Lecture #: 0 Administrative information Chem 142D, Kane 120 (4 :30-5 :20 MWF)
Sections: Chapter 1
Topics: Stoichiometry, the scientific method and the history of molecular structure

Admin: Class starts Sept 28 and Ends December 9
Final exam is on Dec 12 (Monday) in the evening 4:30
Holidays, 3 Holidays: Veterans Day (November 11) and Thanksgiving November 24-25
Lectures: 25 actual lectures,
Seven overhead activities: 2 In Class exams, Three Holidays (including Wed before Thanksgiving) 2 admin lectures, and class evaluations.
Holidays: 11/11/2011 Veterans Day, 11/24-25 Thanksgiving
Final: Monday 12/12/2011 4:30 to 6:20 in Kane 120

There are 432 students, 9 sections of 48 each. There will be 9 TAs.

Sample Problems: Lots of homework every week; keep working on ALEKS. Use in-text problems (that are worked out) as questions for you. Put a sheet of paper over the text stuff, and keep a notebook to work those problems in for yourself. Only look when you are stuck. Use the text not the answer to help you get started; getting a problem started is the hardest part.

Web assign is not the most fun thing to do, so do the problems before you log on. Work the problems in your notebook and show to your TA before you fill them in. There can still be some glitches.
Demonstrations:

Bottom Line Summary: Everybody will do homework (so getting that done is just the baseline for a decent grade). But do your homework problems over during the same week as they are due, to solidify methodology. Homework problems comprise 40 to 60% of the exam. Exams are multiple choice sorry (so there are lots ~20 of questions).

Multiple Choice (M.C.) exams. I will ask you to identify the correct equilibrium expressions and other related expressions as we go along. You must choose from among the ones I give and one (potentially correct) choices may be none of the above or even two of the above. If you use any strategies to guess a pattern in the answers forget it; I use a random letter generator for each problem. So you can have a string of answers that is E E D E (or not), and there is no tie-in with the other versions.

Your homework: In addition to ALEKS work problems at the end of Zumdahl's chapters. Work on the problems for a short time, jot down questions that impede your progress and talk with others (students, TA, instructor, Chem 330 help, etc). Do not copy other peoples work. That is counter productive to doing your own work on the test (it may help in the short run, but you will not be prepared for the exam). About half of the exam will be closely tied to problems at the end of each chapter. So doing the problem for yourself will payoff. Put your worked-problems in a notebook as you go, so you will have your answers to study for the exam. Writing the answers as you go will be most helpful to you to study/review for the exams.

Look over the lecture synopsis (single page for each lecture) before coming to class and maybe skim the related section in the text. This is just to give you a frame of reference for where the lecture is going. Also the ppt are on line to look at any time. I will use some ppt and some overhead material. We will try to do one problem "on the board" (i.e. overhead) each lecture. There are also sample problems to work for class and quiz section. Those sample problems will be used for test and some recast into M.C. format for the exam. The synopsis of each lecture (a single page) is your real assignment for the exams.

Lecture #: 1 Lec2a Structure of Atoms and Molecules
Sections: Chapters 1 and 2
Topics: Stoichiometry, the scientific method and the history of molecular structure
The Structure of the atom. The symbol to keep track of all atomic properties (number of protons, electrons and neutrons). The atomic mass, and the mass number. Why Carbon is not 6 times that of deuterium. Why Chlorine is neither 35 nor 37. The mass spectrometer: How we know atomic masses (at the atomic scale). The structure of simple molecules. The structure of salts. Connect structure with the periodic table; and families of elements.

Sample Problems: What element is 12A6, and how many n,p,e's are there. What is the average molecular weight of chlorine? Given the average molecular weight of chlorine, what percentage is 35Cl vs 37Cl?

Demonstrations: The shapes of simple molecules.

Bottom Line Summary: Identify n,p,es from the general symbols, and give the symbol given n,p,e info. Find elements in periodic table. Understand two sources of molecular weights (binding energy and averaging of isotopes), isotopes and atomic numbers.
Significant figures and proper rounding to report results will be emphasized in laboratory component and ALEKS.

Lecture #: 2 Lec2b Naming simple molecules
Sections: 2.9
Topics: Name simple molecules that we will work with throughout the quarter. The list of molecules and names are given. Name any metal halide (salt). In particular focus on the oxy acids and the salts of the oxy acids. Compare with salts and acids of the halides. The bicarbonate and bisulfate ions. Identify the oxidation states of the transition metals in various salts and complexes. [CoCl4]2- and Co(H2O)6+2, lead and iron.
Naming organic molecules. Ethanol, Methane, Propane, Butane, Acetic Acid, Ethyl Acetate. Ammonia, Methylamine.

Sample Problems: What is periodic acid. If you know the formula of perludicrate ion, what is the formula of ludicrous acid? What is "no salt" salt?

Demonstrations: The shapes of simple molecules, and NO2 in a glass container, as a function of temperature. Demo Co states and Co(II) complexes in particular. Oxidation states of Lead and the Lead Acid Battery.

Bottom Line Summary: Just memorize various classes of molecules; practice the root names so you can name and give the probable formula for making something from Cs and Cl, or Hg and S. It is cumbersome to use the flow charts to name molecules.

Lecture #: 3 Lec3a Stoichiometry
Sections: 3.1 – 3.4
Topics: Why do we bother with mass when molecules combine by number not by mass? Interpret the meaning of the chemical formula for a molecule (even a salt).
The relation between mass and number of molecules. Avogadro's number and the mole. The mass spectrometer and measuring atomic mass with high accuracy.
The mole (or mol) and the units of Avogadro's number. $1 = N_A$. All conversion factors equal 1. Find the mass of each element in a molecule. The amu (or uamu or Dalton) and its relation to the gram. (note the mix of SI and cgs systems a bit). What is the molecular mass (or weight) and how do we compute it from the molecular formula?
Find the mass fraction of each element in a molecule.

Sample Problems: What is the mass of Copper given Cu63 and Cu65 (two isotopes again) What is the percent given the average mass in the periodic table? How many moles and how many atoms are in 6.00 grams of Si? Do we need to worry about the isotopic components in Si? What about Cu? What is the molecular mass (or weight) of your favorite molecule, eg sulfuric acid (compute it from the molecular formula)?
What fraction (by mass) of acetic is carbon? (nitrogen/hydrogen/oxygen???) Substitute you favorite molecule and favorite element, and redo the problem.

Demonstrations:

Bottom Line Summary: Convert among grams, moles, amus, molecular (and atomic masses), use the periodic table to help. A comment about ALEKS computation. Convert from molecular formula to molar mass and molecular mass, and mass fraction of each element.

Lecture #: 4 Lec3b Stoichiometry
Sections: 3.5; and 3.6 – 3.7
Topics: Use the ideas from 3a to turn the problem around. If you are given the mass fractions of each element in a molecule, compute the molecular formula. There is a bit of art in the solution in this direction as one is looking for whole integers for each representative element. Why do we want to go in this direction? It is how we must proceed to analyze molecules for their elemental content and determine the molecular formula (and the empirical formula).

CHANGE: The meaning of a chemical reaction. Follow change as a function of temperature and mixing reactive species.

Sample Problems: What is the empirical formula and the molecular formula of acetic acid? Try also oxalic acid. We need the actual mass to get the molecular formula. How do we get the actual mass of a molecule? How does one determine whether sulfur contains 2, 4 or 8 sulfur atoms per unit? How do we determine the molecular mass of phosphorous (V) oxide? (Why is this challenging?)

Follow people changing from groups of 8 to groups of 6 and visa versa. Distinguish between the chemical reaction and the amounts of reactants available. Change can be incremental or it can go to completion. Identify the unit of the reaction, or the fundamental step of a reaction.

Balance the reaction of different symbols for molecules. Comment about keeping units together to balance. Compare balancing to anagrams. Abstract 11+2=12+1 to symbols; show symbol recombination. Problem Z3.14 in Text.

Demonstrations: Show an elemental analysis device. Show how a mass spectrometer works. Show slow change in a chemical reaction. Show a reaction goes kinetically to equilibrium.

Bottom Line Summary: Go from molecular formula to percent (by mass) composition by elements. Be able to go the other direction and get empirical formula. Using the total molecular mass (or weight) determine the molecular formula. Understand what can be measured and what cannot. Balance a chemical reaction by rearranging the symbols (i.e. elements) from the reaction side to the product side. N.B: reactions are in terms of molecular fragment rearrangements.

Lecture #: 5 Lec3c Stoichiometry
Sections: 3.8 – 3.9
Preamble: Balance a chemical reaction by inspection. Distinguish between the coefficients needed to balance the reaction and the amount of stuff that is available to react. Why should stoichiometric coefficients be integers? Be clear about the units on the stoichiometric coefficients, and the meaning of them: Amount of A (the molecule you choose) that changes per unit change; or change in A per reaction.

Topics: Now allow the reaction to use up some reactant (making product). Determine the mass of the reactant(s) used up and the mass of the product(s) generated, due to the transformation. Fundamental Principle: The mass as well as number of atoms (Stoichiometry) of each atom type are preserved in a chemical reaction. The mass of each element must be conserved (i.e. is not lost or gained) as a result of the transformation.

Sample Problems: Given a balanced chemical reaction. Eg: Burn methane. How many grams of carbon are in 5 grams of methane? How many grams of Carbon are in the product, CO2? How many grams of CO2 do we get by burning 5 grams of methane? (How long does it take your stove to burn 5 grams of methane?) Two ways to do the problem: A) Follow the mass of reactants at the start and finish as products form; go through the stoichiometric coefficients and the molecular weights of each of the molecules. B) Use the fraction of Carbon in reactant and product and know that all carbon by mass moves from reactant (methane) to product (CO_2). Determine masses that way. Method A is more robust (why?).

