

Chapter 17

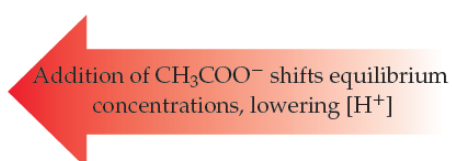
Additional Aspects of Aqueous Equilibria

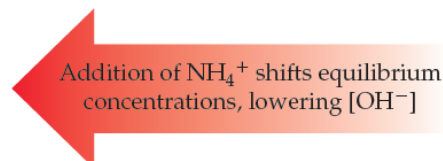
Review

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.




 Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[\text{H}^+]$


 Addition of NH_4^+ shifts equilibrium concentrations, lowering $[\text{OH}^-]$

- **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.

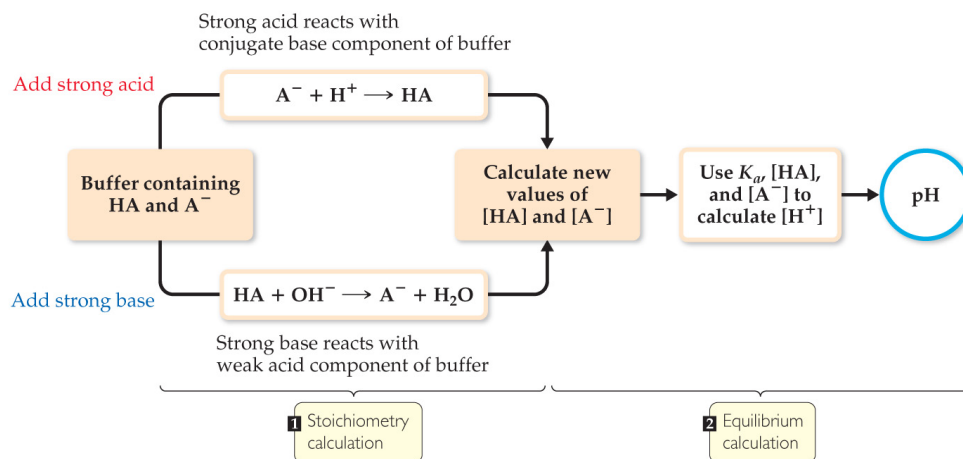
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

where $[\text{base}]$ and $[\text{acid}]$ refer to the equilibrium concentrations of the *conjugate acid–base pair*. Note that when $[\text{base}] = [\text{acid}]$, we have $\text{pH} = \text{p}K_a$.

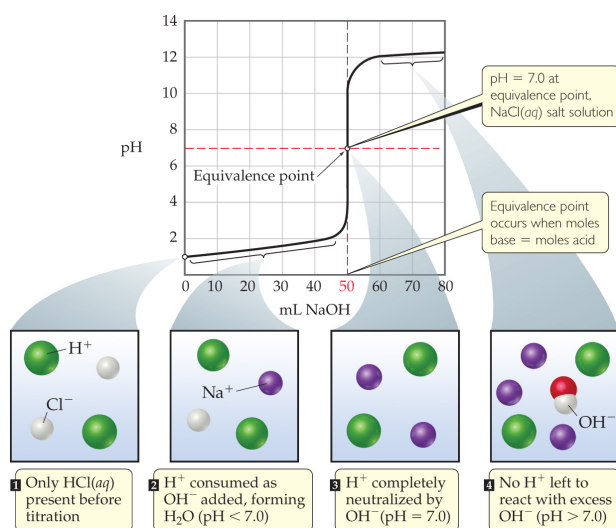
- **Buffer Capacity:** The amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. It depends on the amount of acid and base used to prepare the buffer.
- **pH range:** The range of pH values over which a buffer system works effectively. *Buffers have a usable range within ± 1 pH unit of $\text{p}K_a$ (that is, a range of $\text{pH} = \text{p}K_a \pm 1$).*
Optimal pH: where $\text{pH} = \text{p}K_a$ ($[\text{HA}] = [\text{A}^-]$)

