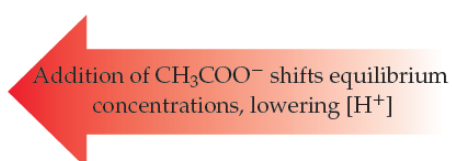# Chapter 17
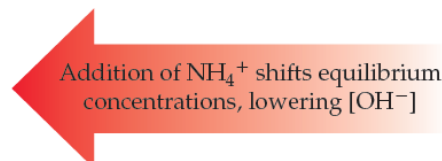## Additional Aspects of Aqueous Equilibria

Review
Definitions:

- **Common-Ion Effect:** Whenever a weak electrolyte and a strong electrolyte containing a common ion are together in solution, the weak electrolyte ionizes less than it would if it were alone in solution.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \qquad NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[H^+]$

Addition of NH_4^+ shifts equilibrium concentrations, lowering $[OH^-]$

- **Buffers:** Solutions that contain high concentrations (10^{-3} *M* or more) of a weak conjugate acid–base pair that resist drastic changes in pH when small amounts of strong acid or strong base are added to them.
  The concentrations of acid and base are approximately equal.
- **Ways to Make a Buffer**
  1) Mix a weak acid and a salt of its conjugate base or a weak base and a salt of its conjugate acid.
  2) Add strong acid and partially neutralize a weak base or add strong base and partially neutralize a weak acid.
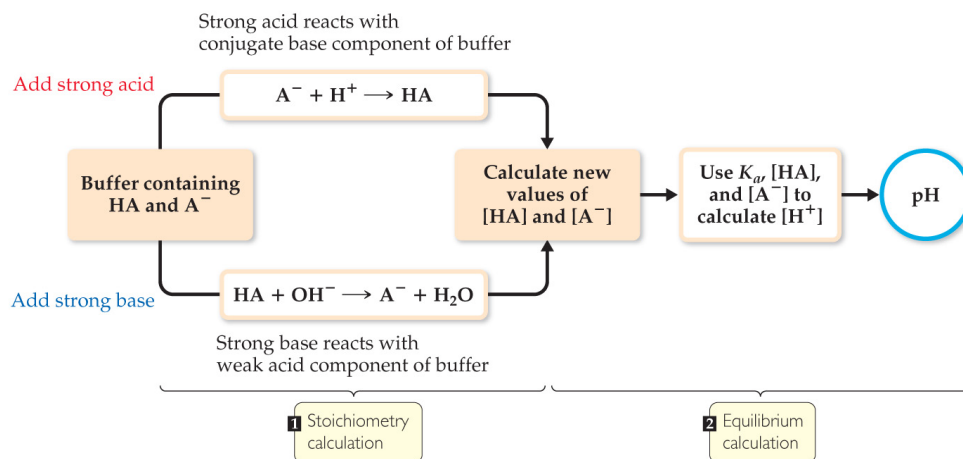- **Henderson–Hasselbalch equation:** applies only to buffers.
$$pH = pK_a + \log([base]/[acid])$$
where [base] and [acid] refer to the equilibrium concentrations of the *conjugate acid-base pair*. Note that when [base] = [acid], we have pH = pK_a.
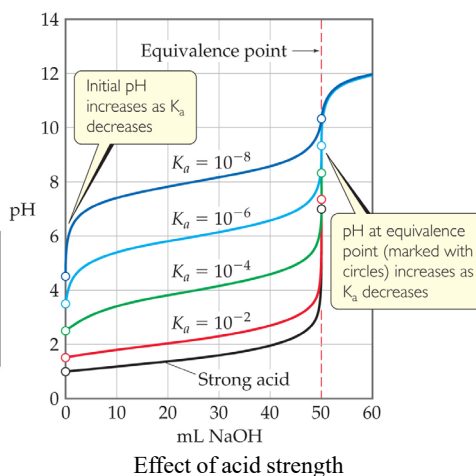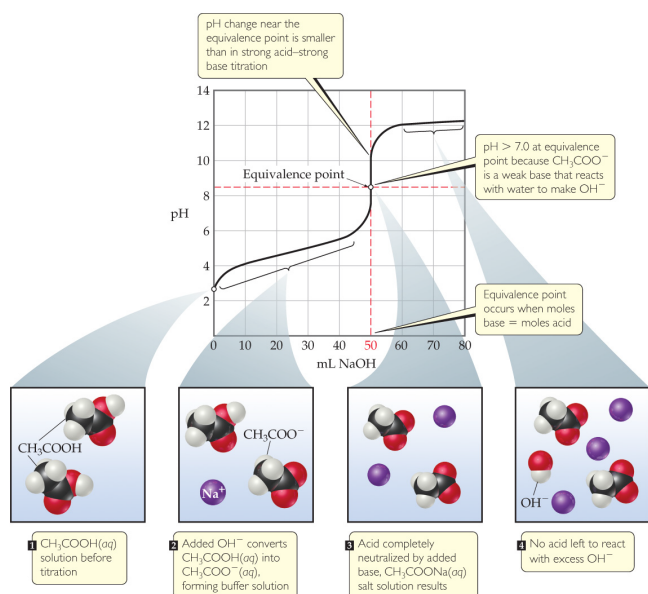- **Buffer Capacity:** The amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. It depends on the amount of acid and base used to prepare the buffer.
- **pH range:** The range of pH values over which a buffer system works effectively. *Buffers have a usable range within ±1 pH unit of pKa (that is, a range of pH = pKa±1).*
  Optimal pH: where pH = pK_a ([HA] = [A$^-$])
- **Addition of a Strong Acid or a Strong Base to a Buffer**
  1) Consider the acid–base neutralization reaction and determine its effect on [HA] and [A$^-$]. *This step is a limiting reactant stoichiometry calculation.*
  2) Use the Henderson–Hasselbalch equation to find pH ((if the concentrations of the weak acid–base pair are very large compared to Ka for the acid).).

