

Lecture Presentation

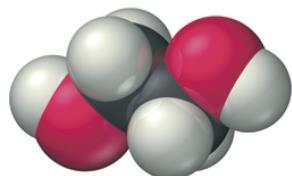
**Chapter 17**

**Aqueous Ionic Equilibrium**

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### The Danger of Antifreeze

- Each year, thousands of pets and wildlife species die from consuming antifreeze.
- Most brands of antifreeze contain ethylene glycol.
  - Sweet taste
  - Initial effect: drunkenness
- Metabolized in the liver to glycolic acid
  - HOCH<sub>2</sub>COOH



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## Why Is Glycolic Acid Toxic?

- In high enough concentration in the bloodstream, glycolic acid overwhelms the buffering ability of the  $\text{HCO}_3^-$  in the blood, causing the blood pH to drop.
- Low blood pH compromises its ability to carry  $\text{O}_2$ .
  - **Acidosis**
$$\text{HbH}^+(aq) + \text{O}_2(g) \rightleftharpoons \text{HbO}_2(aq) + \text{H}^+(aq)$$
- One treatment is to give the patient ethyl alcohol, which has a higher affinity for the enzyme that catalyzes the metabolism of ethylene glycol.

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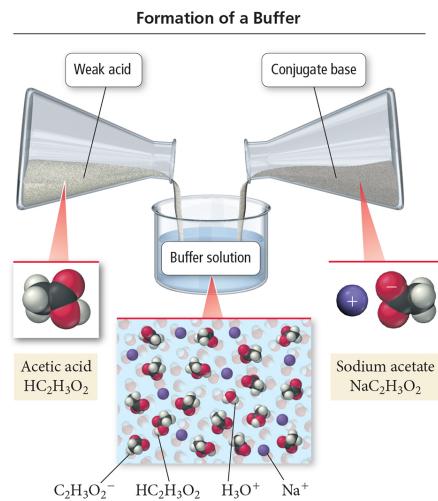
## Buffer Solutions

- A **buffer** resists changes in pH by neutralizing added acid or added base.
- Contains either
  - significant amounts of a weak acid and its conjugate base.
  - significant amounts of a weak base and its conjugate acid.
- Blood has a mixture of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$ .

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## Making an Acidic Buffer Solution

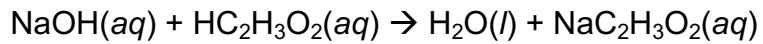
It must contain significant amounts of both a weak acid and its conjugate base.



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## An Acidic Buffer Solution

- If a strong base is added, it is neutralized by the weak acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) in the buffer.



- If the amount of NaOH added is less than the amount of acetic acid present, the pH change is small.

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## An Acidic Buffer Solution

- If a strong acid is added, it is neutralized by the conjugate base ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) in the buffer.



- If the amount of HCl is less than the amount of  $\text{NaC}_2\text{H}_3\text{O}_2$  present, the pH change is small.

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## How Acid Buffers Work: Addition of Base

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{A}^-(aq) + \text{H}_3\text{O}^+(aq)$$

- Buffers work by applying Le Châtelier's principle to weak acid equilibrium.
- Buffer solutions contain significant amounts of the weak acid molecules, HA.
- These molecules react with added base to neutralize it.
 
$$\text{HA}(aq) + \text{OH}^-(aq) \rightarrow \text{A}^-(aq) + \text{H}_2\text{O}(l)$$
  - You can also think of the  $\text{H}_3\text{O}^+$  combining with the  $\text{OH}^-$  to make  $\text{H}_2\text{O}$ ; the  $\text{H}_3\text{O}^+$  is then replaced by the shifting equilibrium.

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## How Acid Buffers Work: Addition of Acid

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{A}^-(aq) + \text{H}_3\text{O}^+(aq)$$

- The buffer solution also contains significant amounts of the conjugate base anion,  $\text{A}^-$ .
- These ions combine with added acid to make more HA.



- After the equilibrium shifts, the concentration of  $\text{H}_3\text{O}^+$  is kept constant.

