

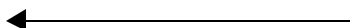
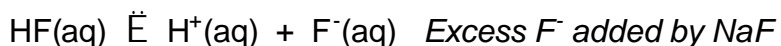
Chapter 15 - Applications of Aqueous Equilibria

Acid-Base Equilibria

15.1 Solutions of Acids or Bases Containing a Common Ion

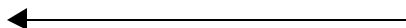
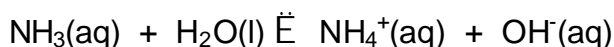
A. Common Ion

1. Ion provided in solution by an aqueous acid (or base) as well as a salt
 - a. HF(aq) and NaF (F^- in common)



Equilibrium shifts away from added component. Fewer H^+ ions present. pH is higher than expected.

- b. NH_4OH and NH_4Cl (NH_4^+ in common)



Equilibrium shifts to the left. pH of the solution decreases due to a decrease in OH^- concentration

B. Equilibrium Calculations

1. Consider initial concentration of ion from salt when calculating values for H^+ and OH^-

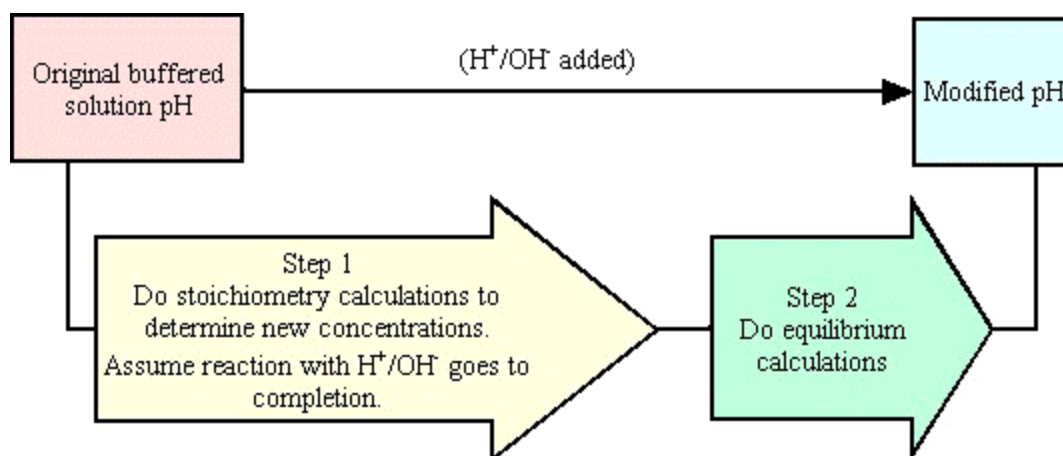
15.2 Buffered Solutions

A. Buffered Solution

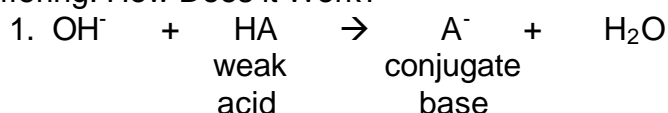
1. A solution that resists a change in pH when either hydroxide ions or protons are added.
2. Buffered solutions contain either:
 - a. A weak acid and its salt
 - b. A weak base and its salt

B. Calculations Involving Buffered Solutions Containing Weak Acids

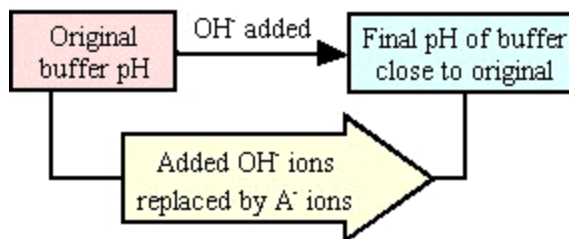
1. "Buffered solutions are simply solutions of weak acids or bases containing a common ion. The pH calculations on buffered solutions require exactly the same procedures introduced in Chapter 14. *This is not a new type of problem.*"
2. "When a strong acid or base is added to a buffered solution, it is best to deal with the stoichiometry of the resulting reaction first. After the stoichiometric calculations are completed, then consider the equilibrium calculations. This procedure can be presented as follows:



