Today's Words of ……..

- Exam has gone to press. 4 pages 14 questions/problems. Only 3 problems require calculations -worth about 30% of the test.
- Bring your calculator, periodic table and a straight edge might be useful in case there are any diagrams.
- Try thinking of 14 questions you would ask if you were writing the exam. Remember that there will be nomenclature and definitions.
- Lab this week-on time and prepared tardiness at this point will not be tolerated.
- HW database reset and new HW assignment posted. Due Thursday of next week.

A couple of comments about problem solving

- Never expect that you will immediately see the path to the solution. If you do-great. If not-no biggie
- Avoid "rush to judgment" which means be certain to read the question carefully and make sure you complete it. "Little things" like K in gases can cause great difficulty.
- Remember that all needed equations will be provided
- It is always more useful to ask
  - "What can be done with the data provided?"
    - than
  - "How the heck am I supposed to solve this?"

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 ΔT_f =>$\boldsymbol{m}$=>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 ºC**) is found to have a freezing point of 50.6 ºC. What is the solute's MW?

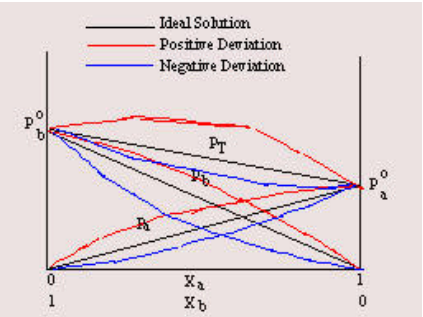
Osmosis

- 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



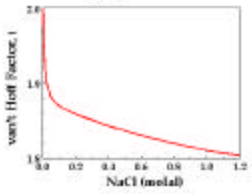
Real Solutions-van't Hoff Factors

- 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,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"

$i_{NaCl} = 2$



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

... so why does it vary with concentration?

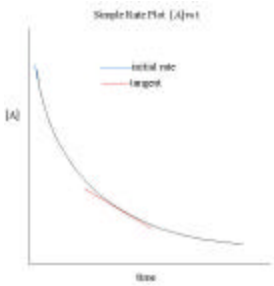
Of Things to Come

- 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 points 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

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 $M sec^{-1}$. However, the time dimension varies a little(hours, years) and in gas systems, as usual, pressures are sometimes used
- Reaction rates are always positive by convention. However, the rate of change for a given compound can be positive or negative.
- 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= $-3/2\Delta[A]/\Delta t$
- 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. Every time a B reacts, 3 Cs are produced, thus the rate for C is 3x that of B.

Following a reaction



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" 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 with 2 occasionally appearing. 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 $([\ ]_o-[\ ]_f)/t$. This is called an initial rate study and is a common approach.
  - Regardless of the method chosen, measuring rates is relatively simple in principle, collect [ ] vs t data.
- To determine a reaction order, one does two rate measurements where the reaction systems vary due to a change in a single concentration. Thus, any rate change can be ascribed to the species whose concentration was changed. If the experiment is designed for easy interpretation, then the data analysis requires little math, most of it mental.
- Assume you wanted the order in A, You do a first rate measurement. The you double the concentration of A while leaving everything else the same.
  - $Rate2/Rate1=([A]_2/[A]_1)^a$
  - no change in the rate (Run 1 vs Run 2)-rate doesn't depend on A=>zero order $Rate2/Rate1=1=(2)^0$
  - rate doubles-first order $Rate2/Rate1=2=(2)^1$
  - rate quadruples-second order $Rate2/Rate1=4=(2)^2$

- This operation is repeated until orders for all of the reactants have been obtained.
- Assume the study yielded the rate law: $rate=k[A][B]^2$
- 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?
- dimension of k and overall order-if the overall order is n then the dimensions of k are $M^{-(n-1)}sec^{-1}$

Using the Rate Law

- Assuming that the rate law and constant have been determined (or provided), what can be done with that information?
- Relative rates
- Determination of rates for different reaction mixtures

Integrated Rate Laws

- The rate should actually be d[A]/dt
- For a 1st order reaction -d[A]/dt=k[A]
- If this equation is rearranged to the form
  - 1) d[A]/[A]= -kdt
  - and then integrated, you get
  - 2) $\ln([A]_t/[A]_o$= -kt
  - 3) ln[A]t=-kt+$\ln[A]_o$
- The key meaning of this is that a plot of ln[A] vs t will give a straightline whose slope = -k (p.540)
- Integrated rate laws are known for all the possible reaction orders, but first order reactions are of particular interest.
- If you examine equation 2) above, you should see that first order processes lend themselves to considerable analysis if only two things are known: the rate constant and the concentration at any time.

Half-lives of 1st order reactions

- $\ln([A]_t/[A]_o$=-kt
- If ½ of the reactant has been consumed t=$t_{1/2}$ and $\ln([A]_t/[A]_o)$=ln(1/2)=-.693.
- Thus $t_{1/2}$ =0.693/k (does the structure of this seem reasonable? What does it say about the relationship between k and $t_{1/2}$?)
- For first order reactions, the half-life is constant, depending only on k. For all other reaction orders, the half life varies with time, as it is concentration dependent. Why is that such a big deal?