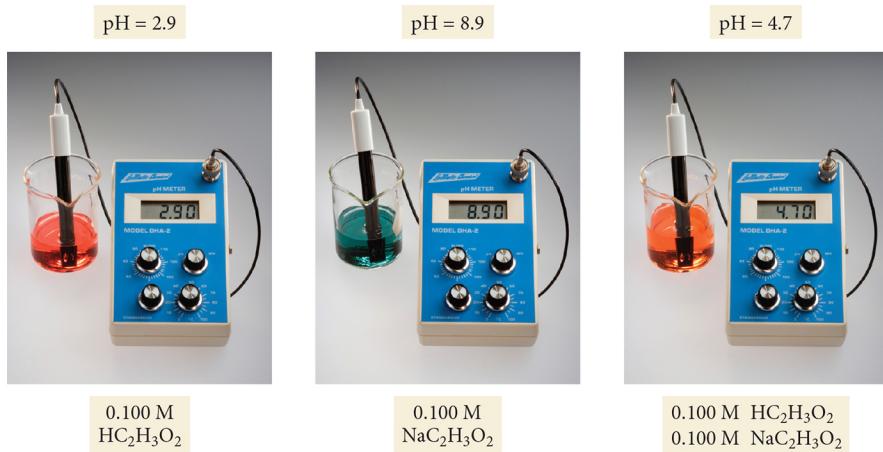
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## Common Ion Effect

- In a weak acid solution, adding a salt containing the anion  $\text{NaA}$ , the conjugate base of the acid (known as the **common ion**), shifts the position of equilibrium to the left.
- This lowers the  $\text{H}_3\text{O}^+$  ion concentration and causes the pH to be higher than the pH of the acid solution.

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## Common Ion Effect



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## Henderson–Hasselbalch Equation

- An equation derived from the  $K_a$  expression that allows us to calculate the pH of a buffer solution
- The equation calculates the pH of a buffer from the  $pK_a$  and initial concentrations of the weak acid and salt of the conjugate base, as long as the “x is small” approximation is valid.

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

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## Deriving the Henderson–Hasselbalch Equation

To derive the equation, consider the equilibrium expression for a generic acidic buffer:



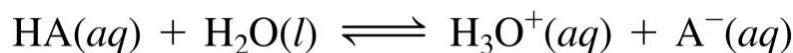
Solving for  $\text{H}_3\text{O}^+$  we have the following:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

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## Deriving the Henderson–Hasselbalch Equation



Taking the logarithm of both sides and expanding, since  $\log(AB) = \log A + \log B$

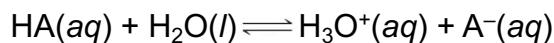
$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

$$-\log[\text{H}_3\text{O}^+] = -\log(K_a \frac{[\text{HA}]}{[\text{A}^-]})$$

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

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## Deriving the Henderson–Hasselbalch Equation



$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

$$-\log[\text{H}_3\text{O}^+] = -\log(K_a \frac{[\text{HA}]}{[\text{A}^-]})$$

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

Multiplying both sides by  $-1$  and rearranging we get the following:

$$-\log[\text{H}_3\text{O}^+] = -\log K_a + \log([\text{A}^-]/[\text{HA}]) \text{ (see page 784)}$$

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## Deriving the Henderson–Hasselbalch Equation



Since  $\text{pH} = -\log[\text{H}_3\text{O}^+]$  and  $\text{p}K_a = \log K_a$

$$\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}]) \text{ (see page 758)}$$

We can then generalize as follows:

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

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## Using the Full Equilibrium Analysis or the Henderson–Hasselbalch Equation?

- The Henderson–Hasselbalch equation is generally good enough when the “ $x$  is small” approximation is applicable.
- Generally, the “ $x$  is small” approximation will work when both of the following are true:
  - The initial concentrations of acid and salt are not very dilute.
  - The  $K_a$  is fairly small.
- For most problems, this means that the initial acid and salt concentrations should be over 100 to 1000 times larger than the value of  $K_a$ .

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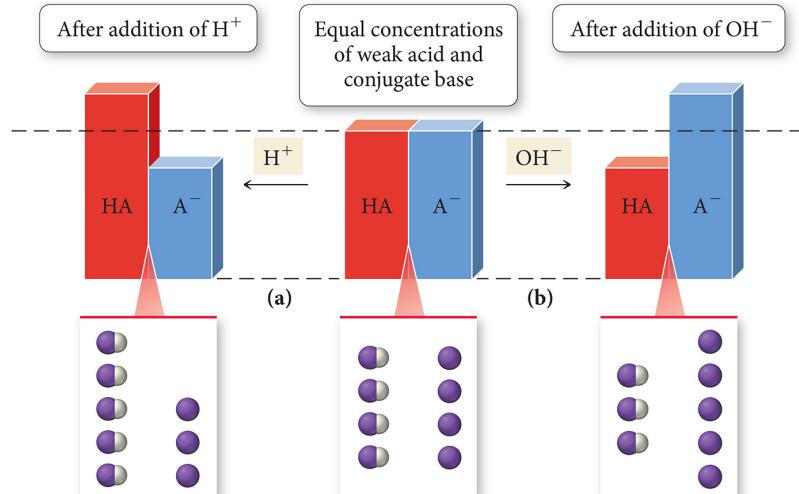
## Calculating pH Changes in a Buffer Solution

