AP Chemistry
Chapter 16 Outline

1. Acids and Bases
   a. Operational Definitions (characteristic properties)
      i. Acids taste sour, turn litmus paper red and react with certain metals to release hydrogen gas.
      ii. Bases taste bitter, feel slippery, turn litmus paper blue and phenolphthalein pink.
   b. Arrhenius acid-base theory (aqueous solutions)
      i. Acids produce H^+ ions in water
         1. Ex. HCl
      ii. Bases produce OH^- ions in water
         1. Example: NaOH

2. Brønsted-Lowry Acids and Bases
   a. An H^+ ion is a bare proton, with no electrons
      i. Tends to form hydronium ions, H_3O^+ in water
   b. Bronsted-Lowry theory emphasizes proton transfer reactions
      i. B-L acid: a substance that can donate a proton to another substance
      ii. B-L base: a substance that can accept a proton
      iii. Amphiprotic: can act as either an acid OR a base
   c. Conjugate acid-base pairs: HX and X^-
      i. One is a reactant, the other is a product
      ii. Formulas differ only by a H^+
      iii. Two sets of conjugate pairs in any B-L reaction
   d. Not all acids and bases are equally good at donating or accepting protons
      i. The stronger the acid, the weaker its conjugate base; the stronger a base, the weaker its conjugate acid.
         1. The conjugate bases of strong acids have practically no tendency to accept protons.
         2. The conjugate bases of weak acids are weak bases.\
      ii. The equilibrium position favors transfer of the proton to the stronger base.
         1. The stronger acid and the stronger base will react to form the weaker acid and the weaker base.

3. The autoionization of water $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$
   a. No individual molecule remains ionized for very long!
   b. $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25^oC **Memorize this!**
      i. This is true in ANY (dilute) aqueous solution
         1. If $[H_3O^+] = [OH^-]$ the solution is "neutral"
         2. If $[H_3O^+] > [OH^-]$ the solution is acidic
         3. If $[H_3O^+] < [OH^-]$ the solution is basic

4. The pH scale   Know this entire section!
    a. $[H_3O^+]$ in a solution is usually very small
        i. $pH = -log[H_3O^+]$ or $pH = -log[H^+]$
    b. the pH of a neutral solution is 7.00 at 25^oC
        i. the pH of an acidic solution is <7
        ii. the pH of a basic solution is >7
    c. for mental math: if $[H_3O^+]$ is 1×10^{-x}, $pH = x$ (you can use this to estimate pH)
    d. $pOH = -log[OH^-]$ Be able to do calculations with these equations!
    e. pH + pOH = 14
    f. Measuring pH
        i. Use a pH meter
        ii. Use indicators (less precise)

5. Strong acids and bases
    a. Strong electrolytes that exist in aqueous solutions are found entirely as ions
        i. 100% dissociation
        ii. Memorize the strong acids: HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4
    b. In aqueous solutions of strong acids, the acid is the only significant source of H^+ ions
        i. Typically ignore the H^+ concentration from the autoionization of water
        ii. $[H^+]$ = the original concentration of the acid for monoprotic acids
    c. Memorize the strong bases: hydroxides of the alkali metals and the heavier alkaline earth metals
        i. Basic anhydrides: metal oxides will form hydroxides when dissolved in water

6. Weak acids
    a. Most acidic substances are weak acids, only partially ionized in solution
        i. Typically less than 5% of the molecules dissociate
    b. $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ or $HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{or} \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

        1. Only H atoms attached to oxygen atoms show acidic behavior
        2. The larger the value of K_a, the stronger the acid
    c. Classic problem type: Calculating K_a from pH
        i. Write out balanced equation & K_a expression
        ii. Set up an ICE table to find concentrations of the species involved
            1. The initial $[H^+] = 10^{-pH}$
            2. Unless you are told otherwise, assume $[A^-] = [H^+]$
            3. Assume that (initial acid concentration – change) $\approx$ (initial acid concentration);
            4. This approximation is acceptable if the % ionization is < 5% or if K_a is 10^{-4} or smaller (this will avoid needing to use the quadratic formula)
        iii. Substitute into K_a expression and evaluate

d. The pH of a weak acid solution is higher than that of a strong acid of the same molarity

    i. $\% \ ionization = \dfrac{change \ in \ [HA]}{initial \ [HA]} \times 100$

e. Polyprotic acids have more than one ionizable hydrogen atom.

    i. $H_2A \leftrightarrow H^+ + HA^-$ K_{a1}

    ii. $HA^- \leftrightarrow H^+ + A^{2-}$ K_{a2}
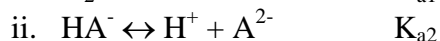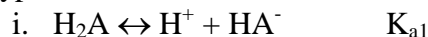
    iii. It is always easier to remove the first proton than following protons.

