AP Chemistry
Chapter 17 Outline

1. The Common-Ion Effect
    i. If you add a salt that contains an ion formed as a product in the equilibrium, the equilibrium will shift to the left.
    ii. Formally: The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte.
        1. Basically, treat these as ICE-strategy problems. The salt is considered an initial source of the common ion. Proceed as with any equilibrium problem.
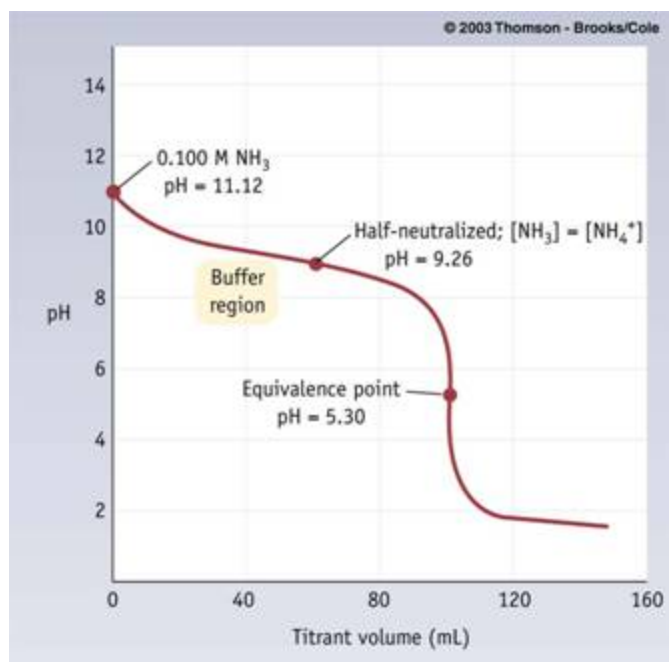
2. Buffers
    a. Solutions which can resist drastic changes in pH when small amounts of strong acid or strong base are added   VERY IMPORTANT TOPIC
    b. Buffers contain a weak acid with a salt of its conjugate base.
        i. OR, a weak base with a salt of its conjugate acid $HX + MX$
        ii. Add OH^- to solution: reacts with the acid to produce X^-:
            1. $OH- + HX \rightarrow H_2O + X^-$
            2. [HX] decreases, [X-] increases but ratio changes only slightly, so pH change is small
        iii. add H^+ to solution: reacts with the conjugate base:
            1. $H^+ + X^- \rightarrow HX$
            2. [X^-] decreases, [HX] increases; if the ratio changes only slightly, pH change is small
    c. Use an ICE approach to calculate the pH of a buffer system
        i. Can use the Ka expression
            1. from rearranging the K_a expression: $[H^+] = K_a \dfrac{[A^-]}{[HA]}$
            2. pH = -log[H^+]
        ii. Can also use the Henderson-Hasselbach equation
            1. $pH = pK_a + \log \dfrac{[base]}{[acid]}$ Be careful—only use this equation for buffer systems!
            2. $pK_a = -\log K_a$
    d. Buffer capacity
        i. the amount of acid or base the buffer can neutralize before the pH begins to change appreciably
        ii. Depends on the amount (moles) of weak acid and conjugate base used to prepare the buffer

e. pH of the buffer depends on the K_a for the acid & relative concentrations of base and acid
  i. The pH range of the buffer is the pH range over which the buffer acts effectively
  ii. Buffers usually have a usable range with ± 1 pH unit of the pK_a of the acid
f. Addition of strong acids or bases to buffers
  i. Can assume that all of the strong acid or base is consumed (as long as we don't exceed the buffering capacity)
    1. Use stoichiometry to calculate the amount of weak acid left, total concentration of weak base present after neutralization of the strong acid or base
    2. Use the H-H equation to calculate new pH (alternatively, use ICE approach and the Ka expression)

3. Acid-Base Titrations
  a. A solution containing a known concentration of base is slowly added to an acid (or, the acid is added to the base)   This is a critically important topic!
  b. Equivalence point = the point at which stoichiometrically equivalent quantities of acid and base have been combined
    i. Use acid-base indicators or pH meter to determine the equivalence point
    ii. Titration curve = plot of pH vs. volume of added titrant
  c. Strong acid-strong base titrations
    i. Low initial pH, very slow pH changes at first (based on concentration of unneutralized acid), then very sudden pH changes near equivalence point
    ii. pH = 7 at equivalence point
    iii. pH levels off, determined by concentration of excess base
    iv. choose indicator to change color in correct pH range: phenolphthalein is often used
  d. Weak acid-strong base titrations   Check out the animations and pay close attention to the predominant chemical species as the titration proceeds
    i. Initial pH depends on Ka value, concentration of weak acid (Section 16.6)
      1. Is higher than pH of a strong acid at the same concentration
    ii. As base is added, a buffer system develops, (can use H-H here)
    iii. At the half-titration point, pH = pKa
    iv. pH > 7 at equivalence point, because the anion of the salt formed is a weak base (KNOW THIS!)
      1. pH change for rapid-rise portion is smaller for weak acid than for a strong acid
    v. pH levels off, determined by concentration of excess base
    vi. choice of indicator is quite important: Choose an indicator with a pKa close to expected pH of endpoint, or with color change in expected pH range

