Chapter 14 - Acids and Bases

14.1 The Nature of Acids and Bases
- A. Arrhenius Model
 - 1. Acids produce hydrogen ions in aqueous solutions
  - 2. Bases produce hydroxide ions in aqueous solutions
- B. Bronsted-Lowry Model
  - 1. Acids are proton donors
  - 2. Bases are proton acceptors
  - 3. H_3O^+ is called the hydronium ion
- C. Conjugate Acid-Base Pairs
  - 1. A conjugate base is what remains after an acid has donated a proton
    - a. Cl^- is the conjugate base of HCl
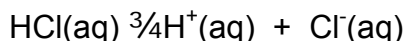 - 2. A conjugate acid is what is formed when a base accepts a proton

    base   acid   acid   base
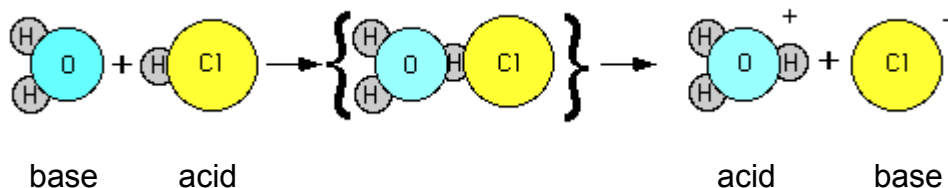
  - 3. HCl is a stronger base than H_3O^+ (H^+) so the equilibrium lies far to the right
- D. Acid Dissociation Constant
  - 1. $K_a = \dfrac{[H^+][Cl^-]}{[HCl]}$
    - a. water is not included because, in dilute solution, the concentration of water is high, and changes so little it is assumed to be constant
    - b. The dissociation constant is the same as for the dissociation equation here:
      $$HCl(aq) \frac{3}{4} H^+(aq) + Cl^-(aq)$$
    - c. K_a is used only for this type of expression
    - d. For strong acids such as HCl, the equilibrium lies so far to the right that [HCl] cannot be measured accurately, and an accurate calculation of K_a is not possible

14.2 Acid Strength
- A. Strong Acids
  - 1. Acids for which the equilibrium lies far to the right
    - a. Strong acids yield weak conjugate bases
  - 2. Common strong acids
    - a. sulfuric, hydrochloric, nitric, perchloric

B. Weak Acids
    1. Acids for which the equilibrium lies far to the left
        a. Weak acids yield relatively strong conjugate bases
C. Acid Terminology
    1. Monoprotic - one acidic proton
    2. Diprotic - two acidic protons
    3. Triprotic - three acidic protons
    4. Oxyacids - acids in which the acidic proton is attached to an oxygen atom
    5. Organic acids - acids containing the mildly
        acidic carboxyl group
        a. Generally weak acids
        b. Equilibrium lies far to the left

$C = O$
O
H ⟵ ionizable hydrogen
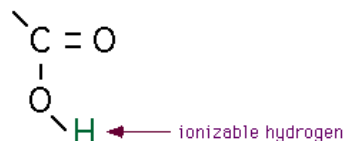
D. Water as an Acid and a Base
    1. Water can act as an acid or as a base
   a. Autoionization of water (Self-ionization)
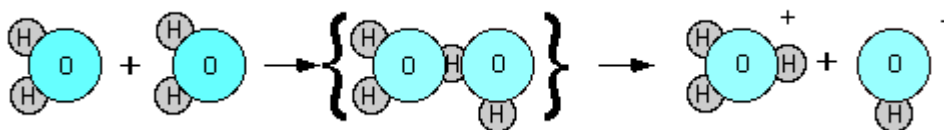
    2. Ion-product constant, K_w (dissociation constant)
        a. At 25°C, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$
        b. $K_w = [H^+][OH^-] = (1.0 \times 10^{-7} \text{ mol/L})(1.0 \times 10^{-7} \text{ mol/L})$
           (1) $K_w = 1.0 \times 10^{-14} \text{ mol}^2/\text{L}^2$ (units often dropped)
    3. Solution characteristics
        a. Neutral solution, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$
        b. Acid solution, $[H^+] > [OH^-]$
        c. Basic solution, $[H^+] < [OH^-]$