- **Addition of a Strong Acid or a Strong Base to a Buffer**

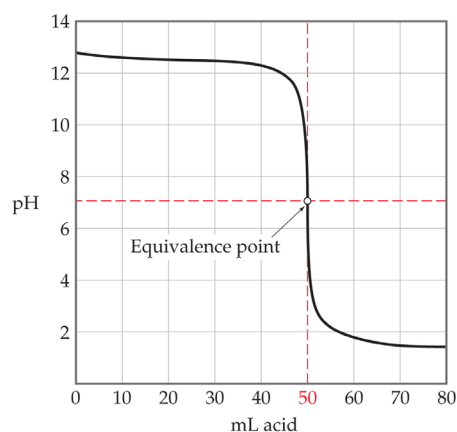
- 1) Consider the acid–base neutralization reaction and determine its effect on $[\text{HA}]$ and $[\text{A}^-]$. *This step is a limiting reactant stoichiometry calculation.*
- 2) Use the Henderson–Hasselbalch equation to find pH ((if the concentrations of the weak acid–base pair are very large compared to K_a for the acid).).



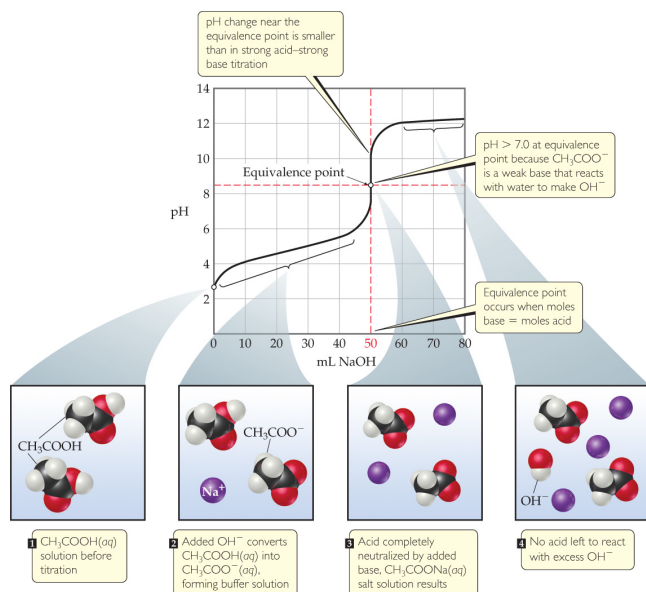
- **Titration:** an acid (or base) solution of known concentration is slowly added to a base (or acid) solution of unknown concentration.
- **Equivalence point:** The amount of acid equals that of base.



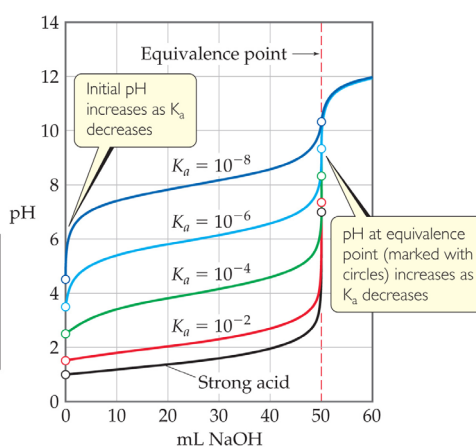
Titration of a Strong Acid with a Strong base