Strong acid reacts with conjugate base component of buffer

Add strong acid

$$A^- + H^+ \longrightarrow HA$$

Buffer containing HA and A^-

Calculate new values of [HA] and $[A^-]$

Use K_a, [HA], and $[A^-]$ to calculate $[H^+]$

pH

Add strong base

$$HA + OH^- \longrightarrow A^- + H_2O$$

Strong base reacts with weak acid component of buffer

1 Stoichiometry calculation

2 Equilibrium calculation

- **Titration:** an acid (or base) solution of known concentration is slowly added to a base (or acid) solution of unknown concentration.
- **Equivalence point:** The amount of acid equals that of base.

pH = 7.0 at equivalence point, NaCl(aq) salt solution

Equivalence point

Equivalence point occurs when moles base = moles acid

1 Only HCl(aq) present before titration

2 H^+ consumed as OH^- added, forming H_2O (pH < 7.0)

3 H^+ completely neutralized by OH^- (pH = 7.0)

4 No H^+ left to react with excess OH^- (pH > 7.0)

Titration of a Strong Acid with a Strong base

Equivalence point

Titration of a Strong Base with a Strong Acid

pH change near the equivalence point is smaller than in strong acid–strong base titration

Equivalence point

pH > 7.0 at equivalence point because CH_3COO^- is a weak base that reacts with water to make OH^-