14.3 The pH Scale
    A. pH and pOH
        1. pH = -log$[H^+]$
           a. The number of decimal places in the log is equal to the number of
             significant figures in the original number
        2. pOH = -log$[OH^-]$
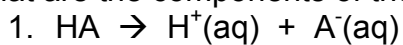   3. pH + pOH = 14
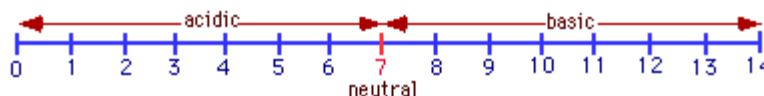
    B. Solving Acid and Base Problems
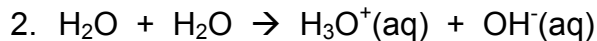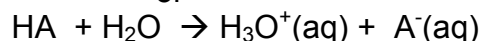   1. Please take time to read the advice at the end of this section (Page 665). It
           applies to far more than acid-base problems!
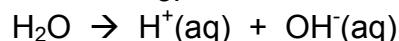
14.4 Calculating the pH of Strong Acid Solutions
    A. What are the components of the solution?
          1. $HA \rightarrow H^+(aq) + A^-(aq)$
              or
          $HA + H_2O \rightarrow H_3O^+(aq) + A^-(aq)$

          2. $H_2O + H_2O \rightarrow H_3O^+(aq) + OH^-(aq)$
              or
          $H_2O \rightarrow H^+(aq) + OH^-(aq)$
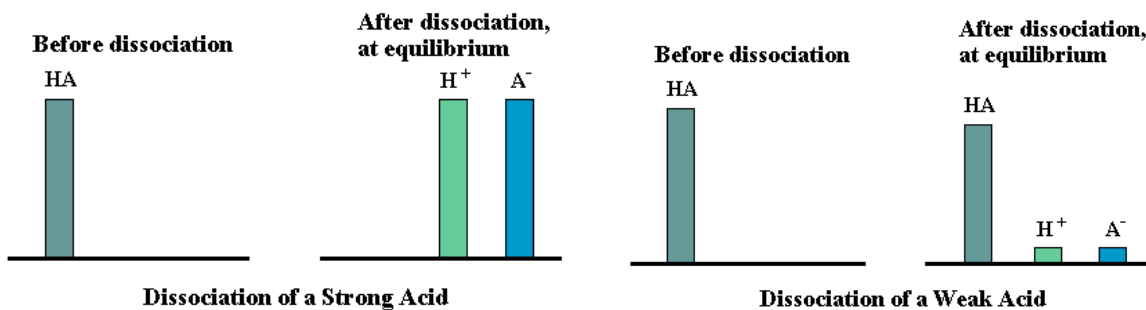   B. Focus on the major species
          1. At high concentrations of strong acids, the autoionization of water is insignificant
          2. For strong acids, the assumption is that HA is completely ionized

Dissociation of a Strong Acid   Dissociation of a Weak Acid

14.5 Calculating the pH of Weak Acid Solutions
    A. Steps (from page 662)
          1. List the major species in the solution
          2. Choose the species that can produce H^+, and write the balanced equations for the reactions producing H^+
          3. Using the values of the equilibrium constants for the reactions you have written decide which equilibrium will dominate in producing H^+
          4. Write the equilibrium expression for the dominant equilibrium
          5. List the initial concentrations of the species participating in the dominant equilibrium
          6. Define the change needed to achieve equilibrium; that is, define x
          7. Write the equilibrium concentrations in terms of x
          8. Substitute the equilibrium concentrations into the equilibrium expression
          9. Solve for x the "easy" way; that is, by assuming that $[HA]_0 - x \approx [HA]_0$
          10. Use the 5% rule to verify whether the approximation is valid
          11. Calculate $[H^+]$ and pH
    B. The pH of a Mixture of Weak Acids
          1. If one acid has a relatively higher K_a value, it will be the focus of the solution
    C. Percent Dissociation

          1. $Percent\ \ dissociation = \dfrac{amount\ \ dissocation\ \ (mol/L)}{initial\ \ concentration\ \ (mol/L)} \times 100\%$

          2. For a given weak acid, the percent dissocation increases as the acid becomes more dilute

14.6 Bases
    A. Strong Bases
        1. Group 1A metal hydroxides
        2. Group 2A metal hydroxides
            a. Less soluble than Group 1A hydroxides; allows use as antacids
    B. Weak Bases
        1. Ammonia and other covalent bases
        2. Compounds with low values of K_b
    C. Calculating the pH of Strong Bases
        1. $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
            a. If you know $[OH^-]$, you can calculate $[H^+]$ from which you can
               calculate the pH
    D. Calculation of pOH
        1. $pK_w = 14.00 = pH + pOH$
        2. $pOH = 14.00 - pH$

14.7 Polyprotic Acids
    A. Stepwise dissociation

        1. $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $K_{a1} = \dfrac{[H^+][HCO_3^-]}{H_2CO_3} = 4.3x10^{-7}$

        2. $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ $K_{a2} = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6x10^{-11}$

    B. Weak Polyprotic acids
        1. $K_{a1} > K_{a2} > K_{a3}...$
    C. Sulfuric Acid, the Strong Polyprotic Acid
        1. $H_2SO_4(aq) \rightleftharpoons H^+(aq) + HSO_4^-(aq)$ K_{a1} is very large
        2. $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$ $K_{a2} = 1.2 \times 10^{-2}$
        2. Sulfuric acid dissociates to a greater extent in even its second step than
            weak acids do in their first step, and the second step cannot be ignored in
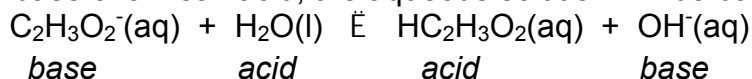   calculation of pH for dilute solutions of H_2SO_4!