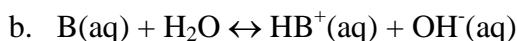   1. $K_{a1} > Ka2$

        2. As long as successive K_a values differ by a factor of 10^3 or more, consider only Ka_1

7. Weak bases

  a. Weak bases may either …

    i. Have a pair of nonbonding electrons that can accept a proton OR

    ii. be the anions of weak acids

  b. $B(aq) + H_2O \leftrightarrow HB^+(aq) + OH^-(aq)$

    i. $K_b = \dfrac{[HB^+][OH^-]}{[B]}$

  c. You must be able to solve equilibrium problems involving weak bases

    1. Start with a balanced equation and K_b expression

    2. Unless you are told otherwise, assume that $[HB^+] = [OH^-]$

    3. Assume that x <<initial concentration in the ICE table

    4. Solve for $[OH^-]$

    5. $[OH^-] \rightarrow pOH \rightarrow pH$

8. Relationship between K_a and K_b

  a. K_a x $K_b = K_w$ for a conjugate acid-base pair! MEMORIZE THIS

    i. If you know K_a for a weak acid, you can use this relationship to solve for K_b of its conjugate base

    ii. In some problems (especially involving weak bases) you may only be given the K_a for conjugate acid!

  b. Often, K_a values are reported as pK$_a$ (-log K_a)

    i. If the pKa is very large, the acid is weak

    ii. If the pKa is very negative, the acid is strong

    iii. $pK_a + pK_b = pK_w = 14.00$ at 25^oC

9. Acid-base properties of salt solutions

  a. Ions can exhibit acidic or basic behavior

  b. Hydrolysis reaction: salt + water $\rightarrow$ acid + base

  c. Predicting the pH of salt solutions:

    i. An anion that is the conjugate base of a strong acid (such as Cl^-, NO_3^-, I^-, Br^-, and ClO_4^-) will not affect the pH.

    ii. An anion that is the conjugate base of a weak acid will produce a basic solution.

        iii. A cation that is the conjugate acid of a weak base will produce an acidic solution.

        iv. The cations of the strong Arrhenius bases (i.e., the group 1 metal cations and the lighter group 2 metal cations) will not affect the pH.

        v. Other metal ions (especially transition metal cations) will produce an acidic solution.

        vi. If both the conjugate base of a weak acid and the conjugate acid of a weak base are present, the ion with the larger K_a or K_b value will determine the pH of the solution.

10. Acid-Base behavior and chemical structure
    a. Three main factors:
        i. A molecule containing hydrogen will transfer a proton only if the H-X bond is polarized so that the H atom has a $\delta+$ charge and the X atom has a $\delta-$ charge
        ii. Very strong bonds are less easily dissociated than weaker ones.
        iii. The greater the stability of the conjugate base, the stronger the acid.
    b. Binary Acids
        i. Acidity decreases down a column
           1. H-X bond strength decreases as X increases in atomic radius
        ii. Acidity increases L-R in a period
        iii. H-X bonds become more polar going L-R
    c. Oxyacids
        i. As central atom becomes more electronegative, acid strength increases
        ii. <u>For the same central atom, acid strength increases as the number of oxygen atoms increases</u>   KNOW THIS
           1. Electron density is pulled away from the OH bond, making the bond more polar
    d. Carboxylic acids
        i. Resonance structures for the conjugate base help to stabilize it

11. Lewis acids and bases—broadest theory of the 3   Know this whole section!
    a. Lewis acid = electron pair acceptor
        i. Lewis acids have an empty valence orbital
        ii. Many cations can act as Lewis acids
    b. Lewis base = electron pair donor
        i. Lewis bases have a lone pair of electrons
    c. Hydrolysis of metal ions
        i. hydration as a Lewis acid-base reaction
           1. As metal cation charge increases, metal ion is more acidic
           2. As radius decreases, the metal ion is more acidic
    Note: <u>Lewis acid-base theory</u> is also relevant for <u>complex ion reactions</u>