

Lecture Presentation

Chapter 17

Additional Aspects of Aqueous Equilibria

James F. Kirby
Quinnipiac University
Hamden, CT

Effect of Acetate on the Acetic Acid Equilibrium

- Acetic acid is a weak acid:
 - $\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$
- Sodium acetate is a strong electrolyte:
 - $\text{NaCH}_3\text{COO}(aq) \rightarrow \text{Na}^+(aq) + \text{CH}_3\text{COO}^-(aq)$
- The presence of acetate from sodium acetate in an acetic acid solution will shift the equilibrium, according to LeChâtelier's Principle:
 - $\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$

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

The 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.”
- This affects acid–base equilibria.
- We will also see (later in the chapter) how it affects solubility.



An Acid–Base Example

- What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?



2) $K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] = 1.8 \times 10^{-5}$

3)

	$[\text{CH}_3\text{COOH}] (M)$	$[\text{H}^+] (M)$	$[\text{CH}_3\text{COO}^-] (M)$
Initial Concentration (M)	0.30	0	0.30
Change in Concentration (M)	$-x$	$+x$	$+x$
Equilibrium Concentration (M)	$0.30 - x$	x	$0.30 + x$

Example (completed)

$$4) 1.8 \times 10^{-5} = (x)(0.30 + x)/(0.30 - x)$$

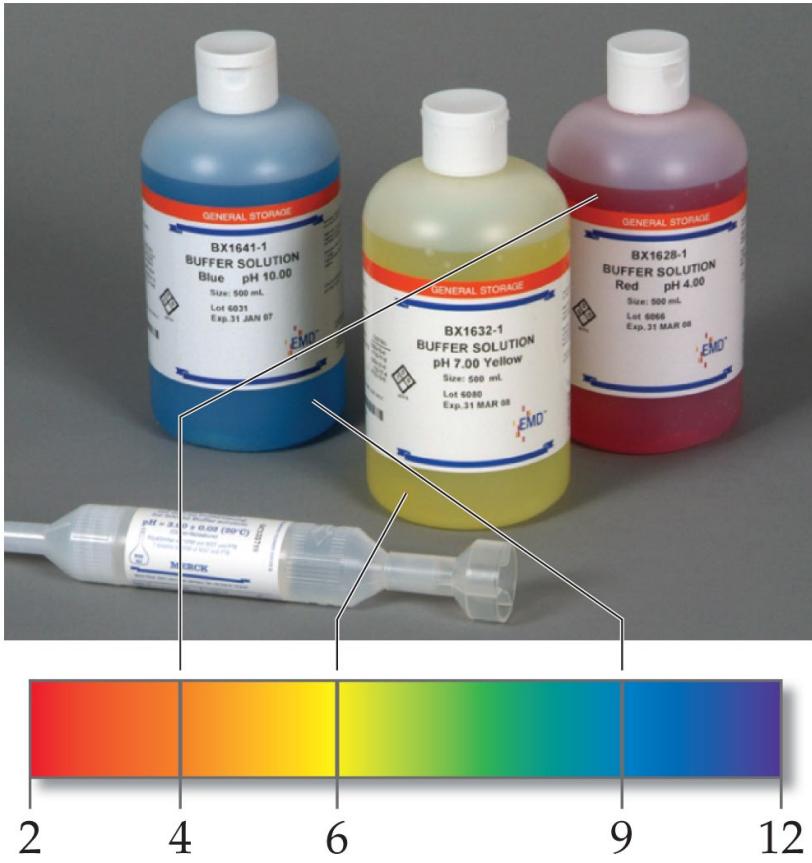
Assume that adding or subtracting x from 0.30 will not change 0.30 enough to matter and the equation becomes

$$1.8 \times 10^{-5} = (x)(0.30)/(0.30)$$

which results in: $x = 1.8 \times 10^{-5} = [\text{H}^+]$

So: $\text{pH} = -\log[\text{H}^+] = 4.74$

Buffers

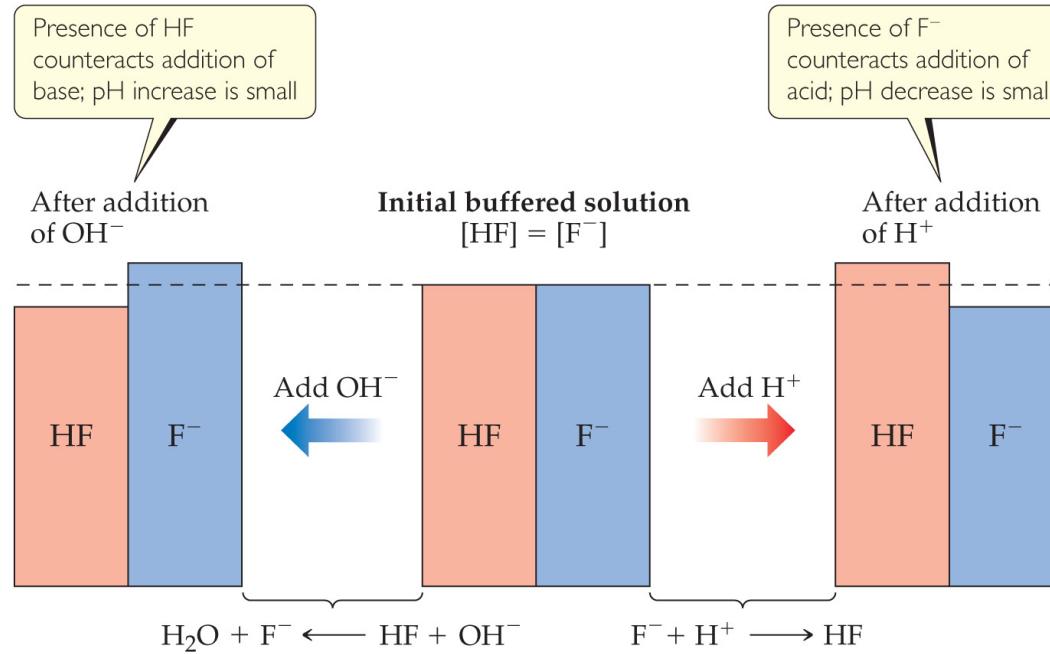


- Solutions of a weak conjugate acid–base pair that resist drastic changes in pH are called **buffers**.
- These solutions contain relatively **high concentrations** ($10^{-3} M$ or more) of both the acid and base. Their concentrations are approximately equal.

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.

How a Buffer Works



- Adding a small amount of acid or base only slightly neutralizes one component of the buffer, so the pH doesn't change much.

Calculating the pH of a Buffer

- For a weak acid: $K_a = [H^+][A^-]/[HA]$
- Take $-\log$ of both sides:

$$-\log K_a = -\log[H^+] + -\log([A^-]/[HA])$$

- Rearrange:

$$-\log[H^+] = -\log K_a + \log([A^-]/[HA])$$

- Which is:

$$pH = pK_a + \log([A^-]/[HA])$$

- This equation is known as the **Henderson–Hasselbalch equation.**

This applies only to buffers.