Demonstrations: Burn Methane, Burn Magnesium and Burn Hydrogen, Thermite Reaction

Bottom Line Summary: Go from mass of reactants to mass of products. Find the limiting reagent. Determine the yields and the theoretical percent yield, given actual yields of reactions. Why do we need the theoretical percent yield?

Lecture #: 6 Lec4a Solution Stoichiometry
Sections: 4:1 – 4:4
Topic: Dissolve weak and strong electrolytes in water. What does water do, how does it support solids to dissolve. Why is it different from cyclohexane (or benzene, or gasoline). Acids and Bases in water, how they ionize. Does water ionize? Use the definition of molarity, to compute moles (run the definition backward). Compare molarity and density. M=n/V. The use of dilution to make a solution of any desired concentration, from a stock solution that has a higher concentration. Show how serial dilutions help make very dilute solutions very accurate.

Sample Problems: Given a balanced chemical reaction for HCl, and H2SO4 in solution, Na2HPO4, and NaOH, and NaCl. Calculate the concentration of each ion based on the mass of the solid (or gas) that goes into solution, and the volume of the solution. E.g. if a bottle is labeled 0.1M NaOH what does that mean; what is actually in the solution?
Want a solution of NaCl that is 1.00M and 300 mLs. From a stock solution that is 3.5M NaCl. How do we make this?

Demonstrations: Compare HCl, NaCl, Acetic Acid, Ammonia, Sugar, ethanol, Water ability to carry current. Make a solution, and a more dilute solution. Do serial dilution, by factors of 2 and 10. Use colored water and the overhead. Show ppt of insoluble salts. Vinegar and baking soda react (acid and base reactions).

Bottom Line Summary: Compute from mass to moles to molarity. Use molarity to do dilutions. Many kinds of reactions take place in solvents. Water is one of the most popular (and most unusual) of solvents. Some salts ppt out and acids and bases react.

Lecture #: 7 Lec4b Solution Stoichiometry
Sections: 4:5 – 4:9
Topic: Reactions in solution. Two types: Acid-Base Reactions and Precipitation. Salts fully ionize in water, unless they don't. The list of ones that don't are in chapter 8. Anything with NH_4^+ and NO_3^- is soluble. Need to keep track of the Stoichiometry, eg Na2SO4 give 2 Na+ ions for every salt unit dissolved. Let us begin to track things that are conserved in a chemical reaction, and apply it to the formation of a ppt. One thing is charge, and another is mass, and number of items (or moles) of components are conserved. A conserved quantity is a very powerful restraint on the system that means we can figure out what happens. Take examples of mixing AgNO3 and NH4Cl. What is really in the solution? What can happen? Ions that can match up (and make a neutral entity) can ppt. And they often do. Do you need to memorize ones that ppt? No. (Table 4.1 provides good guidelines.) When a ppt does from one of the ions will be the limiting reactant. Identify that one and use it to determine how much ppt (moles and mass) is generated; assuming complete ppt.

An acid and a base react to get rid of either excess protons or hydroxide ions in solution. Calculate the amount that reacts. Give the molecular reaction expression, and the net ionic expression. Compare Bronsted-Lowry and Arrhenius definitions of acids and bases. Consider ammonia and methylamine and contrast these molecules with different definitions. Distinguish between the end point of a titration and the stoichiometric point.

Sample Problems: Given two (binary) salts mixed in water identify all ions possible and all possible ppt. Rule out cases that will not ppt. (See table 4.1, and steps – pg 111 – to refine your thinking. If an ion pair is in table 8.5 it ppts.). If a solution (in water) of FeF_2 (0.010 M) and BaS (0.050 M) are mixed together. What ppts? (Hint: By having solutions in the first place you know FeF_2 and BaS are soluble in solvent.) Mix 300 mls of FeF_2 and 100 mls BaS. What is the concentration of each ion in solution? What is the mass of the various ppts? (Identify the Molecular reaction, the ionic reaction and the net ionic reactions in the process and use these to determine the Stoichiometry.)

Mix 200 mls of 0.010 M HCl, and 100 mls of 0.030 M Methylamine. What is the concentration of all the ions (assume reaction goes to completion) Identify the salt that is formed. If the salt were to ppt, what would its mass be?

Demonstrations: PbI2 and AgCl ppt from water.

Bottom Line Summary: Find possible ppt from mixed salts (out of all possible ions). Show the molecular reaction using (aq) and (s) to define whether an ion is in solution or has ppt with a counter-ion. Identify the spectator ions (those that don't ppt). Compute number of moles and mass of ppt when it happens (assume reaction goes to completion). Acids and bases do not ppt but they do form salts when they react. The principle of an acid and a base reaction is to be sure there are no OH- and H+ ions simultaneously around when mixed. Or in the L-B sense, there are no bases available if H+ is around.

Lecture #: 8 Lec4c Oxidation Reduction Reactions
Sections: 4:10 – 4:12
Topic: More reactions in solution. For a Redox or Oxidation-Reduction Reaction the reaction may be in solvent (water) or may be just between solids. Identify the reducing agent (the specific element in the molecule) and the oxidizing agent. Find the oxidation numbers for each species before and after and identify the change (the reducing agent is oxidized). Identify the number of electrons that change partners. Write the net redox expression. Write the net redox expression as two half reactions that transfer electrons. Balance each and add up so that no electrons are in the net redox reaction. To remember what is what, the fundamental oxidizing agent is oxygen, and it want to get electrons. So an oxidizing agent accepts electrons and is reduced in the process. O2 goes from an oxidation number (for each oxygen) of zero to -2 (per O). So it is reduced, as its oxidation number is smaller (i.e. reduced).

Sample Problems: Balance the various redox reactions in the back of the book. Problems 57-63 there are lot of great redox problems. Analyze the lead-acid battery.
(4Z4.62(a) balance. Notice the Mn goes from +7 to +4). Here (one of) the metals is the oxidizing agent (it is reduced); Al is the usual and is a reducing agent (giving up electrons), is oxidized. Contrast this with forming NaCl, compare with the metal Na.

Demonstrations: Thermite, and Mg burning. Reaction of permanganate to oxidize. Burn methane, and analyze the redox reaction. Why CH4 and not H4C? Also NH3 vs H3N? but H2O and HF??

Bottom Line Summary: Find possible ppt from mixed salts (out of all possible ions) show the reaction using (s) and (aq) to define whether an ion in solution or has ppt with a counter-ion. Identify the spectator ions (those that don't dissolve). Compute number of moles and mass of ppt when it happens (assume reaction goes to completion). Acids and bases do not ppt but they do form salts when they reaction (and there are no OH- and H+ ions simultaneously around when mixed).

Lecture #: 9 Lec5a Gas Laws: The gaseous state.
Sections: 5:1-5:3
Topic: The basic properties of a gas. The gas fills the entire volume of its container but actually occupies very little of it. Pressure from a gas arises because the gas molecules hit the walls of the container and push on the container. Know Boyle's (PV is a constant) and Charles' Law (T~V). Boyle was the first to really understand pressure (and that a gas could be compressed). He was way far ahead of anyone else in his time. Charles gave us insight into the idea of an absolute zero. Avogadro's principle (V~n) gives us insight into how a gas really functions: the nature of the gas is irrelevant; all gasses behave the same and it is based on the number of gas molecules not the mass of them.

Demo: Compress a steel container by removing the air; (1 Atm pressure is a big deal). Compare a nearly empty milk carton taken from the refrigerator with a full milk carton. Let both come to room temp (briefly). Which is swelled and which is not? Why? Consider water is 1 g/cc and air is 1 g/l. That is a 1000 fold difference. (You would be very disappointed if you bought a liter of soda and got only one gram of soda.)

Demo: Make a balloon filled with CO2, compare it to balloons of H2, Ar, O2, CH4.

Sample Problems:
Use I.G. equation to determine new V if P and T change (but n does not). Or blow up a balloon using a chemical reaction, burn methane and determine the volume. Can you use a methane balloon to explore? Can you use a CO_2 balloon to go floating? Explain. Why is there a propane/methane tank on board a balloon?

Lavoisier found that when he mixed 1 volume of methane with 2 volumes of O2 (at atmospheric pressure and 250F) the three volumes did not change even though much heat was liberated, after the system returned to 250F. But when he did the same experiment at room temperature, after the reaction and excess heat was dissipated, he got 1 volume of gas and some condensed water when the temperature returned to room temperature. Deduce the Stoichiometry of the reaction, and explain what principle (unbeknownst to him) he was using.

TABLE Variation in the Volume of $H_2(g)$ with Temperature. From:
http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/Charles-s-Law-951.html

Data for 0.0447 mol	H2(g) @ 1Atm	Data for 0.100 mol	H2(g) @ 1 Atm
Temp (Celsius)	Volume (Liters)	Temp (Celsius)	Volume (Liters)
0.00	1.00	0.0	2.24
50.0	1.16	50.0	2.65
100.	1.37	100.0	3.06
150.	1.55	150.0	3.47

Typical data of J. Charles used to deduce an absolute lowest possible temperature. Use this data to see what absolute temperature you get. Would you conclude there was a lowest possible temperature based on this data?

