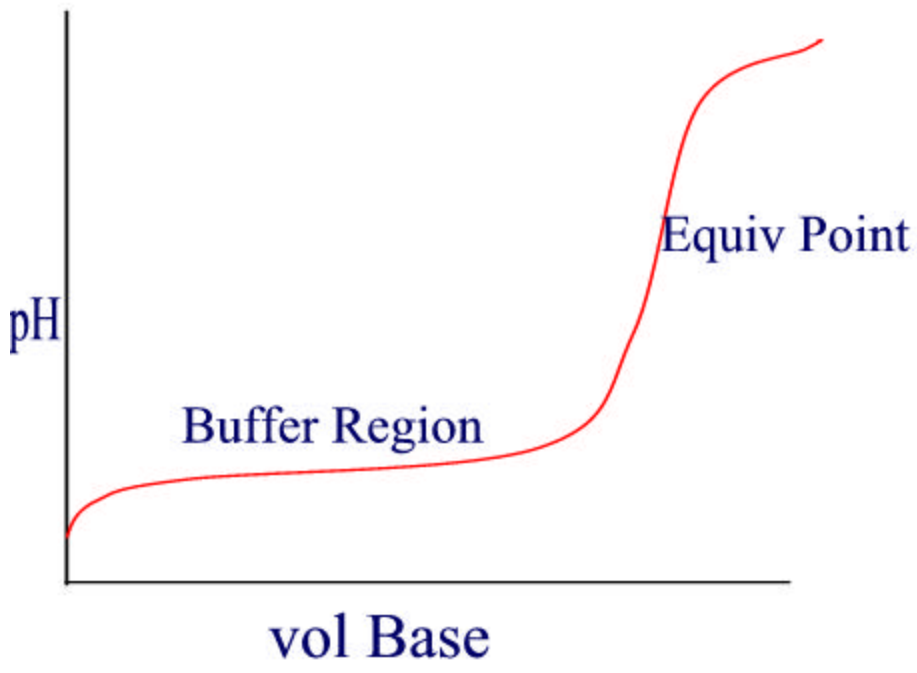
Announcements

- HW and Quiz scores updated-please check
- Windows with the Ks have been added to pages 73 and 81

Buffer Redux

- The behavior of buffers is readily explained by examination of a titration curve



- Details from Tues buffer question
- Adding .50g of NaOH to 100mL of buffer

What chemical reaction occurs when the OH^- is added to the mixture?

CH_3CO_2H + OH- => $CH_3CO_2^-$ + H_2O

- How many moles of all the species, including the hydroxide are present before the reaction?
  - CH_3CO_2H=1.00M*0.100L=0.100moles
  - $CH_3CO_2^-$ =1.10M*0.100L=0.110moles
  - OH^- =0.50g/40g/mole(gfw of NaOH) =.0125moles
- How many moles are present after?
  - CH_3CO_2H=0.100-0.0125=0.087
  - $CH_3CO_2^-$ =0.110+0.0125=0.123
- What is the new pH?
  - pH=4.74+log(0.123/0.087)=4.89

- Adding 10.0mL of 0.10M HCl to 50 mL of buffer

What chemical reaction occurs when the H^+ is added to the mixture?

$CH_3CO_2^- + H^+ \Rightarrow CH_3CO_2H$

- How many moles of all the species, including the H^+ are present before the reaction?
  - CH_3CO_2H=1.00M*0.050L=0.050moles
  - $CH_3CO_2^-$ =1.10M*0.050L=0.055moles
  - H^+ =0.10M*0.010M =.0010moles
- How many moles are present after?
  - CH_3CO_2H=0.050+0.001=0.051
  - $CH_3CO_2^-$ =0.055-.001=0.054
- What is the new pH?
  - pH=4.74+log(0.054/0.051)=4.76
- To illustrate the buffer effect- calculate the pH that would result from adding the acid solution to water, instead of to the buffer.

Buffer Capacity and Optimum Buffer pH

- As noted, the optimum buffer pH is when $pH=pK_a$,. Such a buffer will have equal resistance to both acid and base
- In certain instances (your blood buffer), it is preferable to bias the buffer to be more resistant to acid or base
- The capacity of a buffer is the amount of acid or base needed to “overwhelm” it or remove its buffering ability. This depends on the concentrations and the volume of the buffer solution. As a general rule, the capacity could be viewed as the equivalents of base or acid needed to change the pH of one liter of buffer by one pH unit. Before actually using a buffer in the “real” world, its capacity should be known.

Buffers from conjugates of weak bases

- None of the monoprotic acids in your table has a Ka with exponent of –6, so they are not the best for preparing a 5.x buffer.
- However, if you examine the table of bases, you see that 2 of them, pyridine and hydroxylamine have K_bs with exponents of –9 which means that their conjugate acids will have Kas with exponents of –6. Thus a buffer of pH 5.x could be based upon using a mixture of either of these bases and its conjugate acid.
- Ex: prepare a buffer of pH=5.50 using pyridine and its conjugate acid
  - Ka for $C_5H_5NH^+=10^{-14}/Kb=5.5*10^{-6}$ pKa=5.26
  - using standard methods it can be shown that for the pH to be equal to 5.50 $[C_5H_5N]/[C_5H_5NH^+]=1.74$
  - Is the above result what you would have expected?

