

Chapter 17: Additional Aspects of Aqueous Equilibria

17.1 The Common-Ion Effect

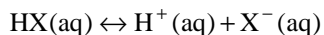
- common-ion effect – dissociation of a weak electrolyte decreases by adding a strong electrolyte to the solution that has a common ion with the weak electrolyte

17.2 Buffered Solutions

- buffers – solutions that resist a change in pH

17.2.1 Composition and Action of Buffered Solutions

- buffers have both acidic and basic species to neutralize H^+ and OH^- ions
- acid dissociation equilibrium in buffered solution



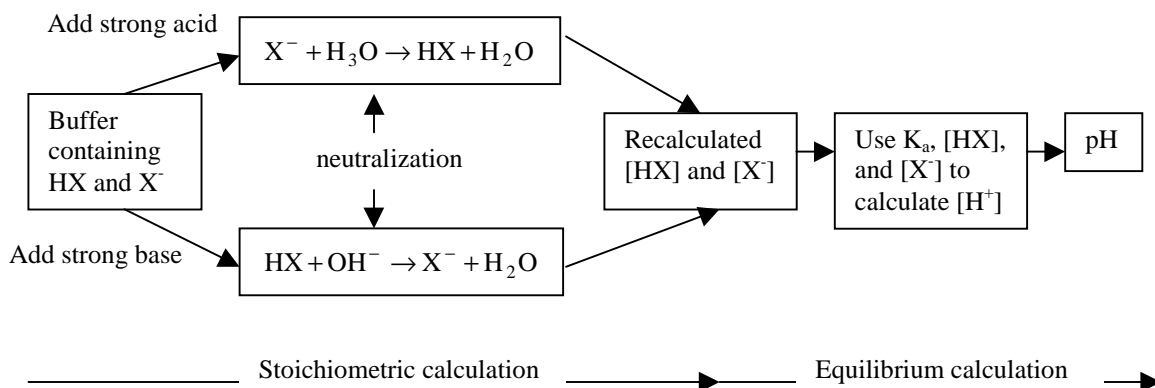
- $K_a = \frac{[H^+][X^-]}{[HX]}$ or $[H^+] = K_a \frac{[HX]}{[X^-]}$
- pH determined by: 1) value of K_a 2) ration of $[HX]/[X^-]$
- if OH^- added:
 - $OH^- + HX(aq) \rightarrow H_2O(l) + X^-(aq)$
 - $[HX]$ decreases, $[X^-]$ increases
 - if amounts of HX and X^- are larger than amount of OH^-
 - ratio $[HX]/[X^-]$ doesn't change much, and pH is small
- when $[HX]$ and $[X^-]$ are about the same, buffers are most effective
 - $[H^+]$ equal to K_a

17.2.2 Buffer Capacity and pH

- buffer capacity – amount of acid or base buffer can neutralize before the pH changes considerably
- capacity depends on amount of acid or base in buffer
- pH depends on K_a for acid and relative concentrations of the acid and base
- Henderson-Hasselbalch equation:
 - $pH = pK_a + \log \frac{[base]}{[acid]}$
 - $[base]$ and $[acid]$ = concentrations of conjugate acid-base pair
 - when $[base]=[acid]$, $pH=pK_a$
 - can use initial concentrations of acid and base components of buffer directly into equation

17.2.3 Addition of Strong Acids or Bases to Buffers

- reactions between strong acids and bases go to completion
- strong base or acid assumed to be completely consumed by reaction with buffer if buffering capacity is not exceeded



17.3 Acid-Base Titrations

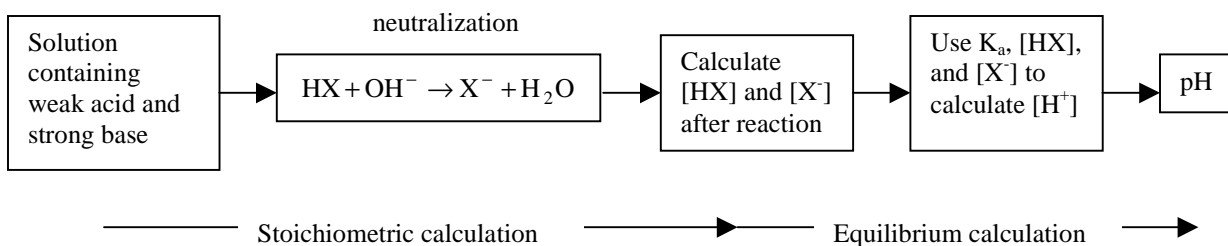
- solution containing a known [base] added to an acid or acid solution added to base
- acid-base indicators used to signal equivalence point
- titration curve – pH vs Volume