Lecture #: 10 Lec5b The Stoichiometry of Gasses
Sections: 5:4-5:5
Topic: For Stoichiometry problems, reactions in the gas phase make it very easy to keep track of the change in the number of moles, because either pressure or volume change (at constant T) with changes in number of moles. The I.G. equation relates two other very useful quantities. The first the gas concentration C (n moles/liter): $C = \frac{n}{V}$. The second quantity is the density of the gas (in grams/liter): $d = \frac{m}{V} = \frac{m}{n} \cdot \frac{n}{V} = M \cdot C$, where M is the molar mass of the gas molecules. From the I.G. $P = CRT$, one cannot tell the difference between He and Xe in the gas as far as the pressure is concerned, but the density certainly goes up a lot with Xe gas. A balloon filled with Xe weighs over 30 times more than a balloon filled with He at the same pressure (and Temp, and Volume).

Avogadro' principle tells us that at STP (0C, 1 Atm) 1 mole of gas occupies 22.4 liters. The I.G. equation gives us the same answer using the gas constant. This tells us that the actual volume of n moles of I.G. (any substance) will give a volume V: $V = n \cdot 22.4\ell$. So (when P and T are fixed at STP) the Volume measures the number of moles of the gas.

In a chemical reaction, which leads to change, both the (individual and overall) densities and concentrations will change. How can we take advantage of these other properties to follow chemical reactions?

If we have a flask of known volume (and P,T) we can measure the mass and determine the molar mass, M (in grams/mole). Once we know M (the molecular weight) we can guess which molecule or element it might be. In an experiment you will do, you fill a flask of known volume at 100C and 1 Atm (boiling water) with gas. Now weigh the flask with the gas and get the mass of the gas. The mass of the gas is m. The number of moles is determined from the I.G. equation $n = \frac{PV}{RT}$. The molecular weight then is: $M = \frac{m}{n}$.
Notice that the molecular weight is related to the density of the gas:

$$M = \frac{m}{n} = \frac{m \cdot RT}{PV} = d \cdot \frac{RT}{P}$$

For I.G. it doesn't matter what the gas is, just the number of moles of gas count. What John Dalton noticed was that the gasses acted independently and that the total pressure of a gas was the sum of the pressures of each of the individual components. This follows because (from the I.G. equation) the total number of moles is just the sum of the number of moles of each component. Therefore:

$$n_{Total} = n_1 + n_2 + n_3 + n_4 + \cdots$$
$$1 = \chi_1 + \chi_2 + \chi_3 + \chi_4 + \cdots$$

The χs are the mole fractions of the different species of gasses present. So the total pressure can be written in terms of the partial pressure of each of the gasses:

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + \cdots \text{ where } P_1 = n_1 \cdot \frac{RT}{V}$$

And V is the total volume where all the gasses are mixed together. This can be turned around, if we know the molar fraction of one gas: $\chi_1 = \frac{n_1}{n_{Total}}$ then $P_1 = \chi_1 \cdot P_{Total}$ etc. so we can determine the partial pressures of each of the gasses from knowing the molar amount of each, (and we get the mole fraction from that).

Sample Problems:
What is the partial pressure of O2 in the air at room temp? O2 is about 20.5% O2. (Dry air is 20.95% but regular air is about 1% water too). What is the vapor pressure of water in air?

The possible chemical reaction for nitrogen dioxide is $2NO_2 \rightleftarrows N_2O_4$. In a flask (of fixed volume) there is 50% NO_2 (by moles) and 50% N_2O_4, at 0C. The mole fraction of each then at the start is ½. The temperature is increased to 100C. What would the new total pressure be (relative to the old one) if no change in the mole fraction of NO_2 occurred? However the total pressure is 20% larger than that expected just due to warming. What happened to the gas? Explain your reasoning. What is the new mole fraction of NO_2? What is the new mole fraction of N_2O_4?

Suppose you want to measure the pressure of a gas relative to a standard (say $P_o = 1Atm$) and the concentration relative to a standard (say $C_o = 1M$) how would you rewrite the ideal gas equation to relate $\frac{P}{P_o}$ to $\frac{C}{C_o}$? Which Gas constant would you use?

Bottom line summary: Daltons Law of partial pressures lets us substitute partial pressures (a quantity rather easy to measure) for concentration of gasses. We want to work in concentration units (just like solutes in liquids) but we can easily convert back and forth to pressure for each species.

Lecture 5C Kinetic Theory of Gasses.

Fun Facts about Gasses (the Air): (An alternative name for the kinetic theory of gasses). The kinetic theory of gasses turns around what is a very general principle that answers the question: What is temperature? Temperature is a direct measure of the internal kinetic energy of all materials (solid, liquid or gas). Because ideal gasses have no intermolecular attraction their only form of energy is kinetic, so the kinetic energy of a gas is directly proportional to its temperature (which is also true for any other substance in the universe). So for motion in the x direction: $m \cdot u_x = RT$, the mass (in kg/mole) times the velocity in the x direction is equal to RT=2.3kJ/mol at 0C.

From Boyle's, Charles', and Avogadro's laws you can prove that the Ideal Gas equation is the only equation possible consistent with those three laws. To show that this is the case, look at text (sec 5.3) where V=an, realize a=a(P,T) ; use the dependence of the constants to sort out fully the ideal gas expression. Getting started: Using PV=k(n,T), from Boyle; multiply Avogadro's equation by P (on both sides): PV= a(P,T)*nP=k(n,T) and rearrange to find that a(P,T)*P= k(n,T)/n. Therefore a*P cannot depend on P so a(P,T)=a'(T)/P, and similarly k(n,T)/n cannot depend on n, so k(n,T)=n*k'(T). Therefore a'(T)=k'(T). You now need to fold in Charles law in a similar way to finish the proof.

If water is 1 g/cc and 10 meters or 32 feet of water is 1 atmosphere (when diving in water) we can conclude (roughly, because air is 1 g/liter) that the earth's atmosphere is about 10 kilo-meters high to give us one atmosphere. This is about right, except that the pressure of the air drops off exponentially with distance up. In an airplane at 35,000 feet, or 10 kilometers (a typical flying altitude) there is still air (for the plane to fly) but the air pressure at that height is ~0.2 of an atmosphere. The cabin is pressurized to about ½ an atmosphere, which is equivalent to about 3.0 miles up. Which is why water boils in Denver (the mile high city, where the air pressure is about 0.8 Atm) at a lower temperature (10F lower) than at the surface of the earth. Pressure comes from the kinetic energy of the gas molecules hitting the surface of the container moving (at the speed of sound!!). All molecules, regardless of mass have the same average kinetic energy. So molecules that are larger (more mass), like argon and CO2, move more slowly than air (nitrogen and oxygen). Moreover, because they are more massive they tend to stay closer to the surface of the earth. To demonstrate that the cabin is pressurized to ½ an atmosphere, after you finish a bottle of water (on the flight at 35,000 feet) that came in a cheap plastic container, close the lid tightly and set it aside. When you get back on the ground, look at the bottle. Estimate the cabin pressure from what you see about the bottle. Why do you think a baby cries on an airplane even though it is being held by its mother?

If all gas molecules are moving (to make pressure) how fast are they moving? The Kinetic theory says it is temperature that makes them move, so the average KE = (3/2) RT. Or 3.6 kJ of energy per mole of gas molecules, at room temperature. What is the mean velocity? Depends on the mass, but since the air is mostly nitrogen The mass of a mole of air is 28 g. From this, the average speed (the r.m.s. velocity) is about 300 m/sec (1 mile in 5 seconds). Need to do everything in S.I. units (safer that way). If gas molecules really move that fast how many gas molecules are hitting your skin every second? At STP (according the I.G. and Avogadro's equation) 1 mole of gas occupies 22.4 liters. The gas bounced from side to side.

This is a cube 0.28 meters in length (~one foot). So each gas hits a wall and returns to hit it again in time t = length/velocity= (2*0.28/300) sec= 1.9e-3 sec. There are Avogadro's number of molecules in this box. Each one hits an area .28*.28 = .08 meters2 or 800 cm^2 every 1.9 milliseconds. That is Na/(time*area) = 3.5*10^27 molecules/m^2/sec. These guys are really busy. This corresponds to a mass of 15 kg hitting each wall of the box every second (just m/t). The same thing is happening on all surfaces including your skin due to the air. Fortunately the collisions are mostly elastic and molecules are individually very light. But these collisions collectively generate a force that develops the pressure 1 Atm (or 10^5 Pa, the SI unit of pressure). Pressure is force per unit area. 1 Atm = 105 Pa (the SI unit of pressure) so this is a force of 10^5 Newtons spread over an area of 1 square meter, or 10 Newtons per square-cm, or a force of 8 kN on each wall of the box (of area 0.08 m^2).

The force (as Newton defined it) comes from the change in velocity per unit time (F=ma = mdv/dt). We have the velocity and the time. The change in velocity of a molecule is for the molecule to be moving from the +X to the –X direction (eg.) so dv=2v, and Force should be F=m*2V/time = 2* (m/t)*v= 2*15kg/sec*300m/sec = 9*10^3 Newtons. Which is very close to the force of 8 kN we predicted based on 1 Atm of pressure above. So the source of the force is each gas molecule hitting the surface and bouncing (elastically) off the surface.