Henderson–Hasselbalch Equation

What is the pH of a buffer that is 0.12 M in lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, and 0.10 M in sodium lactate? K_a for lactic acid is 1.4×10^{-4} .

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log([\text{A}^-]/[\text{HA}]) \\ &= -\log(1.4 \times 10^{-4}) + \log[(0.10 \text{ M})/(0.12 \text{ M})] \\ &= 3.85 + (-0.08) = 3.77\end{aligned}$$

Buffer Capacity

- The amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree
- Using the Henderson–Hasselbalch equation, pH will be the same for a conjugate acid–base pair of 1 M each or 0.1 M each; however, the buffer which is 1 M can neutralize more acid or base before the pH changes.

Higher concentration, higher buffer capacity!

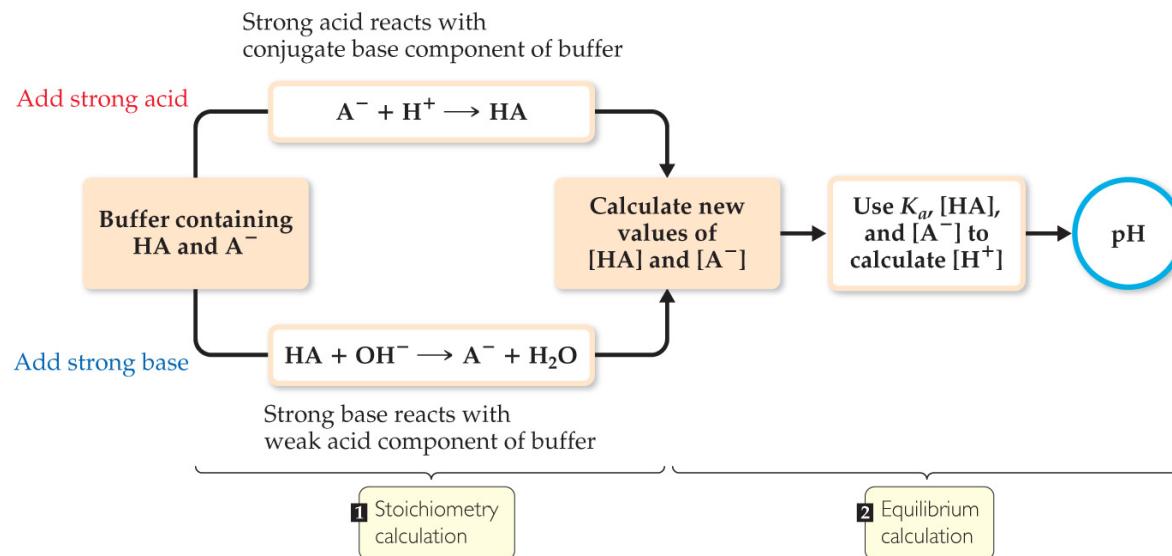
pH Range

- The range of pH values over which a buffer system works effectively
- Optimal pH: where $\text{pH} = \text{p}K_a ([\text{HA}] = [\text{A}^-])$
- If one concentration is more than 10 times the other, the buffering action is poor; this means that the pH range of a buffer is usually ± 1 pH unit from $\text{p}K_a$.

$$\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}])$$

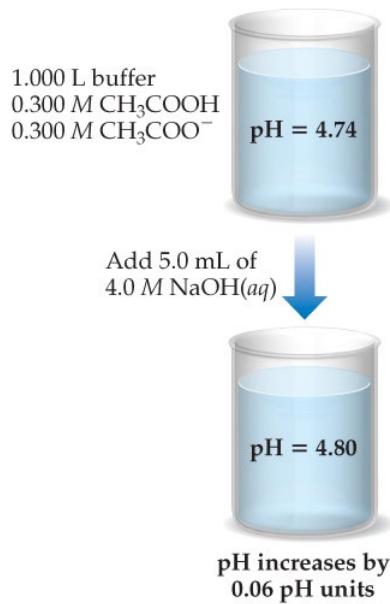
Addition of a Strong Acid or a Strong Base to a Buffer

- 1) Adding of the strong acid or base is a neutralization reaction; calculate like stoichiometry problem to find $[HA]$ and $[A^-]$ when *all* of the added acid or base reacts.
- 2) Use the Henderson–Hasselbalch equation to find pH.



Example

- A buffer is made by adding 0.300 mol $\text{HC}_2\text{H}_3\text{O}_2$ and 0.300 mol $\text{NaC}_2\text{H}_3\text{O}_2$ to enough water to make 1.00 L of solution. Calculate the pH after 0.020 mol of NaOH is added.



1)

	$[\text{CH}_3\text{COOH}]$	$[\text{OH}^-]$	$[\text{CH}_3\text{COO}^-]$
Before reaction (mol)	0.300	0.020	0.300
Change (mol)	-0.020	-0.020 (LR)	+0.020
After reaction (mol)	0.280	0	0.320

Example (completed)

2) Use the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}])$$

Since this is a buffer, the volume for each concentration is the same, so the ratio of molarity can be calculated using a ratio of moles.

$$\text{pH} = \text{p}K_a + \log (n_{\text{HA}}/n_{\text{A}^-})$$

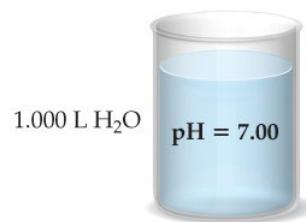
$$\text{pH} = 4.74 + \log(0.320/0.280) = 4.80$$

Buffer

$$\text{pH} = 4.74 + \log(0.320/0.280) = 4.80$$

Change from 4.74 → 4.80

Water



Add 5.0 mL of
4.0 M NaOH(*aq*)