C. Buffering: How Does it Work?

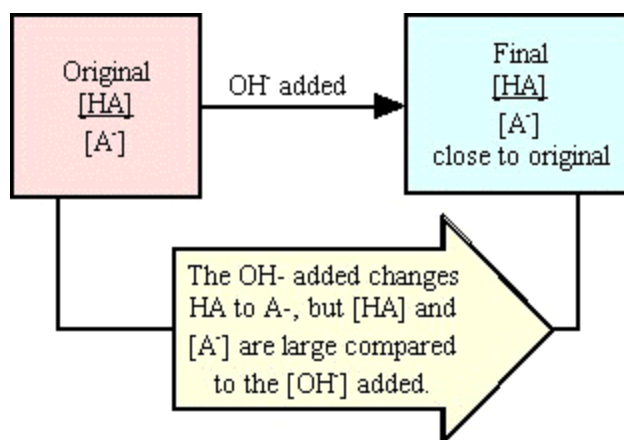


OH^- ions are not allowed to accumulate but are replaced by A^- ions

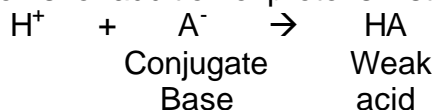


$$2. K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

- a. If the amounts of HA and A^- originally present are very large compared with the amount of OH^- added, the change in $[\text{HA}]/[\text{A}^-]$ will be small. Therefore the pH change will be small



3. Buffering also works for addition of protons instead of hydroxide ions



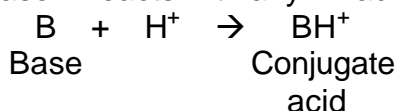
D. The Henderson-Hasselbalch Equation

$$1. \quad pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

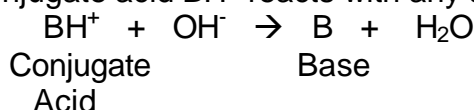
- a. For a particular buffering system (acid-conjugate base pair), all solutions that have the same ratio $[A^-]/[HA]$ will have the same pH

E. Buffering with a Weak Base and Its Conjugate Acid

1. Weak base B reacts with any H^+ added



2. Conjugate acid BH^+ reacts with any added OH^-



F. Summary

1. Buffered solutions contain relatively large concentrations of a weak acid and the corresponding weak base. They can involve a weak acid HA and the conjugate base A^- or a weak base and the conjugate acid BH^+
2. When H^+ is added to a buffered solution, it reacts essentially to completion with the weak base present
3. When OH^- is added to a buffered solution, it reacts essentially to completion with the weak acid present
4. The pH in the buffered solution is determined by the ratio of the concentrations of the weak acid and the weak base. The pH remains relatively unchanged as long as the concentrations of buffering materials are large compared with the amounts of H^+ or OH^- added

15.3 Buffer Capacity

A. Buffering Capacity

1. The amount of protons or hydroxide ions the buffer can absorb without a significant change in pH.
 - a. The pH of a buffered solution is determined by the ratio $[A^-]/[HA]$
 - b. The capacity of a buffered solution is determined by the magnitudes of $[HA]$ and $[A^-]$

B. Preparing a Buffer

1. Optimal buffering occurs when $[HA]$ is equal to $[A^-]$ ($[A^-]/[HA] = 1$)
2. The pK_a of the weak acid to be used should be as close as possible to the desired pH

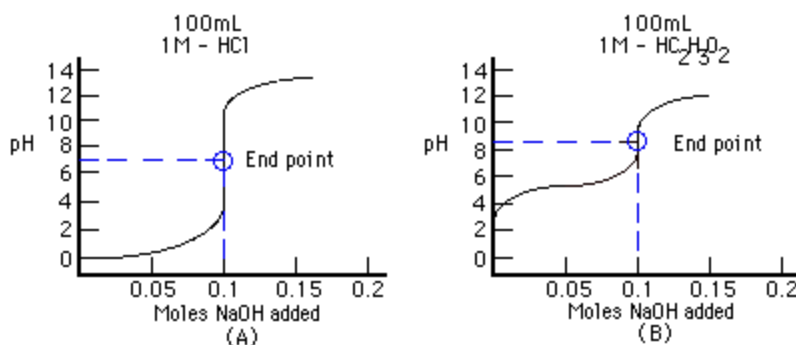
Table 15.1 Change in $[C_2H_3O_2^-]/[HC_2H_3O_2]$ for two solutions when 0.01 mol H^+ is added to 1.0 L of each