Titration of a Strong Base with a Strong Acid



Titration of a Weak Acid with a Strong base

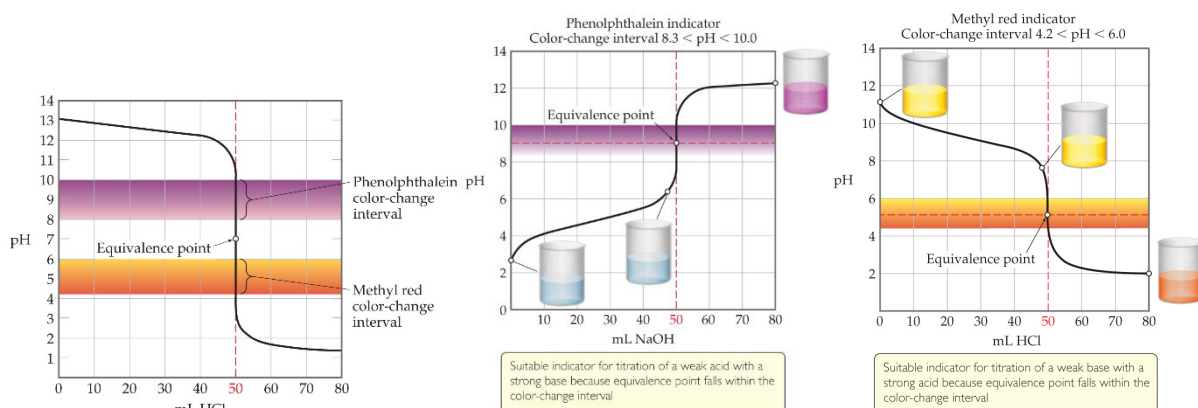


Effect of acid strength

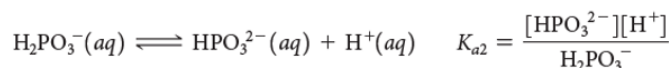
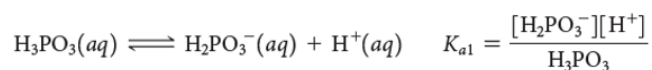
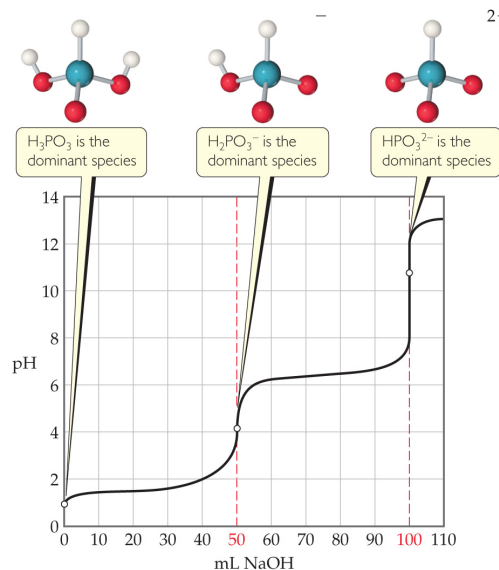
- **Indicator:** a compound that changes color in solution over a specific pH range.
- **End point:** The point in a titration where the indicator changes color is called the end point to distinguish it from the equivalence point that it closely approximates.
- **Use of indicators:**

	pH range for color change													
	0	2	4	6	8	10	12	14						
Methyl violet	Yellow													Violet
Thymol blue		Red			Yellow				Yellow					Blue
Methyl orange			Red			Yellow								
Methyl red			Red			Yellow								
Bromthymol blue				Yellow			Blue							
Phenolphthalein						Colorless			Pink					
Alizarin yellow R							Yellow							Red

▲ **Figure 16.8** pH ranges for common acid–base indicators. Most indicators have a useful range of about 2 pH units.



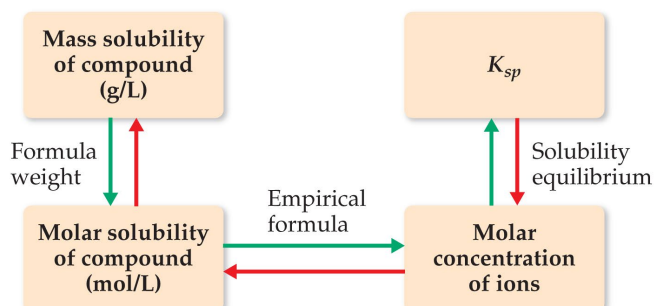
- **Titration of Polyprotic Acids:** there is an equivalence point for each dissociation.