pH increases by
5.30 pH units

$$[\text{OH}^-] = 0.020 \text{ mol}/1.005 \text{ L} = 0.020 \text{ M}$$

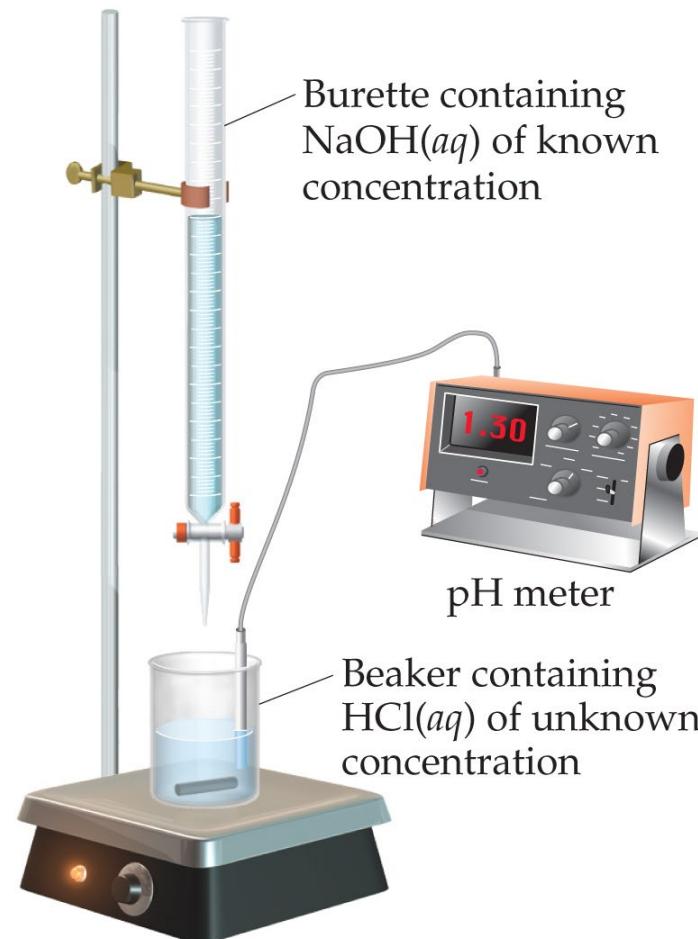
$$\text{pOH} = -\log[\text{OH}] = -\log 0.020 = +1.70$$

$$\text{pH} = 14 - 1.70 = 12.30$$

Change from 7.00 → 12.30

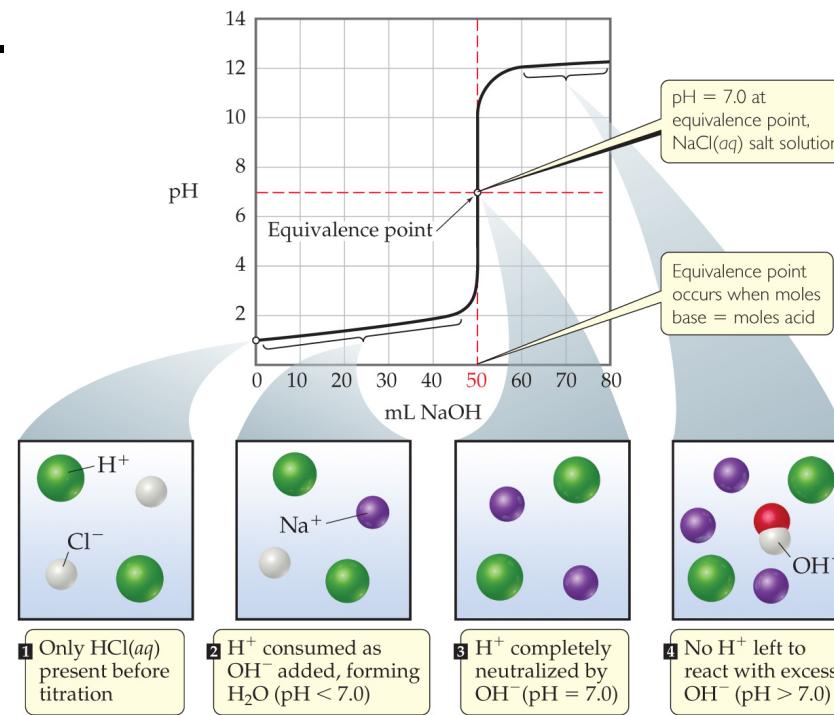
Titration

- In this technique, an acid (or base) solution of known concentration is slowly added to a base (or acid) solution of unknown concentration.
- A pH meter or indicators are used to determine when the solution has reached the **equivalence point**: The amount of acid equals that of base.

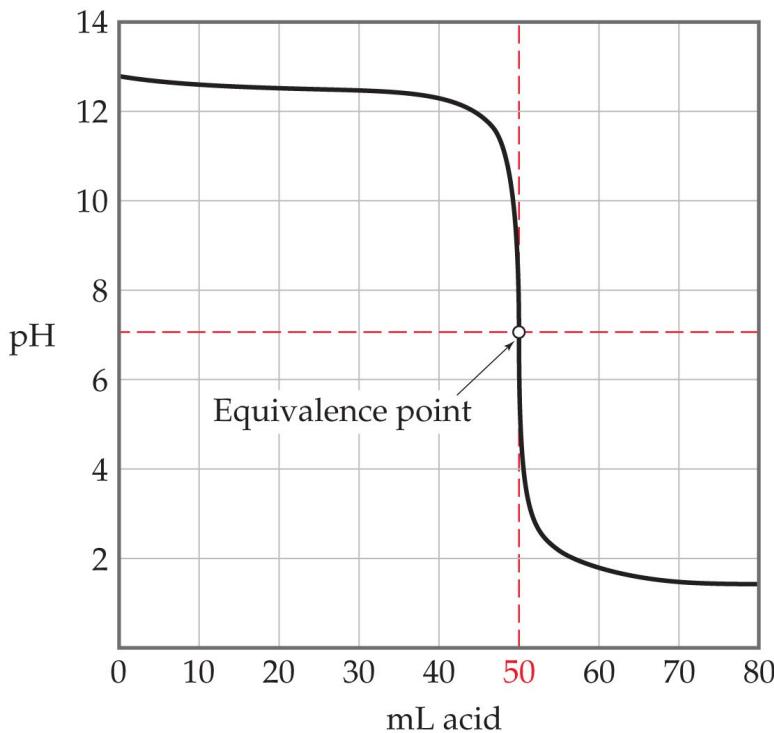


Titration of a Strong Acid with a Strong Base

- From the start of the titration to near the equivalence point, the pH goes up slowly.
- Just before (and after) the equivalence point, the pH rises rapidly.
- At the equivalence point, $\text{pH} = 7$.
- As more base is added, the pH again levels off.



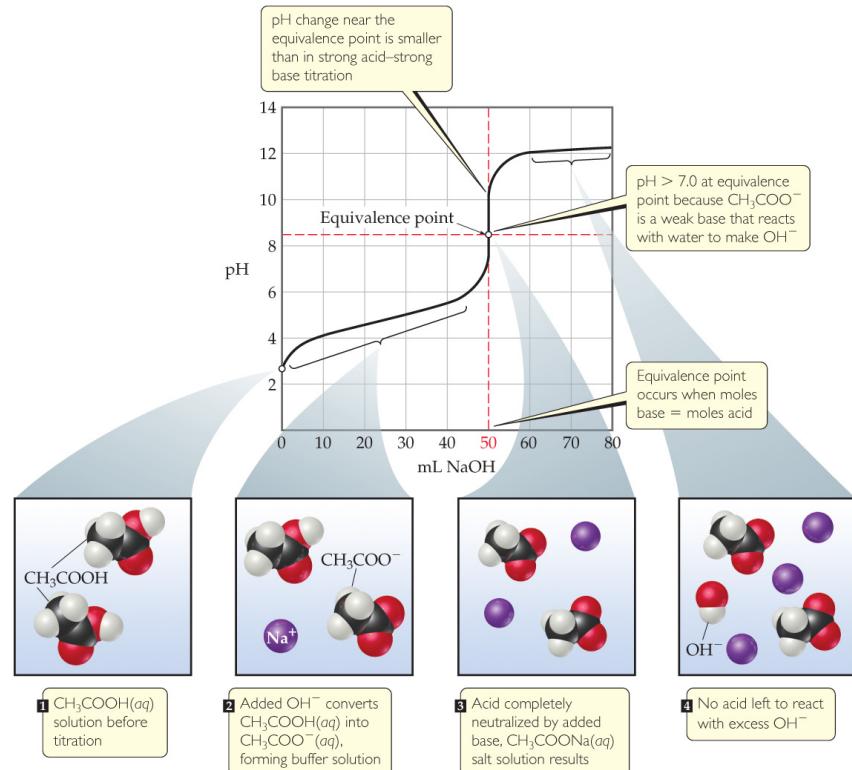
Titration of a Strong Base with a Strong Acid