Solution	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{orig}$	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{new}$	Change	% Change
A	1.00 M/1.00 M = 1.00	0.99 M/1.01 M = 0.98	1.00 \rightarrow 0.98	2.00%
B	1.00 M/0.01 M = 100	0.99 M/0.02 M = 49.5	100 \rightarrow 49.5	50.5%

15.4 Titration and pH Curves

A. Titration

1. The controlled addition of a solution of known concentration (the titrant) in order to determine the concentration of a solution of unknown concentration
2. Equivalence Point (Stoichiometric Point)
 - a. The point in a titration at which the reaction between titrant and unknown has just been completed.
3. Indicator
 - a. A substance which undergoes a color change in the pH interval of the equivalence point
4. Titration Curve (pH Curve)
 - a. Plotting of the pH of the solution as a function of the volume of titrant added



Strong Acid/
Strong Base

Weak Acid/
Strong Base

(Note the initial buffering effect created by the relatively high concentration of H^+ in solution)

B. Strong Acid-Strong Base Titration

1. Before the equivalence point
 - a. $[H^+]$ (thus the pH) can be calculated
2. At the equivalence point, pH = 7.00
3. After the equivalence point
 - a. $[OH^-]$ can be calculated from the excess OH^- and the volume of the solution
 - b. $[H^+]$ and pH can be calculated from $[OH^-]$ and K_w

B. Titrations of Weak Acids and Strong Bases

1. Step 1 - A stoichiometry problem
 - a. The reaction of OH^- with the weak acid is assumed to run to completion
 - b. The concentrations of the acid remaining and the conjugate base formed are determined
2. Step 2 - An equilibrium problem
 - a. The position of the weak acid equilibrium is determined, and the pH calculated
3. The pH at the equivalence point of a weak acid/strong base is always greater than 7
 - a. The anion of the weak acid is a base. The stronger the basic anion, the higher the pH of the equivalence point

C. Titrations of Weak Bases with Strong Acids

1. Identify the major species in solution before, at and after equivalence point
2. Study each reaction to determine if the reaction can run to completion
 - a. Do the stoichiometry problem
 - b. Do the equilibrium problem
3. At the equivalence point, the pH is always less than 7
 - a. The conjugate acid of the weak base lowers the pH

15.5 Acid-Base Indicators

A. Determination of Equivalence Point

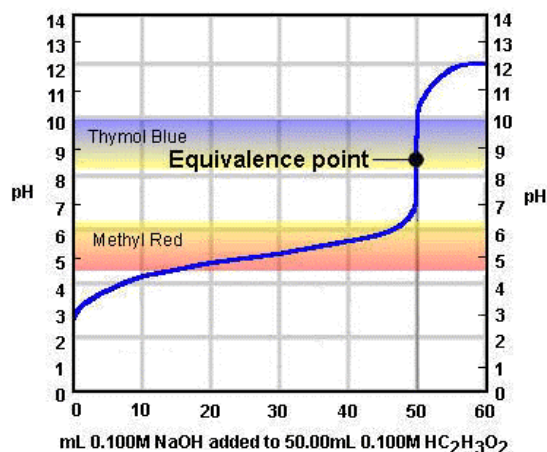
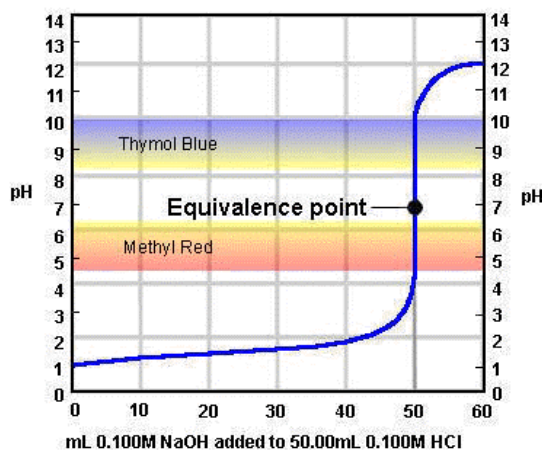
1. Use a pH meter, find midpoint of vertical line in the titration curve
2. Use of indicators

