encounter in a working lab environment is much less than this(probably only a few degrees), it does not seems likely that a significant error will be introduced.

Relating Concentration Measures

- It is important to be able to convert between the three common measures of concentration
- It is also important to recognize that this is not always possible
- In describing a mixture, what sorts of data are available?
- Moles, masses,volumes,densities (of solute,solvent, total solution)
- To calculate a molarity , what datasets will work?
- To calculate mass %?
- To calculate mole fraction?
- If you are given only the molarity , what else is needed to calculate mass%? Mole fraction?
- Given only mass%-to obtain molarity and mole fraction
- Given only mole fraction-to obtain mass% and mole fraction
- Never forget that nomenclature is always lurking in the background here.

Describing Paths

- A 0.25M aqueous solution of calcium hydroxide has a density of 1.095g/mL (I made that up). Can you determine its mass % composition and the mole fractions. If so, present the solution path. If not, what is missing?
- A mixture of methanol (CH_4O) and ethanol (C_2H_6O) is 17.5% methanol by mass. Can you determine its molarity and the mole fractions. If so, present the solution path. If not, what is missing?
- When 1.25g of sodium nitrate are added to 27.3mL of water, the resultant volume is 27.7mL. Present paths to all of the concentration measures that can be determined.

Aqueous Solubilities

- Only materials capable of ionization and/or hydrogen bonding exhibit significant aqueous solubility.There is an exception to this for small, highly polar molecules.
- **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 to work thru exemplary problems
- The appropriate concentration measure is critical to the proper analysis of a problem.

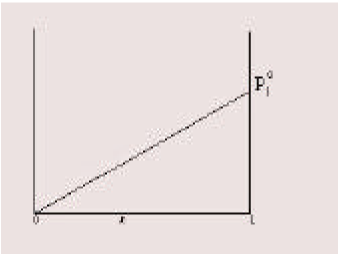
Vapor Pressure Depression

- 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

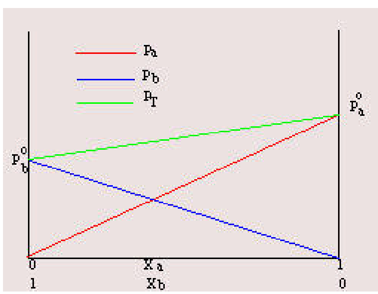
Raoult's Law Plot-a plot of P vs mole fraction is linear



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

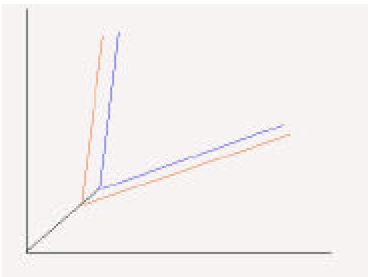


Boiling point elevation

- If the vapor pressure is depressed, the boiling temperature should increase. Why?
- Why should the freezing temperature decrease?
- Although a colligativeproperty 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 2 *m* 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 0.6% These values are not exact, why?
- 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 higher to lower water concentration).
- Why should this happen(simple model)
- What is osmotic pressure and how is it measured?
- Π(this is cap pi)=MRT

Colligative Properties-General Considerations

- 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 (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?(K_f=1.86deg/molal, K_b=.51deg/molal)

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?

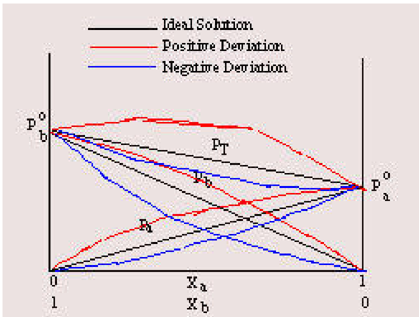
Osmosis

- 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 bycolligative 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,<u>M</u>,*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]