Above we calculated the number of collisoons per second hitting a surface of area A. In the above example the area was 0.08 m^2. We can make it a little clearer how we did the calculation. This is done by knowing the velocity in the x direction from the basic tenet of the (KTG) $m \cdot u_x^2 = RT$ or $u_x = \sqrt{\frac{RT}{m}}$. From here we know there are N gas molecules all moving (on average) like this one. To use this equation properly the mass is the molar mass of the gas molecule and must be in SI units (kg/mole) R must also be in SI units so you must use R=8.31 SI, not the 0.082 l-Atm/mol-K So the number of collisions per second is defined as Z: $Z = \frac{N}{t}$. That is all we need to get the number of collisions per second. The connection between the time t and the velocity is: $u_x = \frac{2\ell}{t}$. The factor of 2 is there because the particle must go down and back to hit the wall again. This is almost the formula Zumdahl gives on page 168. Using the relation that: $V = A \cdot \ell$. Putting all this together we get that

Z= $Z = \frac{N}{t} = N\frac{u_x}{2\ell} = A\left(\frac{N}{\ell \cdot A}\right)\frac{u_x}{2} = A\left(\frac{N}{V}\right)\frac{1}{2}\sqrt{\frac{RT}{m}}$. You can see that this is almost identical to Zumdahl's expression but much easier to find. This formula replaces $\sqrt{2\pi}$ with 2, which is off by 20%.

We commented that the speed of air is the same as the speed of sound. This is close but not exactly correct. For air the speed of sound is 20% greater than the speed (in the x direction) of the gas molecules. $u_{sound} = \sqrt{\gamma} \cdot u_x$, where the gamma is the adiabatic constant of air and is exactly 1.4 for ideal diatomic molecules (like N_2 and O_2). This correction occurs because sound propagates at constant energy in a medium and depends on how the density of the medium changes with the applied sound pressure. The more the material gives under pressure the slower sound will travel.

Lecture #: 11 Lec6a Equilibrium in Chemical Reactions
Sections: 6.1 (part of 6.2)
Topics: The origins of equilibrium. The rate of the reaction in both directions exactly balances. Plot the reaction as a function of time. Follow NO2 dimer formation as an example. Compare with the NIC table for this. Plot all 3 (include X) as a function of time. Find a quantity that does not change with time (because it does not depend on X). {N2O4] vs [NO2] (or pressure). Now plot both vs change or X. If we know X=X(t) we can find equilibrium for every species. The rates are proportional to the amount of stuff there, which is the principle of mass action: That all entities must be present and if one is zero then there is no tendency to make products (so a multiplicative form is required). If we begin with products of concentrations then we must have exponents for the stoichiometric coefficients. The balance of rates at equilibrium gives the condition of an equilibrium constant.

We need to have everything dimensionless so we reference pressure to 1 Atm and concentration to 1M. Use Po and Co to remind ourselves that there are no units. And Kp and KC to distinguish how we write the equilibrium constants and formula.

Sample Problems: 1) From the NO2 reaction, we can follow the amount of NO2 as the absorbance of the sample. If the concentration or partial pressure of the NO2 is .5 and we warm it, and it goes to .7 (Atm) how much change in the N2O4 was there. If the partial pressure of the N2O4 was .4 at the start, what is the new partial pressure. Show that the total partial pressure changed, and show that the invariant quantity did not change. **2)** Find the equilibrium constant in terms of pressure and concentration. (Use the formula we derived from I.G. equation.) First Convert Pressure to Concentration then just do it to the Ks themselves. **3)** Determine Kp for the ammonia reaction. Notice how the Stoichiometric coefficients play into the Kp. Write this rxn from the NIC table and write Kp and Kc, compare them based on equilibrium conditions. **4)** Given Kp, find H2 when two others are equal, etc, find other ways to use X to find equilibrium conditions from non-equilibrium states, qualitatively. Then next lecture, quantitatively. **5)** What would K be for the HD formation reaction? Show that K is independent of the ratio of H and D. We just use probability to guess the fraction of each species present.

Demonstrations: NO_2 gas dimerizes as a function of time and temperature. Follow other chemical reactions in time if possible.

B**ottom Line Summary:** Systems go to equilibrium, and that is not necessarily completion but somewhere in between. The principle of mass action tells us the form of K (which can be C or P when written in terms of Concentrations or Partial Pressures of each gas). Be sure we write K so that it has no units.

Lecture #: 12 Lec6b Equilibrium in Chemical Reactions
Sections: 6.3 and 6.6
Topics: Generalize the functional form for K to any other condition: (not equilibrium necessarily): This is called Q (the proper reaction quotient). Same form as K so when Q=K we are at equilibrium. But think about a battery: The reaction goes and stops (when you open the circuit) and keeps going as long as the battery is not at equilibrium. So Q must be dimensionless and can be written in terms of P or C. The root form of Q and K is in terms of activity. The activity is the pushing power of a substance to create a reaction. So a solid and the solvent have unit activity. The solid will react as long as there is any solid around and the solvent is always there as a support, even if it is used in the reaction. This allows us to write Q or K for any situation that involves solids, liquids or gasses.
Connect Q and the NIC table.
Show how Q depends on the change of concentrations as a reaction proceeds.
Plot Q as a function of X, and Plot K as a function of X.

Sample Problems: 1) What is the partial pressure of CO2 above CaCO3 (a solid that gives off CO2). 2) If Q>K or Q<K what does this imply about the direction of a reaction? 3)

Demonstrations:

Bottom Line Summary: Q and K look a lot alike. How are they same? How are they different? K is a number that does not depend on whether you are at equilibrium or not. Q changes as a reaction occurs and can be computed as X changes. X changes because the reaction happens in time. X stops changing when the reactions stops and the system is in equilibrium.

Lecture #: 13 Lec6c Equilibrium in Chemical Reactions
Sections: 6.5 and 6.6
Topics: Solve for equilibrium from any initial conditions. Use the NIC tables to determine Q at any X value from any initial conditions. Write the NIC table in terms of moles, concentration or partial pressures (of each species). See that X can be moles, concentration or partial pressure change for the reaction, whatever you need X to be. Q and K depend only on concentration or partial pressure (but not just on moles). Follow the change in total number of moles, $\Delta n \equiv \Delta n_{gas}$ to keep track of overall changes in moles of gasses. Use $\Delta n \equiv \Delta n_{gas}$ to convert between K_C and K_P.

Sample Problems: 1) For the reaction $2NO_2 \rightleftarrows N_2O_4$ K_P=4.3 (@25C). What is K_P for the reaction $N_2O_4 \rightleftarrows 2NO_2$? What is K_C for this reaction? **2)** The $K_P = 2.2 \cdot 10^{+6}$ for the reaction $N_2O + NO + 2O_2 \rightleftarrows 3NO_2$. What is Kp for the reaction: $N_2O + NO + 2O_2 \rightleftarrows \frac{3}{2} N_2O_4$ and for $2N_2O + 2NO + 4O_2 \rightleftarrows 3N_2O_4$? Find K_C for this reaction. Where is the equilibrium for this reaction (left, center, right)? **3)** A reaction starts with 5e4 Pa of NO_2. Find the concentration of NO_2 and N_2O_4 at equilibrium. **4)** The ammonia reaction: $N_2 + 3H_2 \rightleftarrows 2NH_3$ is at equilibrium with $[H_2] = 0.5M; [N_2] = 0.8M; [NH_3] = 0.2M$, How much H2 was present at the beginning before the reaction started? What is KC (if the reaction is @25C) what is Kp and what was the total pressure at the start of the reaction and at equilibrium? **5)** With the same initial conditions as (4), what are the concentrations when $[H_2] = [NH_3]$? Is it possible for $[NH_3] = [N_2]$ ever, given the initial conditions? Explain.

Demonstrations:

Bottom Line Summary: Set up Q when given concentrations, compare to K if possible. Be sure you are comparing Qp and Kp and can convert either to C. Remember $\frac{P}{P_o} = \frac{C}{C_o} \cdot \tau$ where $\tau = \frac{RTC_o}{P_o} = 0.082 \cdot T$ (and the Po and Co are understood when using Atm and M units). Use the NIC table to find concentrations anywhere, and find X when equilibrium is the final spot.

Lecture #: 14 Lec6d Equilibrium in Chemical Reactions
Sections: 6.5, 6.7 Finding chemical Equilibrium

Topics: Practice using the principles of the NIC table to find equilibrium (or the ICE/NICE table). Solve for all species' concentrations at equilibrium.

Sample Problems:
1) The H2, D2 equilibrium with HD. What should the equilibrium constant be?
2) The equilibrium of $Cr(Cl4)^{2-}$ with $Cr(H2O)_6^{2+}$ by adding Cl^- and water.
3) Suppose we are at equilibrium. Now add some of one of the species in the reaction. How do we set up the NIC table and what happens as the system reacts to go back to equilibrium? In this case the initial conditions are equilibrium, except for one species. This moves us out of equilibrium. The change moves us back to equilibrium yet again.
4) A reaction $2AsH_3(g) \rightleftarrows 2As(s) + 3H_2(g)$ starts with 1.0 Atm of reactant. After the system has come to equilibrium the total pressure of the cylinder is 1.2 Atm. What is the partial pressure of the H2, and what is the Kp for the rxn? Is it possible for the pressure to decrease from the initial conditions? Explain.

Demonstrations:

Bottom Line Summary:

Lecture #: 15 Lec6e Equilibrium in Chemical Reactions
Sections: 6.8 LeChatelier's Principle

Topics: LeChatelier's Principle provides insight into how chemical systems will react to stress. There are three examples (of chemical stress). The first is the addition of more reactant (or product). The second is the effect of a pressure change on the system. The third is the effect off temperature on the equilibrium point of a reaction. In all cases the system will respond to minimize the impact of the insult.

Looking ahead: $\ln\left(\frac{K(T)}{K(T_0)}\right) = \frac{\Delta H}{RT_0}\cdot\frac{\Delta T}{T}$. So if a reaction is endothermic (DH>0) K will increase with increasing T.