B. How Indicators Work

1. Most are weak acids and shift from acid to conjugate base forms
$$\text{HIn (aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{In}^-(\text{aq})$$
 - a. Color change occurs as the proton is lost or acquired

C. Using Indicators

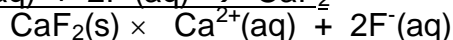
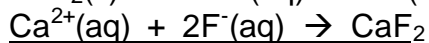
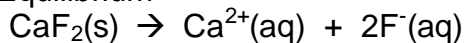
1. Indicator color changes will be sharp, occurring with the addition of a single drop of titrant
2. Suitable indicators must be selected based on the equivalence point
 - a. Strong acid-strong base titrations may use indicators with end points as far apart as pH 5 and pH 9
 - b. Titration of weak acids or weak bases requires more careful selection of an indicator with appropriate transition interval



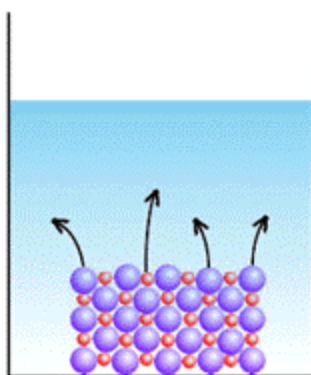
Solubility Equilibria

15.6 Solubility Equilibria and the Solubility Product

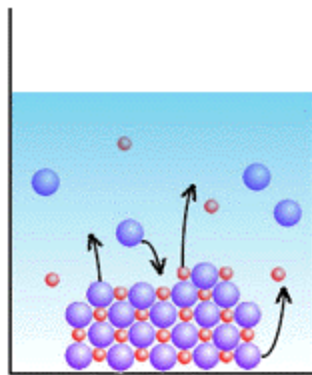
A. Dynamic Equilibrium



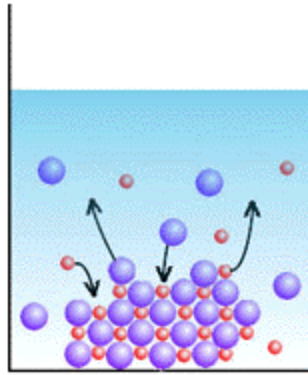
1. Equilibrium occurs when the solution is saturated



Salt is initially put into the water and begins dissolving.



Salt continues to dissolve; however, dissolved ions will also precipitate. Because the salt dissolves faster than its ions precipitate, the net movement is towards dissolution.



Eventually, the rate of dissolution will equal the rate of precipitation. The solution will be in equilibrium, but the ions will continue to dissolve and precipitate.

B. K_{sp} (Solubility Product Constant, Solubility Product)

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

1. Experimentally determined solubility of an ionic solid can be used to calculate its K_{sp} value
2. The solubility of an ionic solid can be calculated if its K_{sp} value is known

C. Relative Solubilities

1. IF the salts being compared produce the same number of ions in solution, K_{sp} can be used to directly compare solubility
 - a. $\text{NaCl}(\text{s})$, $\text{KF}(\text{s})$

$$K_{sp} = [\text{cation}][\text{anion}] = x^2$$

2. IF the salts being compared produce different numbers of ions, K_{sp} cannot be directly compared

- a. $\text{Ag}_2\text{S}(\text{s})$

$$K_{sp} = [2x]^2[x]$$

- b. $\text{Bi}_2\text{S}_3(\text{s}) = [2x]^2[3x]^3$

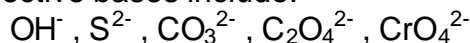
D. Common Ion Effect

1. The solubility of a solid is lowered if the solution already contains ions common to the solid
 - a. Dissolving silver chloride in a solution containing silver ions
 - b. Dissolving silver chloride in a solution containing chloride ions

E. pH and Solubility

1. If anion X^- is an effective base (HX is a weak acid), the salt MX will show increased solubility in acidic solution

- a. Effective bases include:



15.7 Precipitation and Qualitative Analysis

Instructor's Note: We will skim over much of sections 7 and 8, hitting only the high points and performing a lab on selective precipitation

A. Selective Precipitation

1. Mixtures of metal ions in aqueous solution are often separated by using a reagent whose anion forms a precipitate with only one or a few of the metal ions in the mixture