- It looks like you “flipped over” the strong acid being titrated by a strong base.
- Start with a high pH (basic solution); the pH = 7 at the equivalence point; low pH to end.

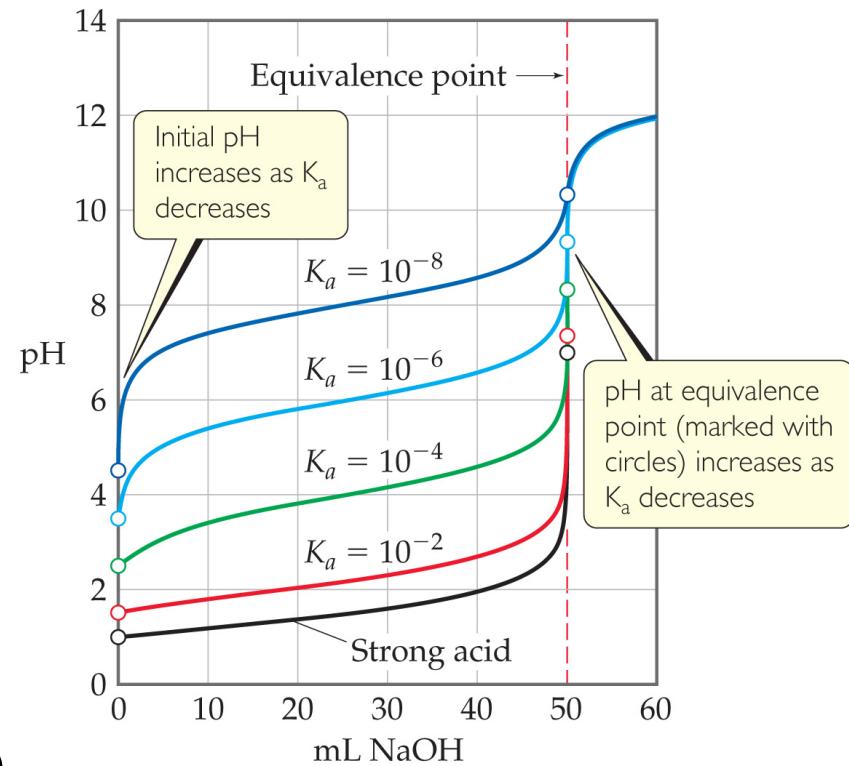
Titration of a Weak Acid with a Strong Base

- Use K_a to find initial pH.
- Find the pH in the “buffer region” using stoichiometry followed by the Henderson–Hasselbalch equation.
- At the equivalence point the **pH is >7**. Use the conjugate base of the weak acid to determine the pH.
- As more base is added, the pH levels off. This is exactly the same as for strong acids.



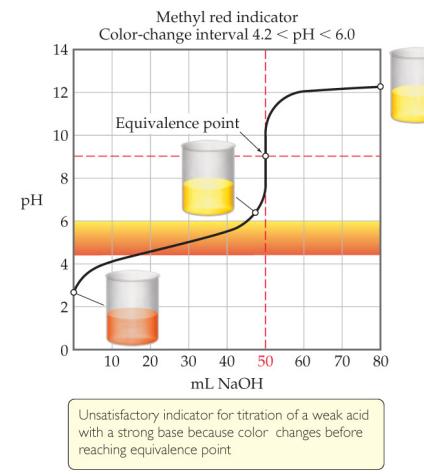
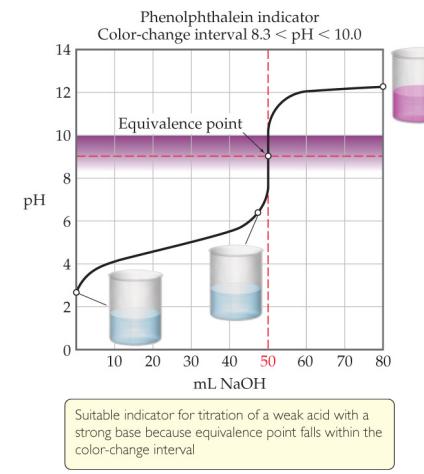
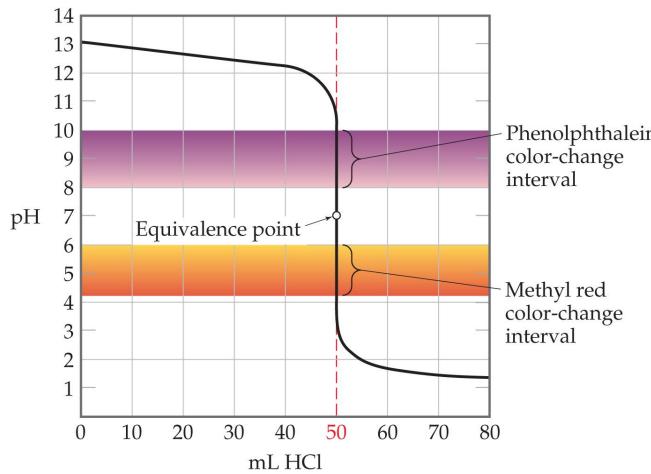
Ways That a Weak Acid Titration Differs from a Strong Acid Titration

- 1) A solution of weak acid has a higher initial pH than a strong acid.
- 2) The pH change near the equivalence point is smaller for a weak acid.
(This is at least partly due to the buffer region.)
- 3) The pH at the equivalence point is greater than 7 for a weak acid.