Sample Problems: **1)** Calculate Q for an imbalance, compare to K and use LeChatelier's principle to say which way the system will move. Put a bound on the amount of change. In the rxn $2AsH_3(g) \rightleftarrows 2As(s) + 3H_2(g)$ Add As, how would the addition of As change the equilibrium or shift the amount of AsH3. Add H2 how does that shift amount of AsH3? **2)** **3)** The NO2 system is at K=4.3 (at 25C). Is the reaction exothermic or endothermic as one makes a bond? $2NO_2 \rightleftarrows N_2O_4$. If the temperature is increased will K increase or decrease, which way will the system move to absorb the insult?

Demonstrations: Effects of Temperature on K, the NO2 reaction again.

Bottom Line Summary: To determine the amount of change when a single reactant is added it is between nothing and the amount of the addition, use the NICE table to find new equilibrium. For pressure, one must change the partial pressure of one of the reacting gasses. Kp does not change when either a reactant is added or when the pressure is changed. The effect of temperature actually changes the K.

Lecture #: 16 Lec8e Equilibrium in Chemical Reactions
Sections: 8.8, 8.9 and 8.10 Reactions of ions in solution and coordination complexes.

Topics: Solubility of Salts; common ion effect; Complex ion formation. We can connect the K_{sp} for a sparingly soluble salt (see Table 8.5, pg 330 for choices) with the solubility. The solubility of a salt is the number of moles of the salt that goes into solution (of a specified volume) if the salt did not dissociate into ions. The K_{sp} is related to the product of the concentration of each of the ions. Therefore the solubility (S) and the Ksp are directly related though the Stoichiometry of the dissociation of the salt into its ions. Many transition metals form aqueous complexes with ammonia, water, halides, and other charged and non-charged small molecules in solution. The equilibrium of such complexes is controlled in a fashion very similar to other equilibrium problems.

Demonstrations: Equilibrium of metal-ammonium; equilibrium of cobalt chloride, precipitation of PbI, AgCl and other sparingly soluble salts.

$$\left[Co\left(H_2O\right)\right]^{2+} + 4Cl^- \rightleftarrows \left[CoCl_4\right]^{2-} + 6H_2O$$

Werner's ammonia complexes are the classic examples. Ag, Co and Ni are good examples with ammonia, water and halides.

Sample Problems: 1) How is the K_{sp} of silver chromate ($\left(Ag_2CrO_4\right)$ related to the solubility (S)? Given the $K_{sp} = 9.0 \cdot 10^{-12}$ how many grams of solid $\left(Ag_2CrO_4\right)$ would dissolve in 100 mls of water? What are the units of Solubility and what are the units of K_{sp}? **2)** Recovery of silver mixes a solution of silver (nitrate) with NaCl. NaCl(s) is added to a solution of 2.5 mM AgNO3 to make a 0.01M NaCl solution. What is the mass of AgCl(s) that will be recovered from 2 liters of this solution? $K_{sp} = 1.6 \cdot 10^{-10}$. Compare the amount of Ag+(aq) in solution with what would be there in a solution made from AgCl(s) in water. **3)** From the demo of Co, we found that the concentration of the two forms were about the same when the Chloride concentration was about 4M. From this compute the K_{sp}, and from that compute the fraction of Co in the CoCl4 form when the concentration is 1M Chloride. Why is the actual concentration of Co2+ in solution not be needed to solve the problem?

Bottom Line Summary:

Solubility of a binary (or ternary) salt and K_{sp} are directly connected. Using the common ion effect the concentration of other ion (of a sparingly soluble salt) the concentration in water (or solubility) of an individual ion can be computed. Watch out for certain species that are solids and therefore are not in the solubility expression (they have unit activity). Also, the solvent, water, has unit activity and is not in the equilibrium expression. Use same rules for K_{sp} as for K_P or K_C, and solve for ion concentrations at equilibrium. Compare Qsp to Ksp to determine whether a salt will ppt.

How to know if a combination of ions precipitates: 1) Think NH_4NO_3 which dissolves as $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$, no other ions will pair with either of these ions to precipitate; 2) Whatever precipitates must be neutral; 3) You must find a K_{sp} for it in the table (Table 8.5, pg 330 or a subset on the test).

Be able to write the K_{sp} expression and relate it to the solubility (S or X). Use the same K_{sp} expression to determine the ion concentrations if other salts are added. Solubility is the concentration the solid would have, had it is just dissolved in the water as the uncharged molecule and did not dissociate. Combined with the volume of the water this tells the number of moles of solid that went into solution.

Lecture #: 17 Lec7a. Water as a solvent to sustain charges.
Sections: 7.1 through most of 7.5.
Topics: Strong and weak acids in water and pH. A brief review of water as a solvent. See chapter 4. Water auto-ionizes and the K = 1e-14. so the pH=7. Define of pH or pX or pQ, etc. Find pH of pure acetic acid. The pH scale; what is the concentration of water; if water were fully ionized, what would the pH be? How to write the KA for an acid and the KB for a base and calculate the pH, pA, pC etc. What is a strong acid or a strong base? The concept of a base conjugate to the acid or an acid conjugate to a base. For an acid HA, the anion A- is a base because it can take an H+ (and go back to HA). If HA is a strong acid the equilibrium lies far to the right and the anion A- is a weak base (LB def).

Sample Problems: Calculate the pH of a strong acid in solution, and the pH of a weak acid in solution. Use the NICE table and comment on the limits of the table. Notice that when KA<CA then H+ is the geometric average of KA and CA, that is, it must be between these two values. Use pH to show this average. But when KA>CA H+ cannot exceed CA. More on the proton pushing power of an acid in the next lecture.

Demonstrations: Conductivity of materials that ionize (or not) in water. Salts and weak and strong acids are compared. pH of common items; Carbonate volcano.

Bottom Line Summary:
Salts and acids dissociate into ions that can conduct electricity. Water (the solvent) itself autoionizes. $H2O \rightleftarrows H^+ + OH^-$ therefore $\left[H^+\right]\left[OH^-\right] = K_W$. In pure water the charge balance requires: $\left[H^+\right] = \left[OH^-\right]$. The pH or $-\log_{10}\left(\left[H^+\right]\right)$ is 7 for pure water because $K_W = 1 \cdot 10^{-14}$, and K_W does depend on temperature (LeChatelier's principle). K_W has no units although it could be M^2. Practice going back and forth between concentration (C) and pC.

$$p \equiv -\log_{10}(\ ) \quad \therefore \quad pX = -\log_{10}(X) \quad and \quad X = 10^{-pX}$$
$$pH = -\log_{10}\left(\left[H^+\right]\right) \quad and \quad pOH = -\log_{10}\left[OH^-\right]$$
$$pC_A = -\log_{10}(C_A) \quad and \quad C_A = 10^{-pC_A}$$
$$eg: C_A = 1 \cdot 10^{-2} \quad or \quad C_A = 2 \cdot 10^{-2} \quad or \quad pC_A = 3$$
$$pH + pOH = 14$$

pH<7 is an acid, and implies pOH>7. pH>7 is a base (or basic solution), and implies pOH=14-pH<7. The difference between HCl and Acetic acid (HAc) in water.
A strong acid is $K_A > C_A \equiv [HA]_o$ and a weak acid $K_A < C_A \equiv [HA]_o$
An acid give off or donates protons and a base accepts protons (Bronsted-Lowry) or produces hydroxides (Arrhenius) which then react with protons. The ability of an acid to generate protons or proton pushing power is generally $P_{HA} = \sqrt{C_A K_A}$, or just C_A whichever is smaller.
Molecules are neutral when they dissolve in water, and separate into charges. The entire solution must remain neutral even when charges are there. Keeping track of the number of different charged species, use: The charge balance relation. Using NICE table for each species: The Mass Balance. (NICE tables and Mass Balance are one and the same.)

Simple method: Calculate the pH of a strong acid; and the pH of a weak acid. $\left[H^+\right] \approx \sqrt{K_A C_A}$

Use the idea of the proton pushing power of an acid. $\left[H^+\right] \le C_A = \left[HA\right]_o$. No acid can produce more protons than acid added (this is the limit of a strong acid), the 'o' subscript means the concentration of HA before dissociation.

The NIC table and mass balance:

$$\left[HA\right] = \left[HA\right]_o - X = C_A - X$$

$$\left[A^-\right] = X$$

$$\left[HA\right] + \left[A^-\right] = C_A$$

If $\left[H^+\right] = X$, then get the simple answer as the approximate pH.

Lecture #: 18 Lec7b. The principles of an Acid (and a base)
Sections: 7.5 and 7.6, 7.10
Topics: Keeping Track of all species in an acid or base solution. The idea of the fraction of an acid dissociated (and the other is the fraction undissociated). Bases are just mirrors or complements of acids. Develop the fundamental equation from the charge balance expression.

Sample Problems: Determine the pH of an acid (and a base) examine different regions: strong/weak acids, include water effects. Compare with NICE table. **1)** pH of .01M HCl; **2)** pH of .01 M HAc (acetic acid) **3)** pH of 1e-8 M HCl; **4)** pH of 1e-6 M HAc.

Demonstrations:

Bottom Line Summary: KAs of monoprotic acids in table 7.2, and monobases in table 7.3. Use these Ks and write the appropriate expressions for related species.

Combine the acid mass balance (from the NIC table) and the KA expression to determine the percent dissociation (i.e the fraction of acid that is the anion form) and the percent association (the fraction of acid in the unionized form).