14.8 Acid-Base Properties of Salts
    A. Salts That Produce Neutral Solutions
        1. Salts that consist of the cations of strong bases and the anions of strong
            acids have no effect on pH, ($[H^+]$), when dissolved in water
        2. Cations of strong bases
            a. Na^+ K^+ (Group 1A)
        3. Anions of strong acids
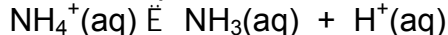   a. Cl^-, NO_3^-
    B. Salts that Produce Basic Solutions
        1. For any salt whose cation has neutral properties and whose anion is the
            conjugate base of a weak acid, the aqueous solution will be basic
                 $C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$
                     base   *acid*   *acid*   *base*

C. Salts that Produce Acidic Solutions
   1. Salts in which the anion is not a base and the cation is the conjugate acid
      acid of a weak base produce acid solutions
$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$
   2. Salts that possess a highly charged metallic ion, such as Al^{3+}
      a. Aluminum ion in water is hydrated, $Al(H_2O)_6^{3+}$
      b. High metallic charge polarizes O - H bond in water
      c. Hydrogens in water become acidic
D. Salts with Acidic and Basic ions
   1. IF K_a for the acidic ion is greater than K_b for the basic ion, the solution is
      acidic
   2. IF K_b for the basic ion is greater than K_a for the acidic ion, the solution is
      basic
   3. IF K_b for the basic ion is equal to K_a for the acidic ion, the solution is neutral

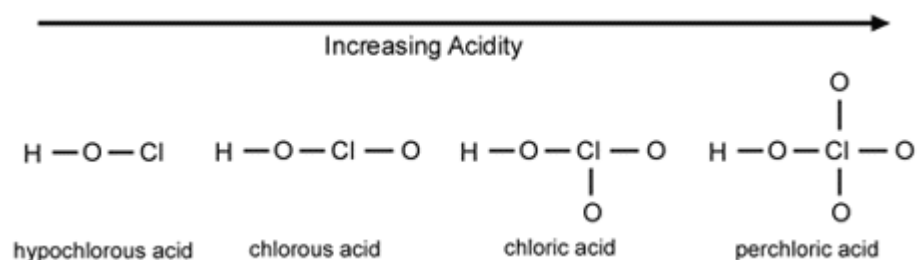14.9 The Effect of Structure on Acid-Base Properties
  A. Factors Determining Acid Characteristics of Molecules with X - H Bonds
   1. Strength of bonds
      a. Strong bonds are reluctant to break, even in solution
   2. Polarity of the bonds
      a. High bond polarity tends to increase the acidity of the hydrogen
  B. Molecules of form H - O - X
   1. IF X has high electronegativity, the hydrogen tends to be acidic
   2. IF X has low electronegativity, the compound tends to be basic (-OH comes
      off)
   3. The more oxygens around X, the more acidic the compound

Increasing Acidity

H —O—Cl   H —O—Cl —O   H —O—Cl —O   H —O—Cl —O

hypochlorous acid   chlorous acid   chloric acid   perchloric acid

14.10 Acid-Base Properties of Oxides
  A. Acidic Oxides (also called acid anhydrides)
   1. Nonmetal oxides that react with water to form acidic solutions
      a. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
      b. $2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$
  B. Basic Oxides (also called basic anhydrides)
   1. Metallic oxides of Group 1A and 2A metals react with water to form basic
      solutions
      a. $K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$
      b. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

14.11 The Lewis Acid-Base Model
    A. Lewis Acids
        1. Electron pair acceptors
    B. Lewis Bases
        1. Electron pair donors

14.12 Strategy for Solving Acid-Base Problems
    Step 1: List the major species in solution
    Step 2: Look for reactions that can be assumed to go to completion, for example, a strong acid dissociating or H^+ reacting with OH^-
    Step 3: For a reaction that can be assumed to go to completion:
        a. Determine the concentration of the products
        b. Write down the major species in solution after the reaction
    Step 4: Look at each major component of the solution and decide if it is an acid or a base
    Step 5: Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.
        a. Write the equation for the reaction and the equilibrium expression
        b. Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, etc)
        c. Define x
        d. Compute the equilibrium concentrations in terms of x
        e. Substitute the concentrations into the equilibrium expression, and solve for x
        f. Check the validity of the approximation
        g. Calculate the pH and other concentrations as required