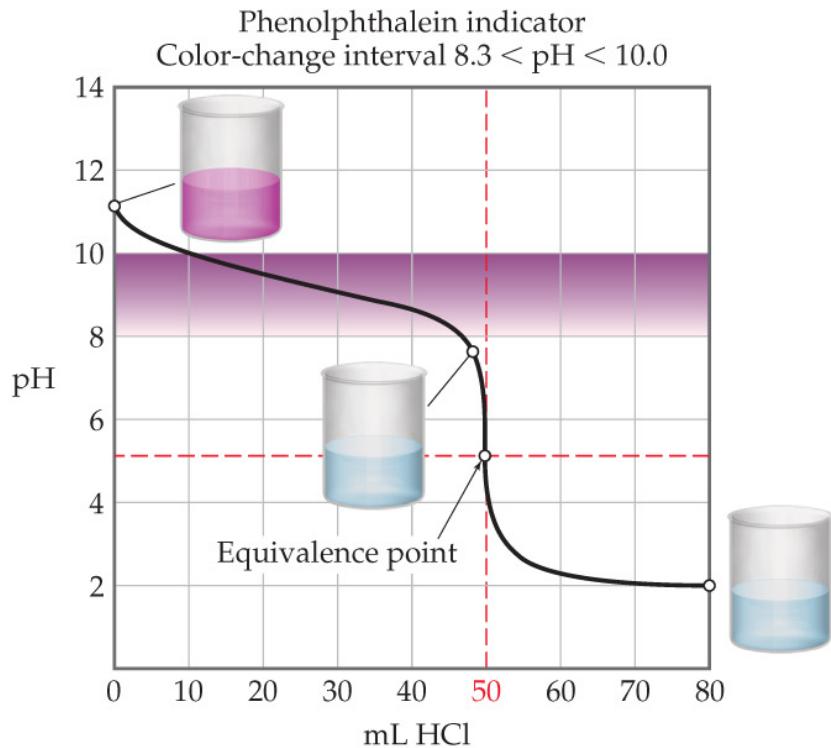


Use of Indicators

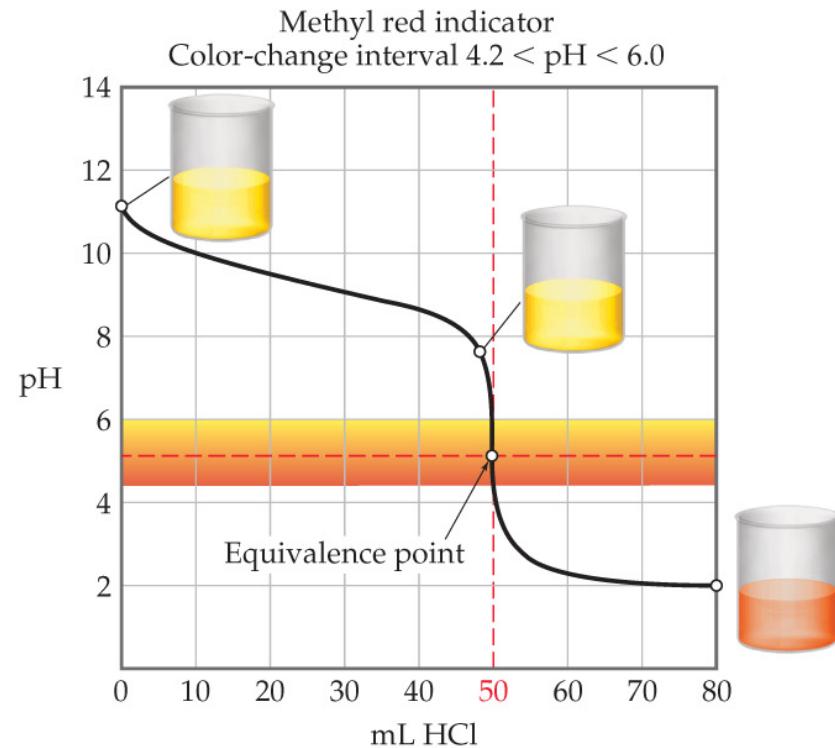
- Indicators are weak acids that have a different color than their conjugate base form.
- Each indicator has its own pH range over which it changes color.
- An indicator can be used to find the equivalence point in a titration as long as it changes color in the small volume change region where the pH rapidly changes.



Indicator Choice Can Be Critical!



Unsatisfactory indicator for titration of a weak base with a strong acid because color changes before reaching equivalence point



Suitable indicator for titration of a weak base with a strong acid because equivalence point falls within the color-change interval

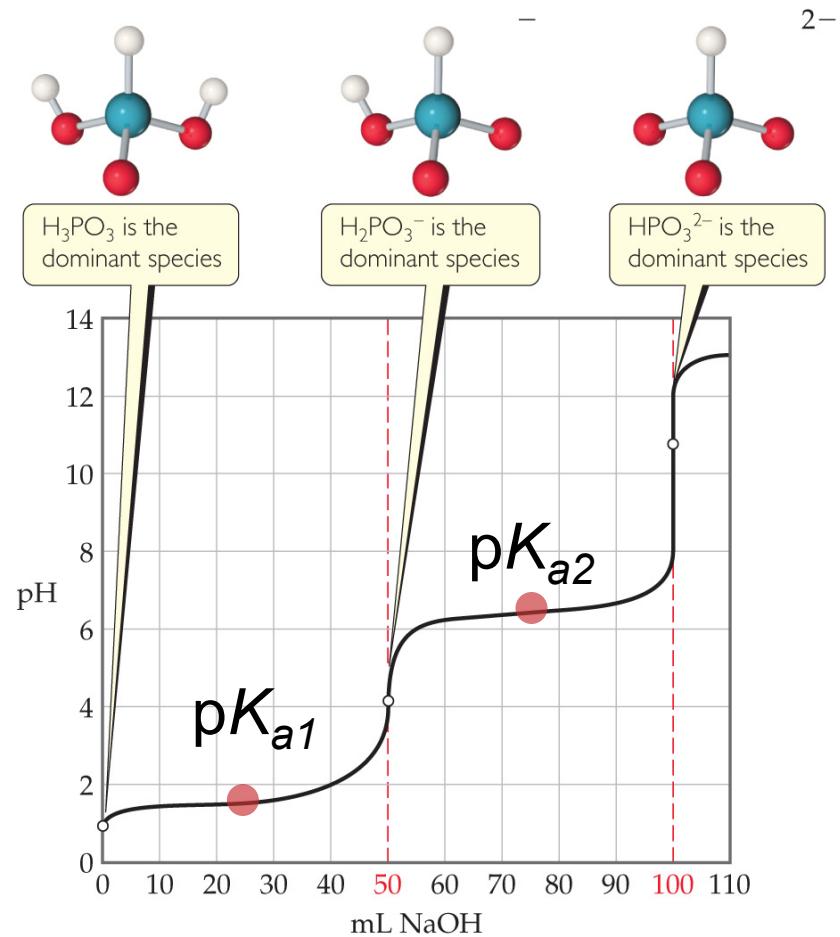
Titrations of Polyprotic Acids

- When a polyprotic acid is titrated with a base, there is an equivalence point for each dissociation.
- Using the Henderson–Hasselbalch equation, we can see that *half way* to each equivalence point gives us the pK_a for that step.