LeChatelier and Acid/base systems

- The table below illustrates % ion as a function of Ci for a weak acid with a Ka=3.5*10^{-4}. The values shown are illustrative of the general trend observed. The exact values for a given weak acid depend on its K_a. Similar results would be found for a weak base. Is this what you'd expect based upon the principle of LeChatelier?

Ci	%ion
0.1	5.7
0.05	8.0
0.01	17
0.005	23
0.001	44
0.0005	56

More LeChatelier-the Common Ion Effect

- Consider a solution of a weak acid where equilibrium has been established according to the general equation:

$$HA + H_2O \Leftrightarrow A^- + H_3O^+$$

- What are the consequences, qualitatively, if a strong acid is added to this mixture? What is the best measure (of the seven magic things) for describing what happens in general terms?
- Does the sequence matter? That is, suppose you added the weak acid to a solution of a strong acid?
- Can the mixture be analyzed quantitatively? That is, how do you determine the % ionization for a solution which contains 0>10M HCl and O.10M HNO_2?
- Under what conditions is this analysis simplified?
- Describe an analogous system for a weak base. What will the common ion be?
- How does a solution of H_2SO_4 represent, in a way, a common ion effect? How would you analyze a 0.10M solution of H_2SO_4?

Indicators

- Logic requires that if changing the [OH-] in a solution can cause an indicator to undergo a color change then the indicator is reacting with the OH^- and it must be an acid.
- $HIn \Leftrightarrow H^+ + In^-$ $K_{a(HIn)}$
- HIn and In- must be different colors(one may be colorless)
- The color observed will depend on [In-]/[HIn]-that ratio should look familiar.
- In general the color change is observed as the above ratio (assuming you're going from low to high pH) goes from 0.10 to 10.
- How is the above transition related to the $pK_{a(HIn)}$?

Relative Strengths of Acids

- The question of why acids vary in their tendency to dissociate in water is clearly fundamental and complex. A complete analysis of this requires a relatively thorough examination of the thermodynamics of the process-most readily done by use of Hess' law-the most beloved of all thermodynamic principles.
- What would a Born-Haber type cycle for the process HA $+H_2O$ => A-(aq) + H_3O+ look like?
- What do you think would be the major factors that would cause variation in the relative acidities?

Lewis Acids and Bases

- As has been noted on a number of occasions, there are quite a few acid/base definitions, of varying popularity. One of the major systems is the Lewis system which, like B-L, focuses not on an individual species, but on a process.
- In the Lewis system an acid is an electron pair acceptor and a base is an electron pair donor. The process is the formation of a covalent pair. The difference here is that the bond is formed when:
  - B: + A => B:A
  - Ex: F_3B + $:NH_3$ => $F_3B:NH_3$
- The bond resulting is called either dative or coordinate covalent.
- You should readily see that B-L theory is included in that as $H^+ + :NH_3$ => $H:NH_3^+$ (shown here in a slightly different fashion than usual) is clearly a Lewis process.
- As expected, the bases will be compounds having atoms with lone pair electrons with the nitrogen bases being the most common. However, it is worth noting that all of the neutral species anions in aqueous media (Cl^-, etc) are Lewis bases.
- The acids are either electron deficient compounds, like BF_3, or metal cations.
- The largest category of Lewis compounds of interest involve the binding of bases to transition metal cations. These will be discussed at a later time.

Solubility Equilibrium

- A saturated aqueous solution of a slightly soluble salt represents an equilibrium between the solid and its product ions
  - $M_aX_b(s) \Leftrightarrow aM^{z+}(aq) + bX^{y-}(aq)$
- Like all other equilibria, it is described by a Q and a K.
  - $Q_{ion} = [M^{z+}]^a[X^{y-}]^b$ –**the ion product**
  - As with all Qs, Q_{ion} has values for all possible solutions and a unique value for the equilibrium condition. For solubility, that value is called K_{sp}, **the solubility product**.
- Just as there were seven quantities of interest in acid/base solutions, there are five in solubility:
  - K_{sp}
  - gs-the gram solubility(mass of solute which will dissolve in 100g of water)
  - s-molar solubility (moles of solute per liter in the saturated solution
  - $[M^{z+}]$-cation concentration in the sat'd solution
  - $[X^{y-}]$-anion concentration in the sat'd solution

Things to ponder

- Is there some real standard that makes a material soluble or insoluble?
- Does the Ksp, by itself, give a good description of the solubility characteristics of a salt? Why is this different from the Ks in acid/base chemistry?
- From a practical standpoint, which of the previously noted measures should we use when trying to understand the degree to which a salt dissolves?
- How are the five quantities related?