Equivalence point occurs when moles base = moles acid

1 $CH_3COOH(aq)$ solution before titration

2 Added OH^- converts $CH_3COOH(aq)$ into $CH_3COO^-(aq)$, forming buffer solution

3 Acid completely neutralized by added base, $CH_3COONa(aq)$ salt solution results

4 No acid left to react with excess OH^-

Titration of a Weak Acid with a Strong base

Equivalence point

Initial pH increases as K_a decreases

$K_a = 10^{-8}$

$K_a = 10^{-6}$

$K_a = 10^{-4}$

$K_a = 10^{-2}$

Strong acid

pH at equivalence point (marked with circles) increases as K_a decreases
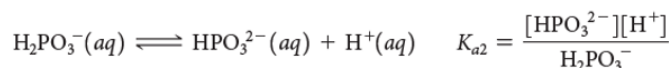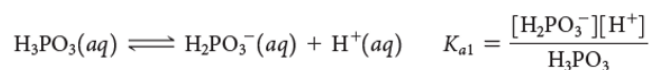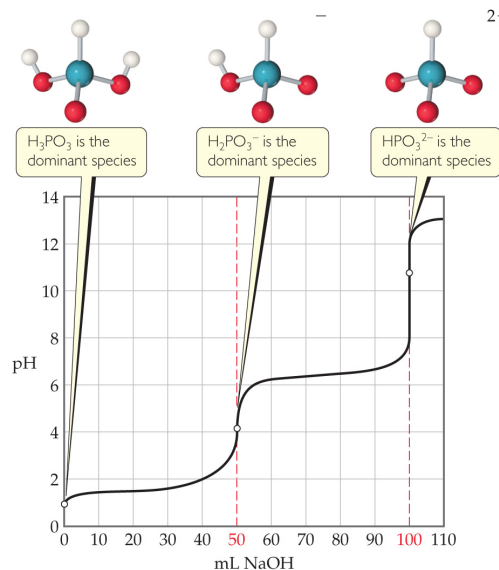
Effect of acid strength

- **Indicator:** a compound that changes color in solution over a specific pH range.
- **End point:** The point in a titration where the indicator changes color is called the end point to distinguish it from the equivalence point that it closely approximates.
- **Use of indicators:**

▲ **Figure 16.8 pH ranges for common acid–base indicators.** Most indicators have a useful range of about 2 pH units.
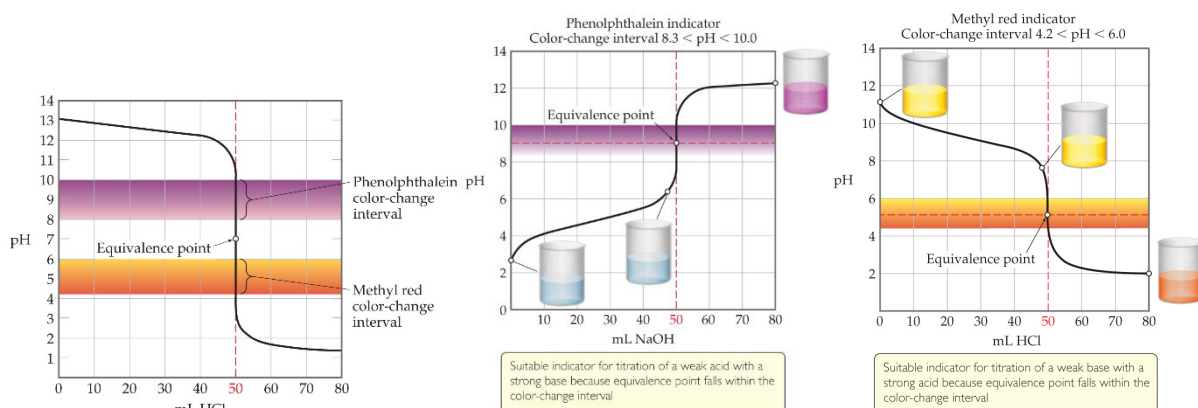
- **Titrations of Polyprotic Acids:** there is an equivalence point for each dissociation.