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

$$\textcircled{c} \quad \text{pH} = pK_{a2} + \log \frac{[\text{HPO}_3^{2-}]}{[\text{H}_2\text{PO}_3^-]}$$

$$\text{pH} = pK_a + \log(\text{[A}^-]/\text{[HA]})$$



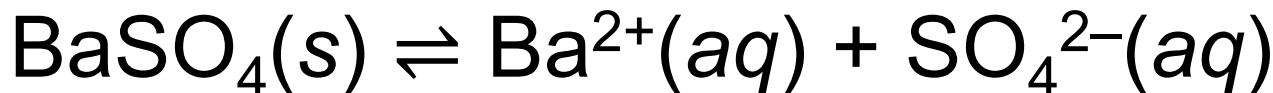
Solubility Equilibria

- Because ionic compounds are strong electrolytes, they dissociate completely to the extent that they dissolve.
- When an equilibrium equation is written, the solid is the reactant and the ions in solution are the products.
- The equilibrium constant expression is called the **solubility-product constant**. It is represented as K_{sp} .



Solubility Product

➤ For example:



➤ The equilibrium constant expression is

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

➤ Another example:

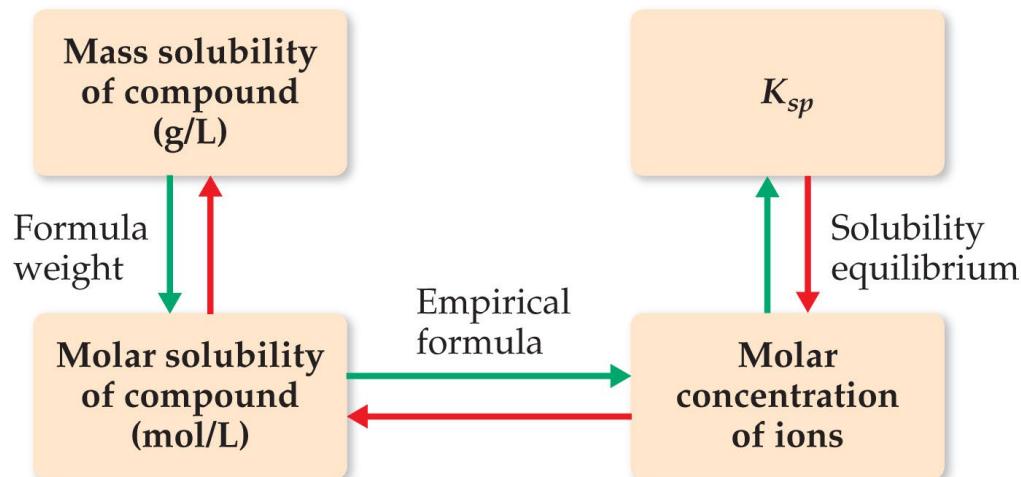


➤ The equilibrium constant expression is

$$K_{sp} = [\text{Ba}^{2+}]^3[\text{PO}_4^{3-}]^2$$

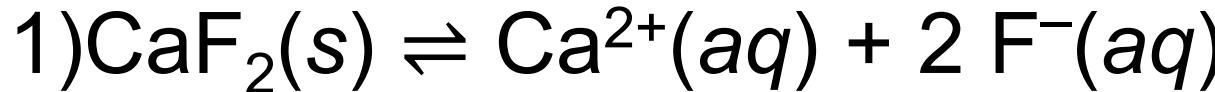
Solubility vs. Solubility Product

- K_{sp} is *not* the same as solubility.
- Solubility is the quantity of a substance that dissolves to form a saturated solution
- Common units for solubility:
 - Grams per liter (g/L)
 - Moles per liter (mol/L)



Calculating Solubility from K_{sp}

- The K_{sp} for CaF_2 is 3.9×10^{-11} at 25 °C. What is its molar solubility?
- Follow the same format as before:



$$2) K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = 3.9 \times 10^{-11}$$

3)

	$\text{CaF}_2(s)$	$[\text{Ca}^{2+}](M)$	$[\text{F}^-](M)$
Initial concentration (M)	---	0	0
Change in concentration (M)	---	$+x$	$+2x$
Equilibrium concentration (M)	---	x	$2x$

Example (completed)

4) Solve: Substitute the equilibrium concentration values from the table into the solubility-product equation:

$$3.9 \times 10^{-11} = (x)(2x)^2 = 4x^3$$

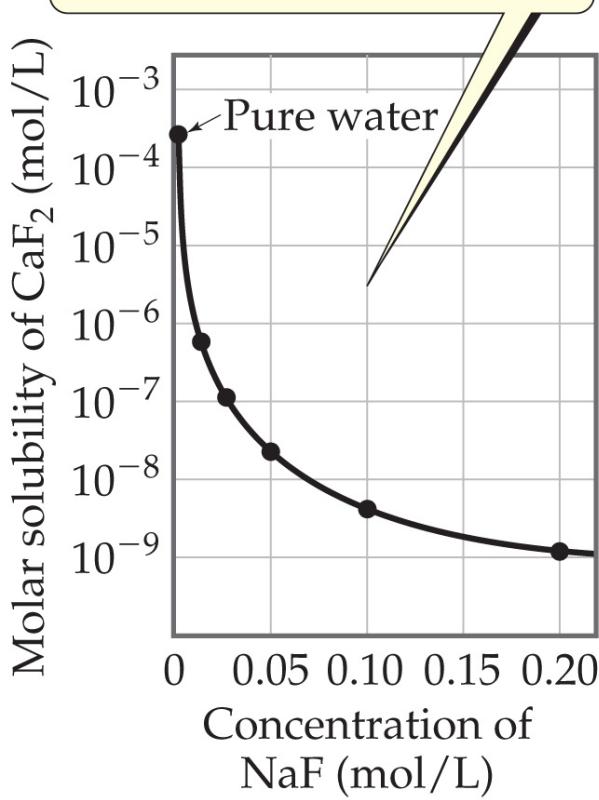
$$x = 2.1 \times 10^{-4} M$$

(If you want the answer in g/L, multiply by molar mass; this would give 0.016 g/L.)

Factors Affecting Solubility

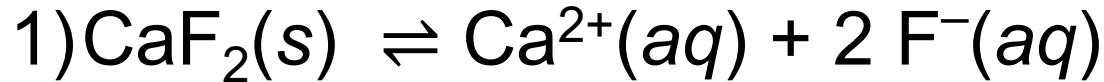
- The Common-Ion Effect
 - If one of the ions in a solution equilibrium is already dissolved in the solution, the solubility of the salt will decrease.
 - If either calcium ions or fluoride ions are present, then calcium fluoride will be less soluble.