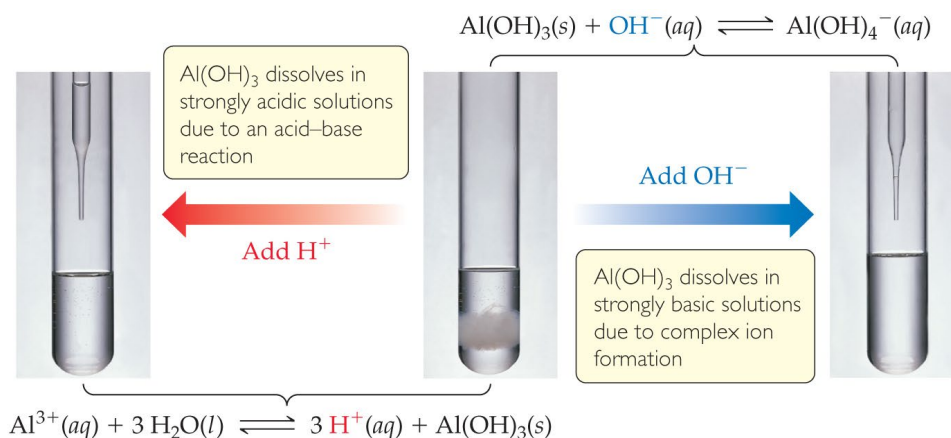
$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$\text{pH} = \text{p}K_{a2} + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

- **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

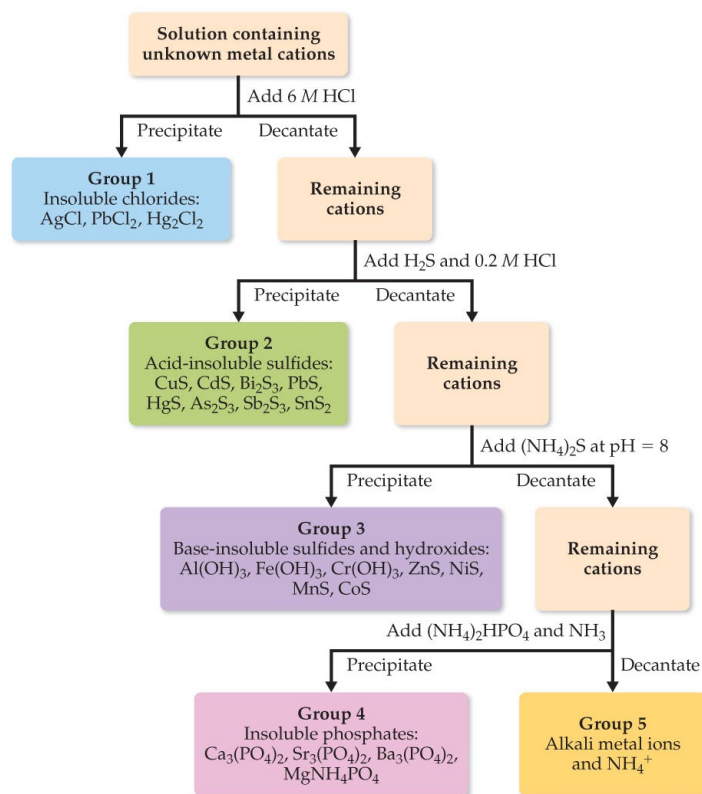


- **Factors Affecting Solubility**
 - ✓ The Common-Ion Effect: In general, the solubility of a slightly soluble salt is decreased by the presence of a second solute that furnishes a common ion.
 - ✓ pH: In general, the solubility of a compound containing a basic anion (that is, the anion of a weak acid) 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.



- **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.



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