General Principles used to solve pH problems:
Principle 0: Water ionizes: $HOH \rightleftarrows H^+ + OH^- \quad and \quad K_W = \left[H^+\right]\cdot\left[OH^-\right] \approx 1\cdot 10^{-14}$
Principle 1: The fraction of an acid that dissociates:
Principle 2: The net charge in the solution must be neutral. Charged Species for an acid (or any solution) must sum to be neutral. This is the Charge Balance expression. (It is central to solving any and all pH problems.)
Principle 3: The pushing power of an acid: $\sqrt{K_A C_A}$ up to C_A. Solving problems will further illustrate the meaning of this.

Principle 4: Solving for the pH or really $\left[H^+\right]$. Show how to obtain the pH without a calculator, and a limited use of calculators, and usually avoiding solving a polynomial problem.

Principle 1: The fraction of each species present. Choices: HA and A-, The sum is constant (i.e. conserved)

$$f_A = \frac{K_A}{\left[H^+\right] + K_A} \quad and \quad f_{HA} = \frac{\left[H^+\right]}{\left[H^+\right] + K_A}$$

$$\boxed{\left[A^-\right] = f_A C_A = C_A \frac{K_A}{\left[H^+\right] + K_A}}$$

The fractions are just weighting of the actual proton concentration and the KA. Show that these fractions Draw a picture like figure 7.6 for Acetic acid. Identify the different species. Show that the fractions sum to 1, regardless of pH, so the mass balance is a constant. So the fraction of dissociation for the acid may be driven by pH which can come from any source. Connect the way the fractions work with LeChatelier's principle: If we add a lot of acid then the reaction is driven to the protonated form (back to reactant).

Lecture #: 19 Lec7c Complex mixtures of Salts and Acids
Sections: 7.5 and 7.6 , 7.7 Topics: The pH of a weak base, and the pH of mixtures of weak acids and forms of a diprotic acid in solution. The fraction dissociation applied to a diprotic acid.
For mixtures of weak acids we use the pushing power (to push protons into solution) of an acid which is $\sqrt{K_A C_A}$ up to the actual concentration of the acid, if KA>CA. In a mixture of acids the charge balance is just extended with more acid anions. If there is one that has a largest pushing power that is all one needs to get the pH. If the mixture is of several with about the same pushing power then we need to add the pushing powers (in a Pythagorean manner).
Generalize the fractional dissociation of a diprotic acid: What are the fractions of each component of a diprotic acid at a given pH? Use the dissociation fraction in conjunction with the charge balance expression. Compare with the NICE table.

A base (in the LB description) can either donate a hydroxide to solution or absorb a proton. In either event B is the base and the fundamental reaction is: $B \rightleftarrows HB^{+} + OH^{-}$. It is this reaction for which KB is defined. To see the general way this works compare ammonia and NaOH. In both cases the starting base is neutral and the conjugate base is a cation. The conjugate acid (which is an acid conjugate to the original base) may or may not contain explicitly an H.

Sample Problems: 1) What is the pH of a .0010 M NaOH solution; **2)** What is the pH of a 0.01 M solution of ammonia? 3) What is the pH of a mixture of 0.001M HF and 0.02M HCH_3CO_2 (acetic acid)? What is the dissociation fraction for each of these acids (or what is the concentration of the base conjugate to the acid)? **4)** Show that Na bisulfate is acidic but Na bicarbonate is basic. In all examples: Compare the NICE table with the charge balance expression.

Bottom Line Summary:
Bases work just like acids. If you just swap H+ and OH- and change the charge on all species, you have exactly the same equations. If you want the pH of a base, you should compute the pOH, and then pH=14-pOH at the end.
The presence of many acids just adds together the pushing power of each acid (including water). The iterative form helps check approximations; one iteration usually does it. The idea of fractions of the acid are generalized for a poly protic acid; generally one can deal with just one dissociation at a time, unless the problem is what is the pH of NaHA (A is the divalent anion).

Lecture #: 20 Lec7d Complex mixtures of Salts and Acids
Sections: 7.9 Revisited/Revised (and 7.10 and 7.11).

Topics: The application of the charge and mass balances to solving the pH of acids, bases and salts. This section goes over charge and mass balance. However, if we combine the equations in different ways, we can see results differently. The strategy. Use the dissociation fractions for the ions (which come from mass balance expressions) and plug those into the charge balance equation. This gives an equation for H (or OH) which can then be directly solved. (The chage balance also naturally includes the autoionization of the solvent, so you get an extra bonus in the expressions)

Sample Problems: 1) The pH of a a weak and a strong acid; the pOH of a weak and a strong base. **2)** The pH of a weak and a strong acid completing with water; **3)** The pH of a mixture of acids **4)** The pH of a salt of a weak acid and the pH of the salt of a weak base. **5)** The pH of a salt that is a mix of a weak acid and a weak base. For NH4CN compare the ratios of charged and uncharged forms of the two species.

Bottom Line Summary:
The entire set of acid base problems can be solved with this strategy. The use of charge balance as the core expression gives iterative forms that converge quickly for a wide variety of problems. See the sample types in the sample problems.

Lecture #: 21 Lec7e Summarize solving pH problems for variety of acids, bases and salts
Sections: 7.5 and 7.6 and 7.8, 7.9, 7.10
Topics: When using the Charge Balance expression, we automatically include the effect of the hydrolysis of water. All equations that arise from the charge balance will be exact unless otherwise indicated. Understand the pH of a salt that contains both a weak acid and a weak base. Be able to qualitatively (i.e. acidic or basic solution) and quantitatively predict the pH. Use LeChatelier's principle to tell us qualitatively whether the salt solution will be acidic/neutral/basic. Then develop an approximate (simple) formula to determine it quickly, based on the Charge Balance expression (What else?). Include the effect of water in all of these expressions just to know that the system goes to pH=7 as the concentration of the salt goes to zero.

Sample Problems: 1) What is the pH of 1M NaCl? **2)** What is the pH of 0.01M NaAc? **3)** What is the pH of 0.1M NH_4Cl? Review charge balance be sure you can write the charge balance for all these cases. You will be asked to recognize the correct charge balance for the corresponding problem on the exam.

Bottom Line Summary:
Principle 3: How to write down the Charge Balance and what does it mean.
Develop the Charge balance for the following cases:
Water; Acid; acid in water; Several Acids in Water; Salt of an acid;
Base in Water; Strong and Weak acid; The salt of a weak acid; the salt of a weak base.
Identify the base conjugate to the acid; and the acid conjugate to the base.

Principle 4: How to solve for the pH? Substitute in the fraction of each species into the charge balance. Arrange the Charge balance to reflect the answer. This provides a path to an iterative form (really don't need to iterate much, other than check the accuracy of the approximation.)

Solve for the salt of a weak acid and weak base. Determine whether it will be acidic or basic. Compare HCN and NaCN in solution, where $K_A = 1\cdot 10^{-10}$ for HCN. HCN is a very weak acid. $C_A = 10^{-2}M$ Identify the base conjugate to the acid; explain qualitatively why the pH of HCN is close to 7 (~6) but the pH of NaCN is very basic pH~11. Identify the $K_{B,A}$, and show that CN- is a base.
Does the salt, $NH_4^+CN^- \rightarrow NH_4^+ + CN^-$, that completely dissociates in water produce an acidic or a basic solution? We examine the relative pushing power of the two ions. NH_4^+ is a weak acid (being the acid conjugate to the weak base, NH_3) and similarly CN^- is a weak base. The concentrations of the two charged species, at the outset are the same: the pushing power (as defined above is) for the acid (to produce protons) is $\sqrt{K_{A,B}C_A}$ and for the base (to produce hydroxides) is $\sqrt{K_{B,A}C_B}$. Because both ions came from the same salt (by the above reaction): $C_A = C_B = C_S$. Therefore we need only compare The $K_{A,B} = \dfrac{K_W}{K_{B(NH_3)}}$ with $K_{B,A} = \dfrac{K_W}{K_{A(HCN)}}$. If $K_{B,A} > K_{A,B}$, then we get more hydroxide than protons and the solution is basic. This inequality is equivalent to $K_{B(NH_3)} > K_{A(HCN)}$ (which saves

us from doing the calculation). This condition is the case for these two species. We can then calculate $\left[OH^{-}\right]=\sqrt{K_{B(NH_3)}\cdot K_{B,A\,(HCN)}}=\sqrt{\left(K_W K_{B(NH_3)}\right)/K_{A(HCN)}}$. This approximation comes from the charge balance expression, which you should be able to write down and use to derive this approximate expression. (This expression is not in your text.)

Lecture #: 22 Lec8a. Make Buffers
Sections: 8.1-8.4
Topics: A buffer is an aqueous solution with an acid and the salt of a weak acid or a similar combination. The buffer relies on the Common ion effect. The point of a buffer is that it will minimize the change in the pH when an insult (either an acid or a base, such as HCl or NaOH, is added to the solution). What is the basic rule for when you have a buffer: $2C_{Na^+} + C_S = C_A + 2C_{Cl^-}$ (This expression comes from the charge balance and will be derived below.) This gives all possible ways to make a buffer from either a base or an acid and the conjugate salt of the base or acid. What you can't do is add NaCl and get a buffer. But you can add the salt of a weak acid, Cs, and co-dissolve it with the acid, $C_S = C_A$, or you can add a weak acid at concentration, C_A, and NaOH at concentration, C_{Na^+} and co-dissolve it at $2C_{Na^+} = C_A$, or add the salt of a weak acid and HCl so that $C_S = 2C_{Cl^-}$. Any of these methods work and lead to the same system where $pH = pK_A$ for a weak acid (such as Acetic Acid). A base may be similarly used.