Solubility of CaF_2 decreases sharply as a common ion (F^-) is added to the solution



Calculating Solubility with a Common Ion

- What is the molar solubility of CaF_2 in $0.010 \text{ M Ca}(\text{NO}_3)_2$?
- Follow the same format as before:



$$2) K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = 3.9 \times 10^{-11}$$

3)

	$\text{CaF}_2(s)$	$[\text{Ca}^{2+}](M)$	$[\text{F}^-](M)$
Initial concentration (M)	---	0.010	0
Change in concentration (M)	---	$+x$	$+2x$
Equilibrium concentration (M)	---	$0.010 + x$	$2x$



Example (completed)

4) Solve: Substitute the equilibrium concentration values from the table into the solubility-product equation:

$$3.9 \times 10^{-11} = (0.010 + x)(2x)^2$$

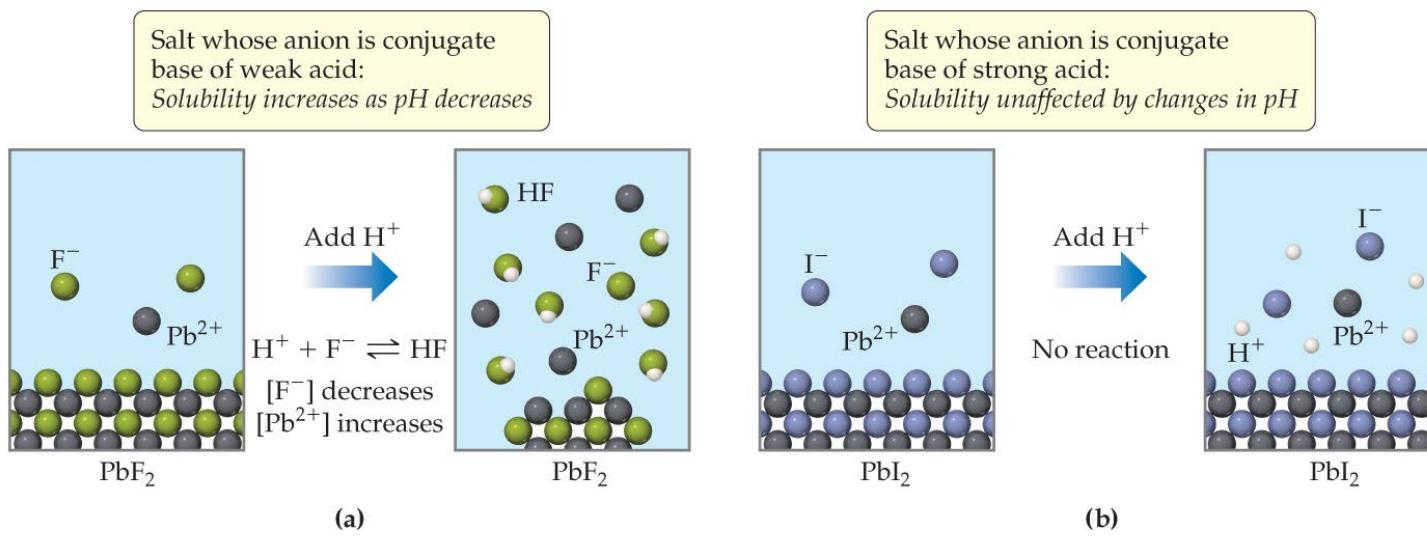
(We assume that $x \ll 0.010$, so that $0.010 + x = 0.010!$)

$$3.9 \times 10^{-11} = (0.010)(2x)^2$$

$$x = 3.1 \times 10^{-5} M$$

Factors Affecting Solubility

- pH: If a substance has a basic anion, it will be more soluble in an acidic solution.
- Remember that buffers control pH. When a buffer is used, there is *no change* in concentration of hydroxide ion!



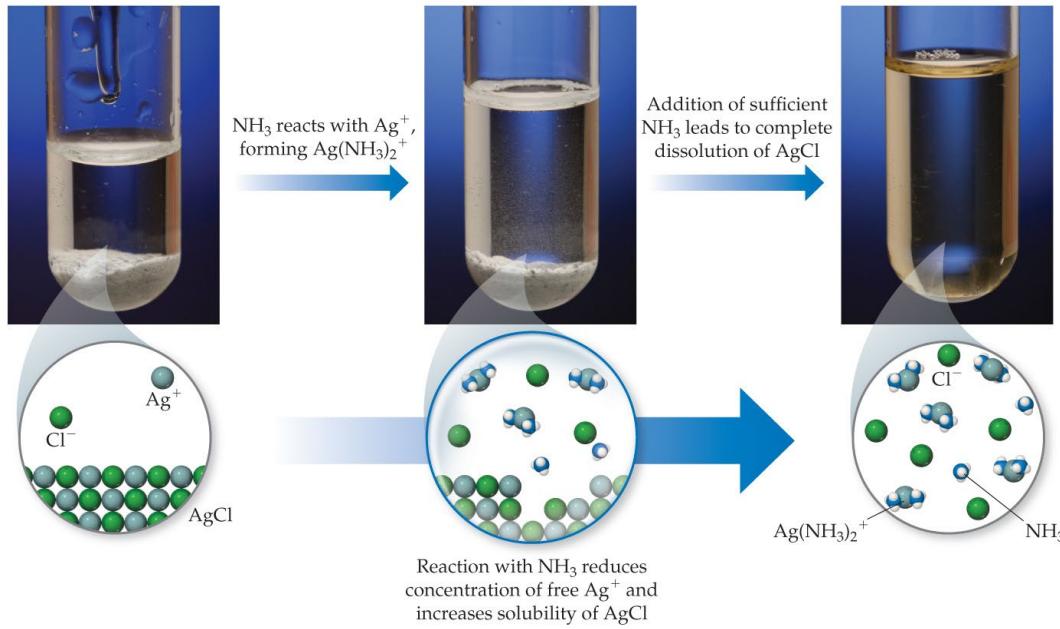
Complex Ion Formation

- Metal ions can act as Lewis acids and form complex ions with Lewis bases in the solvent.
- The formation of these complex ions increases the solubility of these salts.

Table 17.1 Formation Constants for Some Metal Complex Ions in Water at 25 °C

Complex Ion	K_f	Equilibrium Equation
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7	$\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+ (aq)$
$\text{Ag}(\text{CN})_2^-$	1×10^{21}	$\text{Ag}^+(aq) + 2 \text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2.9×10^{13}	$\text{Ag}^+(aq) + 2 \text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$
CdBr_4^{2-}	5×10^3	$\text{Cd}^{2+}(aq) + 4 \text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$
$\text{Cr}(\text{OH})_4^-$	8×10^{29}	$\text{Cr}^{3+}(aq) + 4 \text{OH}^-(aq) \rightleftharpoons \text{Cr}(\text{OH})_4^-(aq)$
$\text{Co}(\text{SCN})_4^{2-}$	1×10^3	$\text{Co}^{2+}(aq) + 4 \text{SCN}^-(aq) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(aq)$
$\text{Cu}(\text{NH}_3)_4^{2+}$	5×10^{12}	$\text{Cu}^{2+}(aq) + 4 \text{NH}_3(aq) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(aq)$
$\text{Cu}(\text{CN})_4^{2-}$	1×10^{25}	$\text{Cu}^{2+}(aq) + 4 \text{CN}^-(aq) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(aq)$
$\text{Ni}(\text{NH}_3)_6^{2+}$	1.2×10^9	$\text{Ni}^{2+}(aq) + 6 \text{NH}_3(aq) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
$\text{Fe}(\text{CN})_6^{4-}$	1×10^{35}	$\text{Fe}^{2+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN}_3)_6^{4-}(aq)$
$\text{Fe}(\text{CN})_6^{3-}$	1×10^{42}	$\text{Fe}^{3+}(aq) + 6 \text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(aq)$