- Calculating the new pH after adding acid or base requires breaking the problem into two parts:
  1. A stoichiometry calculation for the reaction of the added chemical with one of the ingredients of the buffer to reduce its initial concentration and increase the concentration of the other
    - Added acid reacts with the  $A^-$  to make more HA.
    - Added base reacts with the HA to make more  $A^-$ .
  2. An equilibrium calculation of  $[H_3O^+]$  using the new initial values of  $[HA]$  and  $[A^-]$

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## Action of a Buffer

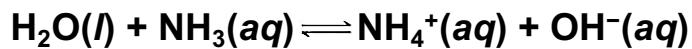
### Action of a Buffer



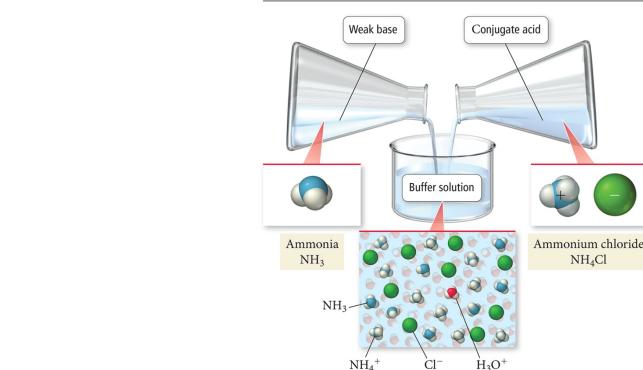
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## Basic Buffers

- Buffers can also be composed of a weak base and its conjugate acid, usually in the form of a salt.



Formation of a Buffer



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## Buffer Effectiveness

- An effective buffer neutralizes moderate amounts of added acid or base.
- However, there is a limit to how much can be added before the pH changes significantly.
- The **buffer capacity** is the amount of acid or base a buffer can neutralize.
- The **buffer range** is the pH range in which the buffer can be effective.
- The effectiveness of a buffer depends on two factors: (1) the relative amounts of buffer acid and base, and (2) the absolute concentrations of buffer acid and base.

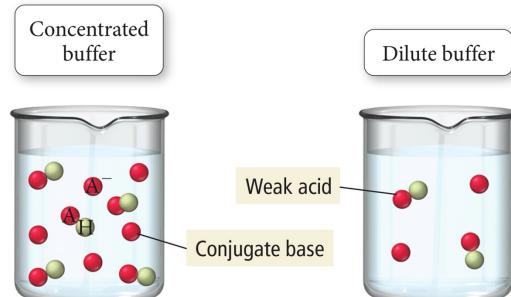
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## Buffer Capacity

- **Buffer capacity** is the amount of acid or base that can be added to a buffer without causing a large change in pH.
- The buffer capacity increases with increasing absolute concentration of the buffer components.

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## Buffer Capacity



A concentrated buffer can neutralize more added acid or base than a dilute buffer.

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## Effectiveness of Buffers

- A buffer will be **most** effective when the ratio  $[\text{acid}]:[\text{base}] = 1$ .
  - Equal concentrations of acid and base
- A buffer will be effective when  $0.1 < [\text{base}]:[\text{acid}] < 10$ .
- A buffer will be most effective when the [acid] and the [base] are large.

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## Buffer Range

- We have said that a buffer will be effective when  $0.1 < [\text{base}]:[\text{acid}] < 10$ .
- Substituting into the Henderson–Hasselbalch equation, we can calculate the maximum and minimum pH at which the buffer will be effective.

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

<b>Lowest pH</b> $\text{pH} = \text{p}K_a + \log(0.10)$	<b>Highest pH</b> $\text{pH} = \text{p}K_a + \log(10)$
$\text{pH} = \text{p}K_a - 1$	$\text{pH} = \text{p}K_a + 1$

Therefore, the effective pH range of a buffer is  $\text{p}K_a \pm 1$ . When choosing an acid to make a buffer, choose one whose  $\text{p}K_a$  is closest to the pH of the buffer.

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## Buffer Capacity

- As the  $[\text{base}]:[\text{acid}]$  ratio approaches 1, the ability of the buffer to neutralize both added acid and base improves.
- Buffers that need to work mainly with added acid generally have  $[\text{base}] > [\text{acid}]$ .
- Buffers that need to work mainly with added base generally have  $[\text{acid}] > [\text{base}]$ .

