Chapter 16: Acid-Base Equilibria

16.1 Acids and Bases: A Brief Review

- acids have sour taste and turn litmus paper red
- bases have a bitter taste and feel slippery
- Svante Arrhenius (1859-1927)
    - Acids associated with H^+ ions
    - Bases associated with OH^- ions
- Solution is acidic if there is more H^+ than OH^-
- Solution is basic if there is more OH^- than H^+

16.2 The Dissociation of water

- autoionization of water - dissociation of H_2O molecules to H^+ and OH^- ions
- at room temperature only 1 out of 10^9 molecules are ionized
- exclude water from equilibrium expressions involving aqueous solutions
- ion-product constant
    - $k_w = k[H_2O] = [H^+][OH^-] = 1.0 \times 10^{-14}$ (at 25°C)
- solution is neutral when $[H^+] = [OH^-]$
- solution is acidic when $[H^+] > [OH^-]$
- solution is basic when $[H^+] < [OH^-]$

16.3.1 The Proton in Water

- H^+ ion is a proton with no valence electrons
- H^+ ion react with H_2O molecule to form H_3O^+, hydronium ion
- H_3O^+ ion can bond with other H_2O molecules to form hydrated hydrogen ions
- H^+ and H_3O^+ used interchangeably

16.3 The pH Scale

- concentration of $[H^+]$ expressed in terms of pH
    - $pH = -\log [H^+]$
- acidic solutions
    - $[H^+] > 1.0 \times 10^{-7}$
    - $[OH^-] < 1.0 \times 10^{-7}$
    - $pH < 7.00$
- neutral solutions
    - $[H^+] = [OH^-] = 1.0 \times 10^{-7}$
    - $pH = 7$
- basic solutions
    - $[H^+] < 1.0 \times 10^{-7}$
    - $[OH^-] > 1.0 \times 10^{-7}$
    - $pH > 7$

16.3.1 Other "p" Series

- $pOH = -\log [OH^-]$
- $pH + pOH = -\log K_w = 14.00$

16.3.2 Measuring pH

- pH meter
    - has a pair of electrodes connected to a meter that measures in millivolts
    - voltage generated when electrodes placed in solution, and is measured by meter
- red litmus paper for pH of 5 or lower
- blue litmus paper for pH of 8 or higher

16.4 Brθnsted-Lowry Acids and Bases

- Arrhenius definition of acids and bases
    - Acids when dissolved in water increase H^+ concentration

- Bases when dissolved in water increase OH^- concentration

16.4.1 Proton Transfer Reactions

- Brθnsted-Lowry definition of acids an bases
  - Acid is a proton donor
  - Base is a proton acceptor
  - Can be applied to non-aqueous solutions
- Brθnsted-Lowry acid must be able to lose a H^+ ion
- Brθnsted-Lowry base must have a non bonding pair of electrons to bind to H^+ ion
- Amphoteric - substance that can act as an acid or base

16.4.2 Conjugate Acid-Base Pairs

- conjugate acid - product formed by adding a proton to base
- conjugate base - product formed by removal of a proton from acid

16.4.3 Related Strengths of Acids an Bases

- the stronger the acid, the weaker the conjugate base
- the stronger the base, the weaker the conjugate acid
- equilibrium favors transfer of proton from stronger acid to stronger base

16.5 Strong Acids and Bases

- strong acids and bases are strong electrolytes

16.5.1 Strong Acids

- strongest monoprotic acids
  - HCl, HBr, HI, HNO_3, $HclO_3$, $HclO_4$, and diprotic H_2SO_4
  - For strong monoprotic acid concentration of $[H^+]$ equals the original concentration of the acid

16.5.2 Strong Bases

- most common strong bases are ionic hydroxides of alkali metals and the heavier alkaline-earth metals
- complete dissociation

16.6 Weak Acids

- $HA_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+ + A^-_{(aq)}$
- $HA_{(aq)} \leftrightarrow H^+_{(aq)} + A^-_{(aq)}$
- $K_a = \frac{[H^+][A^-]}{[HA]}$
- K_a = acid - dissociation constant
- The lager the K_a the stronger the acid
- K_a usually less than 10^{-3}

16.6.1 Calculating pH for Solutions of Weak Acids

- 1) write ionization equilibrium
- 2) write equilibrium expression
- 3) I.C.E. Table
- 4) substitute equilibrium concentrations into equilibrium expression
- $\text{percent inonization} = \frac{[\text{initial}]}{[\text{final}]} \times 100\%$
- in weak acids $[H^+]$ is small fraction of concentration of acid
- percent ionization depends on temperature, identity of acid and concentration
- as percent ionization decreases, concentration increases