Strategies for dealing with ln

- A first order reaction has k=0.034sec$^{-1.}$ In what directions can you go from this point?
- What is $t_{1/2}$?
- General reaction progress analysis
- How long will it take until……
- After 18secs, how…….
- With the exception of calculating $t_{1/2}$, all such problems require pressing that " ln" key on your calculator that you may be wondering about. The key issue is to use the ln and e key properly and at the correct stage in the problem.

More on 1st order processes

- ln([A]t/[A]o=-kt
- Always calculate the half-life since it's a useful signpost in any problem.

When given [A]t and [A]o, evaluate the ln term immediately

Pay close attention to wording: "remains" vs "consumed" are totally different problems

If the question is in %, then set [A]o=100

- When t is given (and assuming k is known), the
- equation becomes, from a practical standpoint,
- $[A]t/[A]o = e^{-kt}$

- In this case, the right side should be fully evaluated, before proceeding.
- Generic:
- How much remains (is consumed) after…
- It is found that … remains (is consumed)
- after..how much did you begin with?
- Again-pay very close attention to wording and to
- the time dimension.

Trials and Tribulations-First Order Processes

- Even a seemingly simple idea-a first order process is filled with potential pitfalls
- A first order process has k=x or $t_{1/2}$=0.693/xsecs. Either of these could be given.
- Scenarios
  - What is k (or $t_{1/2}$)
  - How long will it take until
    - []remains
    - [] has reacted
    - % remains
    - % has reacted
  - After a given period
    - []remains
    - [] has reacted
    - % remains
    - % has reacted
- Note-% questions do not require that any quantities be known and actually work better if you ignore any quantities given.
- The above gives you about 16 basic questions without even considering issues like changes in time dimensions, etc.

One (well, sort of two) Quick Example(s)

- A first order process has $k=0.010 sec^{-1}$
- If the initial concentration of A=0.50M(this quantity could be in many different dimensions)
  - How long will it take until 0.30M remains?
  - How long until 0.30M has reacted?
  - How long until 65% has reacted?
  - How long until 65% remains?
- A first order process has $t_{½}$=43 sec
  - After 1.2 minutes, how much remains?
  - After 1.2minutes, how much has reacted?
  - After 1.2minutes, what % remains?
  - After 1.2 minutes, what % has reacted?

Why do reactions have rates?

- We know that reactions take place at different rates and that a kinetics study allows us to determine the value of k, the rate constant, which tells us what the rate of the process will be. **However, it does not tell us why.**
- Consider a process such as A+B=>C
- What fundamental requirements are there for this to occur?
- A and B must collide
- The collision must have the required orientation
- $H^{\cdot} + {}^{\cdot}H \Rightarrow H_2$ any collision brings the atoms together correctly
- $CH_3CH_2CH_2Cl + OH^- \Rightarrow CH_3CH_2CH_2OH + Cl^-$ only collisions of the OH^- on the carbon containing the Cl will have the chance of being productive.
- The collision factor, Z, is the product of the number of collisions and the fraction which are productive. Suppose you had 57 collisions/sec and 0.045 of those could be productive then Z=2.65 (these numbers are not real. Remember, I make stuff up all the time.)

Does Temperature Matter?

- How do temperature changes affect reaction rates?
- In general, for every 10deg increase in T, the rate will double . This is a very useful "rule of thumb."
- Increasing T increases k, but it is not a simple linear relationship. Rather lnk is related to T(K).

  There must be some minimum energy needed for the process to proceed (sound familiar?)
- This energy is called the activation energy Ea
- The rate constant, the collision factor and the activation energy are related by the Arrhenius equation:
- $k=Z*e^{-Ea/RT}$ or
- $\ln(k2/k1)=(-Ea/R)(1/T2-1/T1)$ (this should look very familiar)
- a plot of lnK vs 1/T permits determination of Ea
- The actual use of the Arrhenius equation in calculations is a web only exercise.

How many steps would it take

- 2A + 3B => C + 2D
- What is the likelihood that 2As come together with 3Bs and in one great conflagration kick out a C and 2Ds?
- What's the alternative?
- Given that overwhelmingly, particularly in the gas phase, the most likely event is a two body collision, the reaction probably occurs as a result of a series of "bimolecular" steps.

Elementary Reactions and the mechanism

- A chemical reaction which describes two or more species directly reacting to produce product is called elementary.
- Not surprising, most elem. reactions have only two species reacting
- The step by step process consisting of a series of elementary reactions which yields the overall reaction is called a mechanism
  - The sum of these elementary reactions will be the overall process
  - When more than one step is involved, there will be a slow step- called the rate determining step(rds). Only species involved up to and in the rds will appear in the rate law.
- In a reaction mechanism it is common for species to be produced (and then consumed) which don't appear in the overall reaction, These are called intermediates.

Mechanisms and Rate Laws

- For each of the following, what is the overall reaction? Write the rate law and identify any intermediates.

A+C=>D+E **fast**
B+C=>D **slow,rds**

A+B=>D **fast**
B+C=>D **slow,rds**
A+C=>E+E **fast**

A+C=>D **fast**
A+B=>E **fast**
B+C=>E **slow,rds**
B+C=>D **fast**

A+C=>N+D **slow,rds**
C+N=>M **fast**
A+M=>E+D **fast**