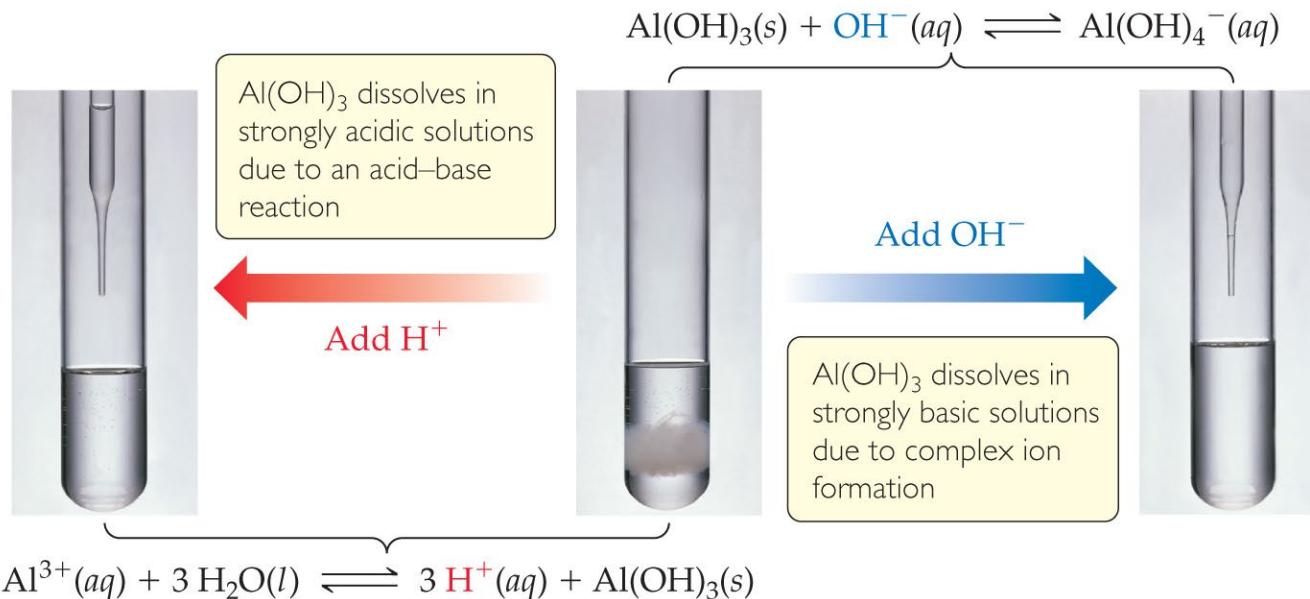
How Complex Ion Formation Affects Solubility



- Silver chloride is insoluble. It has a K_{sp} of 1.6×10^{-10} .
- In the presence of NH₃, the solubility greatly increases because Ag⁺ will form complex ions with NH₃.

Amphotericism and Solubility

- **Amphoteric oxides and hydroxides** are soluble in strong acids or base, because they can act either as acids or bases.
- Examples are oxides and hydroxides of Al^{3+} , Cr^{3+} , Zn^{2+} , and Sn^{2+} .

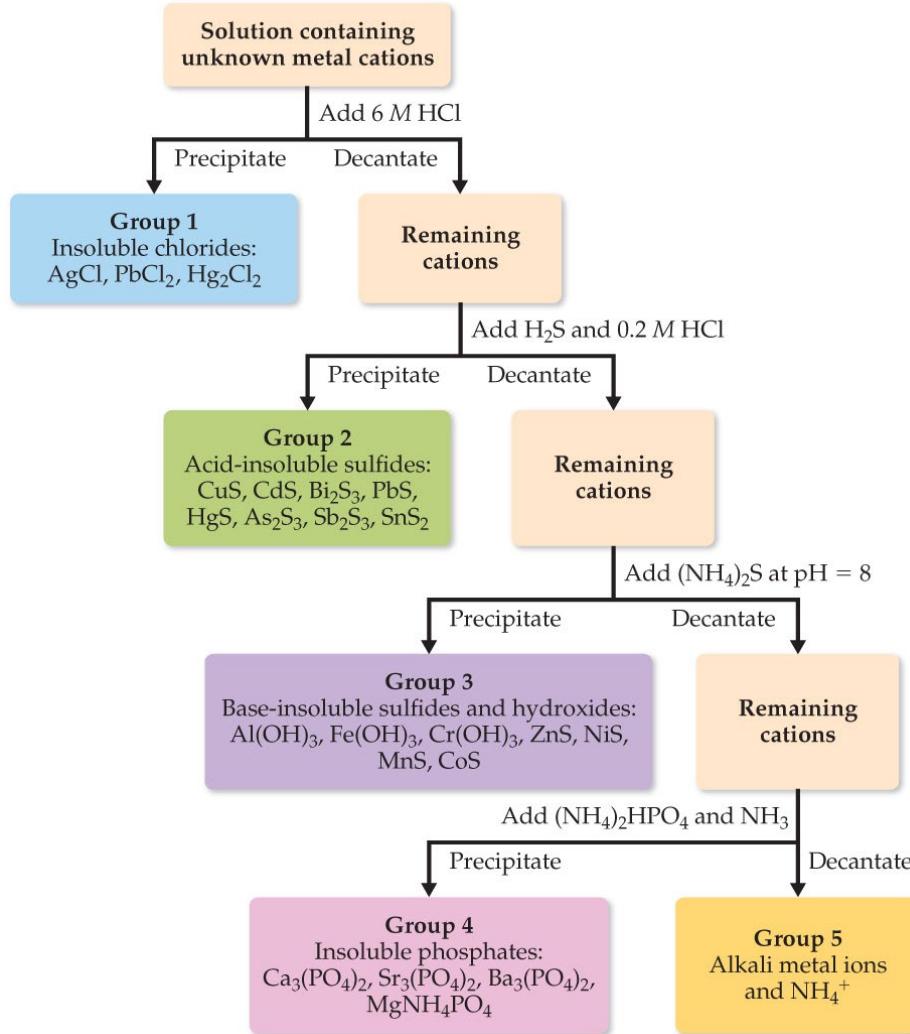


Will a Precipitate Form?

- To decide, we 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 of Ions



One can use differences in solubilities of salts to separate ions in a mixture. This has been used for qualitative analysis of the presence of ions in a solution.