e. <u>Weak-base strong acid titrations</u>
    1. Starts at a high initial pH (depends on the Kb and concentration of the weak base)
    2. As acid is added, the pH drops
    3. pH < 7 at endpoint, because the weak acid is formed
    4. Choose an indicator that will change color near the pH of the expected endpoint

f. <u>Titrations of polyprotic acids</u>
    i. Reactions with OH- proceeds in a series of steps, each with a distinctive equivalence point

© 2003 Thomson - Brooks/Cole

0.100 M NH$_3$
pH = 11.12

Half-neutralized; [NH$_3$] = [NH$_4^+$]
pH = 9.26

Buffer region

Equivalence point
pH = 5.30

pH

Titrant volume (mL)

4. Solubility equilibria: <u>K$_{sp}$ problems</u>   CRITICAL PROBLEM TYPE
  a. If $AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$ if $AB_2(s) \rightleftharpoons A^+(aq) + 2B^-(aq)$
    i. $K_{sp} = [A^+][B^-]$ $K_{sp} = [A^+][B^-]^2$
    ii. Note that the solids are always the reactants in the equations
    iii. K$_{sp}$ values are generally very small; it's an equilibrium constant & is unitless
    iv. Solubility of a substance = the quantity of that substance that dissolves to form a saturated solution; may be expressed as g/L or molarity
  b. 2 main types of K$_{sp}$ problems:
    i. Calculate K$_{sp}$ from solubility
    ii. Calculate solubility from K$_{sp}$
    iii. For both types:
        1. start with a balanced equation for the undissolved solid and its ions in solution
        2. write a K$_{sp}$ expression
        3. set up an ICE table to determine relative concentrations of ions, then solve!

5. Factors that affect solubility
  a. Common ion effects
    i. In general, the solubility of a slightly soluble salt is decreased by the presence of a second solute that contains an ion in common with the slightly soluble salt.
        1. Use an ICE approach and solve as an equilibrium problem
            a. In the ICE table, use the concentration of the common ion in solution as the initial concentration
            b. Usually, x << [initial]

b. Solubility and pH
    i. If the anion of the solute is basic, the solubility of the salt will increase as pH is lowered.
        1.   Basic anions: carbonate, phosphate, cyanide, sulfide, fluoride, hydroxide
            a. These are the conjugate bases of weak acids
    ii. Salts whose anions are the anions of strong acids are unaffected by pH.
c. Formation of complex ions
    i. Complex ion = assembly of a metal ion and the Lewis bases attached to it
    ii. Transition metal ions can act as Lewis acids
        1. Water molecules and other Lewis acids can react with metal ions
        2. Lewis acid-base reactions that result in complex ions can dramatically increase the solubility of a slightly soluble salt
            a. Metals that often form complex ions: Al^{3+}, Ag^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} (this is not an exhaustive list)
            b. Lewis bases (aka ligands) often found in complex ions: NH_3, H_2O, CN^-, OH^- especially if they are stated to be concentrated or "in excess"
            c. Rule of them: when in doubt, number of ligands = 2x the charge of the metal cation
    iii. Amphoteric acids and bases
        1. can be made to dissolve in either acidic or basic conditions
        2.   Oxides and hydroxides of Al^{3+}, Zn^{2+}, Cr^{3+}, Sn^{2+}
            a. they dissolve in acidic solutions because they have basic anions
            b. they dissolve in strongly basic solutions because they form complex ions involving hydroxides

6. Precipitation and Separation of Ions
    a. Use the reaction quotient, Q
        i. If Q > K, too much product—thereforem precipitation will occur (until Q = K)
        ii. If Q = K, solution is saturated and is at equilibrium
        iii. If Q < K, too much reactant—therefore solid will dissolve (until Q = K)
    b. Selective precipitation of ions
        i. Use the K_{sp} values and K_{sp} expressions to determine the concentration of the common ion needed to precipitate each salt
            1. The salt with the lowest K_{sp} is the least soluble and would precipitate first
            2. Be careful about comparing salts with different total numbers of ions—you will need to do Q calculations before determining which will precipitate first

7. Qualitative analysis for metallic elements
    a. Know your solubility rules!
        i. Do the most selective separations first: the ones that take out the smallest number of ions
        ii. Can do additional testing, as well:
            1. Flame tests:

2. Metal ion	3. Flame color
4. Potassium	5. Lavender
6. sodium	7. Yellow-orange
8. Copper	9. green
10. Strontium	11. red