16.6.2 Polyprotic Acids

- more than one ionizable H atom
- easier to remove first proton than second
- acid dissociation constants are K_{a1}, K_{a2}, etc…
- K_a values usually differ by 10^3

16.7 Weak Bases

- base-dissociation constant, K_b
  - equilibrium at which base reacts with H_2O to form a conjugate acid and OH^-
  - contain 1 or more lone pair of electrons

16.7.1 Types of Weak Bases

- weak bases have NH_3 and anions of weak acids

16.8 Relationship Between K_a and K_b

- when two reactions are added together than equilibrium constant of third reaction is equal to the product of the equilibrium constants of the added reactions
  - reaction 1 + reaction 2 = reaction 3
  - $K_1 \times K_2 = K_3$
  - $K_a \times K_b = [H^+][OH^-] = K_w$
  - Acid-dissociation constant times base-dissociation constant equals the ion-product constant for water
  - $K_a \times K_b = K_w = 1.0 \times 10^{-14}$
  - $pK_a \times pK_b = pK_w = 14$; ($pK_a = -\log K_a$ and $pK_b = -\log K_b$)

16.9 Acid-Base Properties of Salt Solutions

- hydrolysis - ions reacting with water to produce H^+ and OH^- ions
- anions from weak acids react with water to produce OH^- ions which is basic
- anions of strong acids are not basic and do not influence pH
- anions that have ionizable protons are amphoteric
  - behavior depends on K_a and K_b
- all cations except those of alkali metals and heavier alkaline earth (Ca^{2+}, Sr^{2+} and Ba^{2+}) are weak acids in water
- alkali metal and alkaline earth cations do not hydrolyze
  - do not affect pH
- strengths of acids and bases from salts
  - 1) salts derived from strong acid and base
    - no hydrolysis and solution has pH of 7
  - 2) salts derived from strong base and weak acid
    - strong conjugate base
    - anion hydrolyzes and produces OH^- ions
    - cation does not hydrolyze
    - pH greater than 7
  - 3) salts derived from weak base and strong acids
    - cation is strong conjugate acid
    - cation hydrolyzes to produce H^+
    - anion does not hydrolyze
    - solution has pH below 7
  - 4) salts derived from weak acid and base
    - both cation and anion hydrolyze
    - pH depends on extent on hydrolysis of each ion]

16.10 Acid-Base Behavior and Chemical Structure

16.10.1 Factors that Affect Acid Strength

- strength of acid depends on:
  - 1) polarity of H-X bond

- 2) strength of H-X bond
- 3) stability of conjugate base, X^-
- molecule will transfer proton if H-X bond is polarized
- in ionic hydrides H^- acts as proton acceptor because of negative charge
- nonpolar bonds produce neither acidic or basic solutions
- strong bonds less easily dissociated that weak bonds
- the greater the stability of conjugate base, the stronger the acid]

16.10.2 Binary Hydrides

- metal hydrides are basic or have no acid-base properties in water
- nonmetal hydrides can be between having no acid-base properties to being acidic
- in each group of nonmetallic elements, acidity increases with increasing atomic number
    - bond strengths decrease as central atom gets larger and overlap of orbitals get smaller

16.10.3 Oxyacids

- Y-O-H bond
- Oxyacids - have OH bonded to central atom
- Base if bonded to a metal because pair of electrons shared between Y-O is completely transferred to O
    - Ionic compound with OH^- is formed
- When bonded to nonmetal the bond is covalent and compounds are acidic or neutral
- As electronegativity of Y increases , acidity also increases
    - O-H bond becomes more polar
    - Conjugate base usually an anion and stability increases as electronegativity of Y increases
- Relating acid strengths of oxyacids to electronegativity of Y and to number of groups attached to Y
    - 1) same number of oxygen atoms, acid strength increases as electronegativity of central atom increases
    - 2) same central atom Y, acid strength increases with increasing number of bonded oxygen atoms to central atom
    - acidity increases as oxidation number of central atom increases

16.10.4 Carboxylic Acids

- carboxyl group - COOH
- acidic behavior of carboxylic acids
    - addition oxygen atom in carboxyl group draws density from O-H bond which increases the polarity
    - conjugate base ion have resonance forms
    - acidity increases as number of electronegative atoms in acid increases

16.11 Lewis Acids and Bases

- Lewis acid - electron pair acceptor
- Lewis base - electron pair donor
- Any Brθnsted-Lowry is a Lewis base
- Lewis acids have molecules that have incomplete octets

16.11.1 Hydrolysis of Metal Ions

- hydration - attraction of metal ions to water molecules
    - metal ion acts as Lewis acid
    - water molecule acts as Lewis base
    - electron density drawn from oxygen atom to water molecule
    - O-H bond becomes more polarized
- For hydrolysis reactions K_a increases with increasing charge and decreasing radius of ion