The ability of a buffer to hold the pH is given by its buffer capacity, B.C.: For the buffer made from an acid and its salt: $B.C. = 2.3\left(\frac{C_A C_S}{C_A + C_S}\right) \sim C_A$, where when $C_S = C_A$ the B.C. is about the same as the concentration of the acid. When an insult is added (at concentration C_I) the pH will change by: $\Delta pH = \frac{C_I}{B.C.}$ as long as the insult is less than the B.C. If you want to adjust the pH to be near the pK_A but not equal then the SHH formula is useful: $pH = pK_A - \log_{10} \cdot \left\{\frac{C_A - C_{Na^+} + C_{Cl^-}}{C_{Na^+} + C_S - C_{Cl^-}}\right\}$. All of these conditions can be found from the charge balance expressions.

Sample Problems: Make a buffer of Acetic Acid with the acid and sodium acetate. The buffer must be able to absorb 1mM NaOH. Make a buffer of the same buffer capacity with NaAc and HCl. Explain how the buffer capacity is the same as the first solution, and be careful to explain how the concentrations work out to have the same buffer capacity. Adjust the HAc and NaAc concentrations so that pH=pK-1. What is the buffer capacity in this case?

Demonstrations: Compare two solutions at pH~4, one is HCl, the other is HAc. How much base can we add to move the pH by 2 units, to pH~6? The surprise is a large amount of un-dissociated acid can be hidden (or latent or sequestered) in the Acetic acid/Na Acetate buffer, and it will take a lot of base to move the pH of that solution. Similarly show what happens as we dilute with water.

Bottom Line Summary: Buffers are used everywhere in nature. Your blood (and other fluids) are controlled in their pH by the buffering action of the salts and blood itself in the body. For proper enzyme function (for metabolism and protein synthesis) it is necessary to control the pH of the system. Add a salt and an acid, A- is the common ion, which comes from two sources. The salt makes a basic solution, the acid makes an acidic solution, when you mix 1:1 you get an intermediate case where

$pH = pK_A$. Set up the mass balance and the charge balance expressions for adding C_A acid HA @ concentration C_A. and salt NaA @ concentration C_S.

Create a buffer: Make the pH be within one unit of the pKA of the acid. The buffer can come from the acid and its salt or the acid plus a strong base or the salt plus a strong acid (or any combination that gets the job done). Let us look at the charge balance expression for a complicated situation that covers all cases, we add a weak acid, concentration, C_A, and the salt of the weak acid, concentration, C_S, and we add a strong base (NaOH) concentration C_{Na^+}, and a strong acid (HCl) concentration C_{Cl^-}.

The charge balance is $\left[Na^+\right]+\left[H^+\right]=\left[OH^-\right]+\left[A^-\right]+\left[Cl^-\right]$

Substituting in the various concentrations, and using $\delta=\left[H^+\right]-\left[OH^-\right]$, and setting $pH = pK_A$, or $f_{A^-}=\frac{1}{2}$, we get: $\left(C_{Na^+}+C_S\right)+\delta=\left(C_A+C_S\right)\frac{1}{2}+C_{Cl^-}$. Therefore (neglect δ): $2C_{Na^+}+C_S=C_A+2C_{Cl^-}$.

When we meet this condition (or are close to it, the pH will be the pKA) and we will have a buffer. The full charge balance can be rearranged to be equivalent to the full Henderson-Hasselbalch form (FHH), which can be simplified (neglect δ) to the simple HH or SHH from.

$$\text{FHH:}\quad \left[H^+\right]=K_A\cdot\frac{C_A-C_{Na^+}+C_{Cl^-}-\delta}{\left(C_{Na^+}+C_S-C_{Cl^-}\right)+\delta}$$

Or in terms of pH: SHH: $pH = pK_A-\log_{10}\cdot\left\{\frac{C_A-C_{Na^+}+C_{Cl^-}}{C_{Na^+}+C_S-C_{Cl^-}}\right\}$

For the case of a buffer from only the salt and the acid, C_S and C_A:

$$pH = pK_A-\log_{10}\cdot\left\{\frac{C_A}{C_S}\right\}=pK_A-\log_{10}\cdot\left\{\frac{\left[HA\right]_o}{\left[A^-\right]_o}\right\}$$

Now we have a buffer. What is so great about that? A buffer resists change in the pH even when a strong base or strong acid is added. The change in the pH is related to the concentration of added base (called an insult) or C_I and $\Delta pH = pH_2-pH_1=-\log_{10}\left(\frac{\left[H_2^+\right]}{\left[H_1^+\right]}\right)=\frac{C_I}{B.C.}$ $\quad B.C.=2.3\left(\frac{C_AC_S}{C_A+C_S}\right)\sim C_A$

Buffers can resist change until the insult is greater than the amount of acid/salt present. Details depend on direction of change and relative amount of acid and salt. To compute the change in pH for the addition of an acid, the insult concentration must be considered as a negative number.

Lecture #: 23 Lec8b. Titration of a Weak Acid by a Strong Base
Sections: 8.5
Topics: Read by pH meter and by indicator. The titration of an acid by a strong, known base (e.g. NaOH) of known concentration ($C_B = C_{Na^+}$) is a great way to learn what the concentration of the acid, C_A, is. This works for a weak or a strong acid. A titration is a plot of the pH of the acid solution as base is progressively added. So pH is plotted as a function of the volume of the base added. Throughout the entire titration the charge balance is:

$C_{Na^+} + \left[H^+\right] = \left[A^-\right] + \left[OH^-\right] = f_{A^-}C_A + \left[OH^-\right]$ where $f_{A^-} = \dfrac{K_A}{K_A + \left[H^+\right]}$

The equivalence point (of a titration curve) is where one unit of base, equivalent to one unit of acid has been added. At the equivalence point the concentrations are $C_B = C_{Na^+} = C_A$ andd are further related through the charge balance: . Rearranging the charge balance expression for the hydroxide:

$\left[OH^-\right] = C_{Na^+} - f_{A^-}C_A + \left[H^+\right] = C_A - f_{A^-}C_A + \left[H^+\right] = f_{HA}C_A + \left[H^+\right]$

If the acid is a strong acid $f_{HA} = 0$ then $\left[OH^-\right] = \left[H^+\right] = 1\cdot 10^{-7}$. If the acid is a weak acid then $f_{HA} > 0$ and $\left[OH^-\right] > \left[H^+\right]$. Notice the equation for the pOH at the equivalence point is the same as that of the salt of a weak acid. For a titration we must compute the actual concentration in the beaker because the acid and base volumes dilute each other. If the titration starts with original volume $V_{o,A}$ and original acid concentration $C_{o,A}$ and you add V_B of base then the concentration of each is diluted, but the number of moles of acid is not changed:

$n_A = C_A\left(V_{o,A} + V_B\right) = C_{o,A}V_{o,A}$ or $C_A = C_{o,A}\dfrac{V_{o,A}}{\left(V_{o,A} + V_B\right)}$. And same type of dilution for the base $C_B = C_{o,B}\dfrac{V_B}{\left(V_{o,A} + V_B\right)}$. How do I know the equivalence point? If it is a strong acid then it occurs at pH=7. If the acid is weak, then the pH>7, but it will take very, very little more base to go from pH=7 to the equivalence point. In the next lecture, we discuss how to determine the K_A as well.

Sample Problems: 1) Start with 50 mls of a strong acid at 5 mM. This acid is titrated by 5, 10, 15 and 20 mls of 20.0mM base. Find the pH at each step of the titration. Hint: To help you see how the problem works: First find the number of mls of base needed to reach equivalence. **2)** Redo the same problem but the acid is a weak acid with K_A=1e-5. **3)** Redo the problem (exactly) to find the amount of base needed (C_B) to get the pH to 5 and 7 (why these places?); then to pH = 2, 4, 6 and 8.

Demonstrations: Titration of Acetic acid and Hydrochloric acid by NaOH.

Bottom Line Summary: Use the charge balance expression to determine the pH of a titration as a function of the amount of base added. Examine the amount of base added. There are four regions to consider. 1) No base (find pH of a weak acid), 2) Some base, use SHH form of the charge balance expression; 3) Equivalence point $C_B = C_{Na^+} = C_A$, use charge balance for the salt of a weak acid: 4) $C_B > C_A$, find pOH from charge balance assuming $f_{A^-} = 1$ so

$\left[OH^-\right] \approx C_{Na^+} - C_A + \left[H^+\right] \approx C_{Na^+} - C_A$.

It is much easier to find the amount of base needed to reach a certain pH than to find the pH after a certain amount of base has been added. Then determine how much (i.e. the volume) of the base that is needed $V_B = V_{o,A}\frac{C_B}{\left(C_{o,B} - C_B\right)}$ to reach that pH. What if the concentration is negative?

Use the charge balance expression to obtain a unified theory for the entire titration curve. Add base C_B to the acid C_A, the charge balance is

$$\left[Na^+\right] + \left[H^+\right] = \left[OH^-\right] + \left[A^-\right]$$

:
$$C_B = \left[OH^-\right] - \left[H^+\right] + C_A f_{A^-} = \frac{K_W}{\left[H^+\right]} - \left[H^+\right] + C_A\frac{K_A}{K_A + \left[H^+\right]}$$

This expression lets you compute the amount of base needed to give a certain pH, because the r.h.s. depends only on $\left[H^+\right] = 10^{-pH}$. So you just compute C_Bs for lots of values of pH over a range say 2 to 12, and then plot C_B on the x axis (abscissa) and pH on the y axis (ordinate) as though you had done the really hard problems, of solving a cubic polynomial, but you didn't. What does it mean if C_B is negative?