$$H_3PO_3(aq) + OH^-(aq) \longrightarrow H_2PO_3^-(aq) + H_2O(l)$$

$$H_2PO_3^-(aq) + OH^-(aq) \longrightarrow HPO_3^{2-}(aq) + H_2O(l)$$

$$H_3PO_3(aq) \rightleftharpoons H_2PO_3^-(aq) + H^+(aq) \qquad K_{a1} = \frac{[H_2PO_3^-][H^+]}{H_3PO_3}$$

$$H_2PO_3^-(aq) \rightleftharpoons HPO_3^{2-}(aq) + H^+(aq) \qquad K_{a2} = \frac{[HPO_3^{2-}][H^+]}{H_2PO_3^-}$$

$$pH = pK_{a1} + \log\frac{[H_2PO_3^-]}{[H_3PO_3]}$$

$$pH = pK_{a2} + \log\frac{[HPO_3^{2-}]}{[H_2PO_3^-]}$$

- **Solubility-product constant (K_{sp}):** the equilibrium constant indicates how soluble the solid is in water, it equals the product of the concentration of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation.
- **Solubility vs. Solubility Product (K_{sp})**
  Solubility is the quantity of a substance that dissolves to form a saturated solution. Common units for solubility: g/L & mol/L
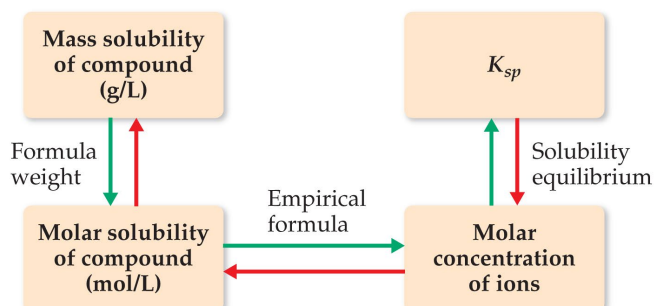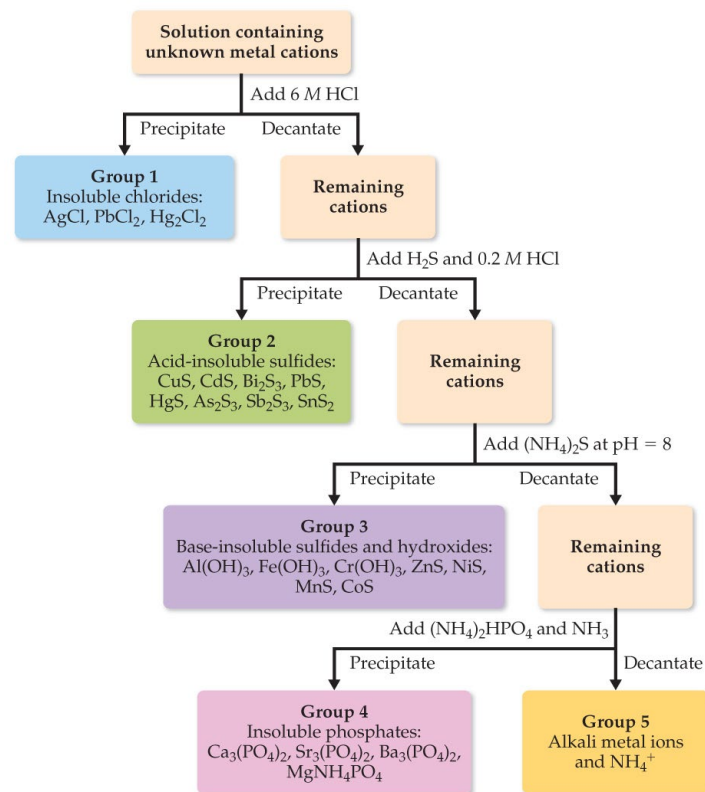

- **Factors Affecting Solubility**
  ✓ The Common-Ion Effect: In general, the solubility of a slightly soluble salt is decreased by the presence of a second solute that furnishes a common ion.
  ✓ pH: In general, the solubility of a compound containing a basic anion (that is, the anion of a weak acid) increases as the solution becomes more acidic.
  ✓ Complex Ion Formation: Metal ions can act as Lewis acids and form complex ions with Lewis bases in the solvent, increasing the solubility of these salts.
- **Amphoteric oxides and hydroxides:** Some metal oxides and hydroxides (such as Al^{3+}, Cr^{3+}, Zn^{2+} and Sn^{2+}) that are relatively insoluble in water dissolve in strongly acidic and strongly basic solutions.