17.3.1 Strong Acid – Strong base Titrations

- pH starts out low ends high
- pH before equivalence point is pH of acid not neutralized by base
- pH at equivalence point is pH of solution
- pH equals 7.00
- for strong base titrations, the pH starts high ends low

17.3.2 The Addition of a Strong Base to a Weak Acid

- reaction between weak acid and strong base goes to completion
- calculating pH before equivalence point
 - 1) stoichiometric calculations: allow strong base to react to completion producing a solution containing a weak acid and its conjugate base
 - 2) equilibrium calculation: use K_a and equilibrium expression to find equilibrium concentrations of the weak acid and its conjugate base, and H^+



17.3.3 Titration Curves for Weak Acids or Weak Bases

- differences between strong acid-strong base titrations:
 - 1) solution of weak acid as higher initial pH than solution of a strong acid with same concentration
 - 2) solution of weak acid rises more rapidly in early part of titration and more slowly as it reached the equivalence point
 - 3) pH is not 7.00 at equivalence point
- before equivalence point solution has mixture of weak acid and its salt
 - also called the buffer region of curve
- at equivalence point solution contains only salt
 - weakly basic due to hydrolysis of anion
- after equivalence point solution has mixture of salt and excess strong base
 - pH determined by [base]

17.3.4 Titrations of Polyprotic Acids

- reaction occurs in series of steps
- titration curve shows multiple equivalence points

17.4 Solubility Equilibria

17.4.1 The Solubility-Product Constant, K_{sp}

- saturated solution – dissolved and undissolved solute are at equilibrium
 - expressed by g/L
- molar solubility – moles of solute dissolved to form a liter of saturated solution (mol/L)
- K_{sp} equilibrium constant for the equilibrium between an ionic solid and its saturated solution

- Solubility of compound (g/L) → molar solubility of compound (mol/L) → [molar] of ions → K_{sp} of ions

17.5 Factors That Affect Solubility

- solubility affected by temperature and presence of other solutes
- solubility of ionic compound affected by:
 - 1) the presence of common ions
 - 2) pH of solution
 - 3) presence of complexing agent

17.5.1 Common-Ion Effect

- solubility of slightly soluble salt decreases when a second solute has a common ion

17.5.2 Solubility and pH

- solubility of any ionic compound affected if solution is acidic or basic
- change only noticeable if both ions are moderately acidic or basic
- solubility of slightly soluble salts containing basic anions increase as $[H^+]$ increases (as pH is lowered)
- the more basic an anion is, the greater the solubility will be affected by pH

17.5.3 Formation of Complex Ions

- metal ions act as Lewis acids in water
- complex ion – metal ion and Lewis base bonded together
- K_f – formation constant, equilibrium expression for formation of a complex ion
- Solubility of metal salts increases in acceptable Lewis bases if metal forms a complex base
 - Lewis bases – NH_3 , CN^- , OH^-

17.5.4 Amphoterism

- amphoteric substances – hydroxides, oxides of Al^{3+} , Cr^{2+} , Zn^{2+} , and Sn^{2+}
- dissolve in strongly basic solutions
 - formation of complex anions containing, typically four, hydroxides bound to metal ion
- amphoterism also associated with behavior of water molecules that surround and bond to metal ions by Lewis acid-base interactions

17.6 Precipitation and Separation of Ions

- Q = ion product
- If $Q > K_{sp}$, precipitation occurs until $Q = K_{sp}$
- If $Q = K_{sp}$, equilibrium exists, have a saturated solution
- If $Q < K_{sp}$, solid dissolves until $Q = K_{sp}$

17.6.1 Selective Precipitation of Ions

- separation of ions in aqueous solution using a reagent that precipitates only with selected ions

17.7 Qualitative Analysis for Metallic Elements

- qualitative analysis – determines presence or absence of a particular metal ion
 - 1) ions separated into broad groups on basis of solubility
 - 2) ions separated by dissolving selected members in group
 - 3) ions identified by specific tests