Lecture #: 24 Lec8c Titration
Sections: 8.5, 8.6 and figure 8.4.
Topics: What to look for in a titration curve. (See figure 8.4 in text). The strong acid and strong base have the equivalence point at pH=7. But when the acid is a weak acid, the equivalence point has a pH>7. All parts of the titration curve can be obtained from the single charge balance expression. The volume of base added from the burette, V_B^B, to reach the equivalence point is almost the same as that to obtain pH=7, and almost the same as that to obtain the endpoint of an indicator. At this point: $C_B \approx C_A$, therefore at half volume $C_B \approx \frac{1}{2} C_A$. This point, when put into the charge balance expression shows that $f_{A^-} = \frac{1}{2}$ (nearly), and that gives $pH = pK_A$. So the pK_A of an acid can be found graphically by looking to ½ way to the equivalence point and reading the pH off the graph. Notice you are in the center of the buffer zone and SHH form of the charge balance expression works very well. To use this method to obtain the pK_A you need to see the sharp rise in the pH when first adding base. What does that tell you? Why can't you get a pK_A=1.5 for a strong acid from the curve?

Sample Problems: 1) How much more base must be added to move the pH from 7 to the equivalence point? Consider a weak acid with $C_A = 1 \cdot 10^{-3} M$ and $K_A = 1 \cdot 10^{-5}$ (Neglect volume dilution). What is the incremental base concentration (then volume) relative to the amount of bases added to reach the equivalence point? Try to find the incremental amount without any numbers. 2) Graphically determine the pK_A and C_A of an unknown acid from the titration curve.

Demonstrations: Titration of Acetic acid and Hydrochloric acid.

Bottom Line Summary: Titration and the visual plot.
The sequential addition of a strong base (NaOH) to a flask containing a fixed amount of a weak acid. (or strong acid (HCl) with a weak base). Titration is done to determine the concentration of an acid, C_A, and determine the pK_A of the acid.
The titration curve consists of 5 regions.
1) Start, pure acid; 2) buffer region and midpoint of buffer region; 3) $pH = 7$; and 4) equivalence point $pH \geq 7$; 5) Past the equivalence point, solution basic. The underlying equation (the charge balance) is the same for all regions, the simplifying assumptions in each region give different looking expressions.

Be able to explain how one unambiguously determines the C_A and pK_A of the acid. Apply the principles to an unknown weak base. Computing the entire titration curve, no approximations no Balkanized formulae, from the root charge balance expression. Calculate the pH at each of the five places (listed) along the titration curve. Be sure to be able to identify from a graph each place, and be able to draw a graph (when given C_A and pK_A).

At start, pure acid, so we know how to determine the pH but we don't know either pCA or pKA. The midpoint is the half way point when $C_B = \frac{1}{2} C_A$. At this point $pH = pK_A$. To find this point we need to find the equivalence point (which is often taken as the endpoint) when $C_B = C_A$. From here we can go back and find the midpoint and then get the $pH = pK_A$ at that point. The equivalence point is when the change in pH with base is maximal (i.e. the rise of pH is steepest at this point and for a weak acid is slightly basic, usually in the 8 to 9 pH range). The equivalence point is exactly what it means, when $C_B = C_A$. The endpoint is a property of the indicator used, and is an optical estimate to the equivalence point. So an indicator is optimal when its pK_I is close to 8 or 9. This is when you can see the color change and why phenolphthalein is so popular for weak acids. The approximate/working expressions the 5 regions are:

$$1 \quad \left[H^+\right] = \sqrt{K_A C_A} \qquad 2 \quad \left[H^+\right] = K_A\left(\frac{C_A - C_B}{C_B}\right) \qquad 3 \quad C_B = C_A \frac{K_A}{K_A + 1\cdot 10^{-7}}$$

$$4 \quad \left[OH^-\right] = \sqrt{K_{B,A} C_A} \qquad 5 \quad \left[OH^-\right] = C_B - C_A$$

Be sure to correct for volume dilution of both the acid and the base. If the initial concentration of the acid is C_A^0 in volume V_A^o, and we add volume V_B^B from the burette of base at concentration C_B^B in the burette, then $C_A = C_A^0 \cdot \frac{V_A^o}{V_A^o + V_B^B}$ and $C_B = C_B^B \cdot \frac{V_B^B}{V_A^o + V_B^B}$, the is true because moles are conserved and thee correction factors are volume dilution factors; the ratio of each contribution to the total volume (the denominator).

Lecture #: 25 Lec8d Titrations Continued
Sections: 8.5, 8.6, 8.7
Topics: The titration of a weak base with a strong acid (HCl). Set up and use the charge balance expression (again) and the appropriate form of the fraction of base that is positively charged (either protonated or dehyroxlyated). In either event, the undissociated form of the base is neutral (and does not show up directly in the charge balance). As a check, compare with the titration of a weak acid with a strong base and exchange H^+ and OH^- in all expressions (and the signs of all charges reverse from the acid cases) and solve for pOH (rather than pH).

Consider a diprotic acid titrated by NaOH. Uses the charge balance expression; and generalizes fractions of species). How much base is needed to achieve the first and second equivalency points, and what is the pH at these two points. Find the pH at the half way points and find both pK_{A1} and pK_{A2}. Need to start with a charge balance expression. The first equivalence point occurs when $C_B = C_A$, $\left[H^+\right] = \sqrt{K_{A1}K_{A2}}$ and the second when $C_B = 2C_A$. Use the charge balance to develop an expression for the pH at these points. Generalize the titration to find what the pH is when $C_B = \frac{1}{2}C_A$ (use K_{A1} reaction only) and $C_B = \frac{3}{2}C_A$, (use K_{A2} reaction only) and relate to the pK_As.

Sample Problems: 1) What is the pH of a solution of 0.01M ammonia (in water), and then what concentration of strong acid (HCl) will be need to bring the pH to 8, to 7 and to the equivalence point. (Neglect volume dilution.) **2)** Read the pKAs and the concentration of base from a curve of a weak base titrated by a strong acid (HCl). **3)** Compare the pH of Na-bisulfate and Na-bicarbonate. Notice that this problem can be used as an experimental method to determine the pK_{A1} of sulfuric acid.

Demonstrations: Titrate carbonic acid with NaOH; Show the pH of different polyprotics like phsporic acid, compare to coke. Show the pH using an indicator of $NaHSO_4$ and $NaHCO_3$.

Bottom Line Summary:
Calculate the pH at all the places along the titration curve. Add base at concentration C_B in the flask. Correct the Base and Acid concentrations for the volume dilution effect. Use approximate expressions to obtain close results. Identify: start, midpoint and equivalence point. What can you learn from just the endpoint with an indicator?

Titrating a weak base with HCl:
Use the charge balance expression to obtain a unified theory for the entire titration curve for the titration of a weak base with a strong acid (HCl). Add the acid $C_A = C_{Cl^-}$ to the weak base (in the beaker) $C_B = B + HB^+$. The charge balance is

$$\left[OH^-\right]+\left[Cl^-\right]=\left[HB^+\right]+\left[H^+\right]$$

:

$$C_A = C_B f_{BH^+} + \left[H^+\right] - \left[OH^-\right] + = C_B \frac{K_B}{K_B + \left[OH^-\right]} + \left\{ \frac{K_W}{\left[OH^-\right]} - \left[OH^-\right] \right\}$$

This expression lets you compute the amount of acid needed to give a certain pOH, because the r.h.s. depends only on $\left[OH^-\right] = 10^{-pOH}$. So you just compute C_As for lots of values of pOH over a range say 2 to 12, and then plot C_A on the x axis (abscissa) and $pH = 14 - pOH$ on the y axis (ordinate) as though you had done the really hard problems, of solving a cubic polynomial, but you didn't.

The Diprotic Acid titration curve (an extension of a monoportic acid):

At the beginning of the titration, before any strong base is added, the pH is determined by the first KA, KA1. During titration to the first equivalence point, the first midpoint is pH=pKA1 and CB=(1/2)CA, and the SHH (using only the first dissociation reaction) works in this first buffer region, about pK1 to give the pH. Then at the (first) equivalence point $\left[H^+\right] = \sqrt{K_{A1}K_{A2}}$ or $pH = \frac{1}{2}\left(pK_{A1} + pK_{A2}\right)$, and CB=CA at this first equivalence point. (This is the same problem as finding the pH of the salt NaHA). The titration continues and the second proton is removed around the region of the second midpoint, when pH=pKA2, the SHH gives the correct pH in the second buffer region using only the equilibrium for the second proton coming off the acid; you need to remove the base used to titrate the first acid off. At the second midpoint CB=(3/2)CA. The second and final equivalence point, where OH~sqrt(CaKB,A2). And CB=2CA, so both protons are now titrated (off). Beyond this point OH=CB-2CA, all of the acid has been titrated and the acid is fully ionized to the A(2-1) ion. All of these specific points and all points in between are determined from various solutions to <u>the same</u>, single charge balance expression.

You should be able to identify the region of the titration curve from the values of CB relative to CA, and from the pH relative to the pKAs.
Finding the first (internal) equivalence point for a diprotic acid is (not obviously) found as the geometric average of the pKAs around the equivalence point.

$$\left[H^+\right] = \sqrt{K_{A1}K_{A2}}$$

You will need to be able to identify the correct charge balance expression, mass balance expression, Henderson-Hasselbalch forms and fraction of each species and relevant approximations in each part of the titration curve. You will need to be able to compute the correct pH given a CB and go the other way, compute the correct CB given a pH.

The condition that $\left[H^{+}\right]=\sqrt{K_{A1}K_{A2}}$ is the same one found for determining the pH of sodium bisulfate and sodium bicarbonate, for the same reason, and comes from the requirement that: $f_{H_2A} = f_{A^{2-}}$.