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$$

$$Al^{3+}(aq) + 3\,H_2O(l) \rightleftharpoons 3\,H^+(aq) + Al(OH)_3(s)$$
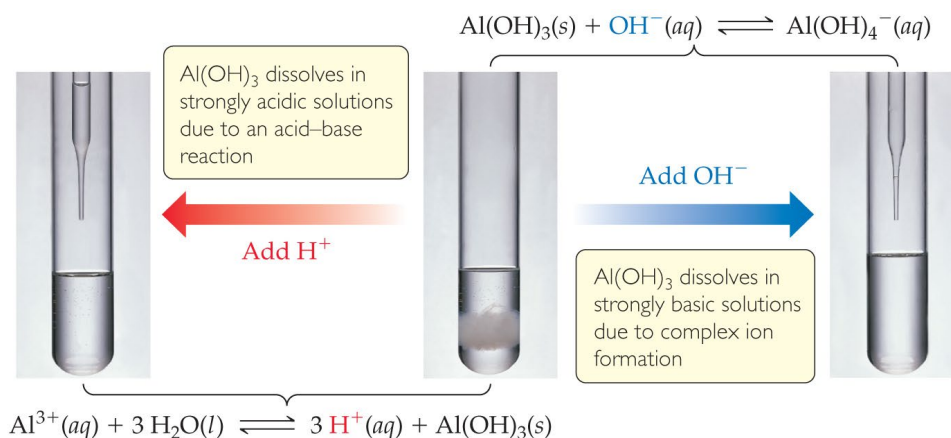
- **Precipitation of ions:** calculate the reaction quotient, Q, and compare it to the solubility product constant, K_{sp}.
  ✓ If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.
  ✓ If $Q < K_{sp}$, more solid can dissolve, so no precipitate forms.
  ✓ If $Q > K_{sp}$, a precipitate will form.
- **Selective precipitation:** Separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or more (but not all) of the ions.

- **Qualitative analysis:** determines only the presence or absence of a particular metal ion relative to some threshold.

```
                    ┌──────────────────────┐
                    │  Solution containing │
                    │ unknown metal cations│
                    └──────────────────────┘
                              │ Add 6 M HCl
                 Precipitate  │  Decantate
          ┌──────────────┐    │
          │   Group 1    │    │
          │ Insoluble    │    ┌──────────────┐
          │ chlorides:   │    │  Remaining   │
          │ AgCl, PbCl₂, │    │   cations    │
          │ Hg₂Cl₂       │    └──────────────┘
          └──────────────┘          │ Add H₂S and 0.2 M HCl
                        Precipitate  │  Decantate
```

Group 1
Insoluble chlorides:
$AgCl$, $PbCl_2$, Hg_2Cl_2

Remaining cations

Add H_2S and 0.2 M HCl

Group 2
Acid-insoluble sulfides:
CuS, CdS, Bi_2S_3, PbS, HgS, As_2S_3, Sb_2S_3, SnS_2

Remaining cations

Add $(NH_4)_2S$ at pH = 8

Group 3
Base-insoluble sulfides and hydroxides:
$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, ZnS, NiS, MnS, CoS

Remaining cations

Add $(NH_4)_2HPO_4$ and NH_3

Group 4
Insoluble phosphates:
$Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ba_3(PO_4)_2$, $MgNH_4PO_4$

Group 5
Alkali metal ions and NH_4^+

- **Quantitative analysis:** determines how much of a given substance is present.