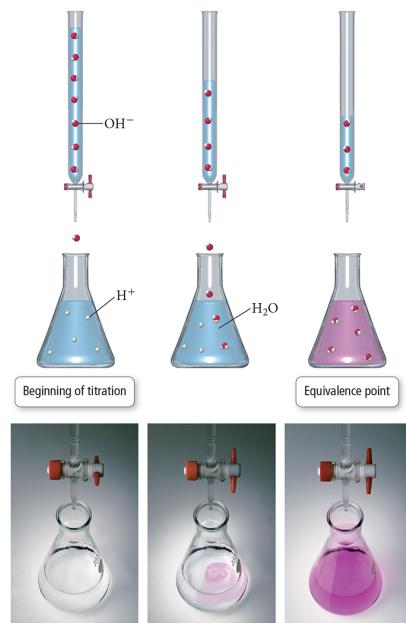
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## Titration

- In an **acid–base titration**, a solution of unknown concentration (**titrant**) is slowly added to a solution of known concentration until the reaction is complete.
- When the moles of acid are stoichiometrically equal to the moles of base, the titration has reached its **equivalence point**.
- An **indicator** is a chemical that changes color when the pH changes.

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## Titration



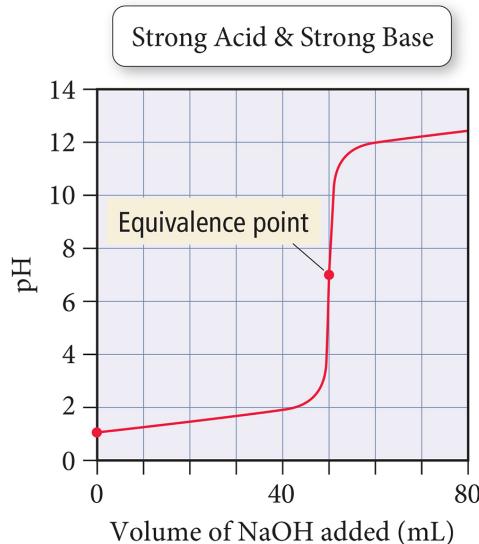
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## Titration Curve

- It is a plot of pH versus the amount of added titrant.
- The inflection point of the curve is the equivalence point of the titration.
- Prior to the equivalence point, the original solution in the flask is in excess, so the pH is closest to its pH.
- The pH of the equivalence point depends on the pH of the salt solution.
  - Equivalence point of neutral salt, pH = 7
  - Equivalence point of acidic salt, pH < 7
  - Equivalence point of basic salt, pH > 7
- Beyond the equivalence point, the unknown solution in the burette is in excess, so the pH approaches its pH.

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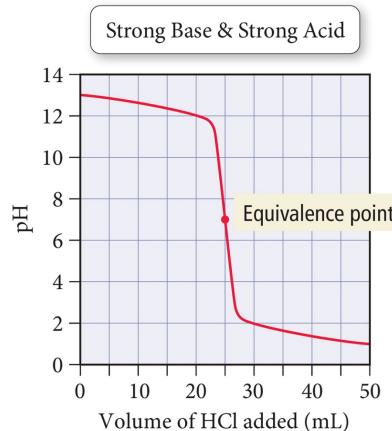
## Titration Curve: Strong Base Added to Strong Acid



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## Titration of a Strong Base with a Strong Acid

- If the titration is run so that the base is in the flask and you are adding the acid, the titration curve will be the reflection of the previous curve.



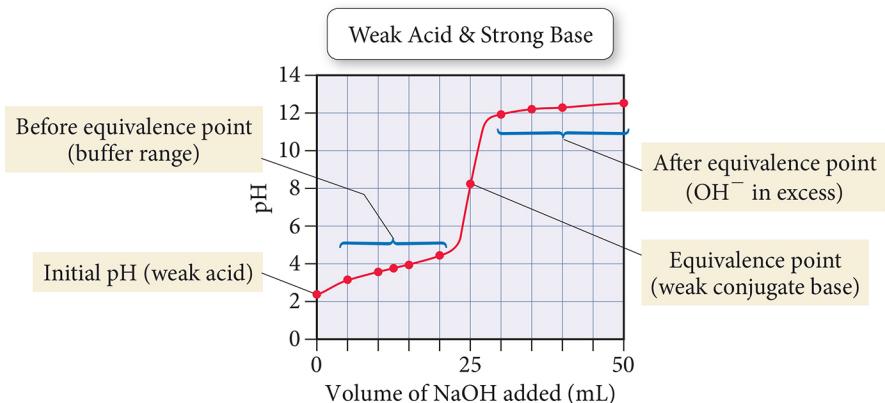
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## Titration of a Weak Acid with a Strong Base

- Titrating a weak acid with a strong base results in differences in the titration curve at the excess acid region and the equivalence point.
- The initial pH is determined using the  $K_a$  of the weak acid.
- The pH in the excess acid region is determined as you would determine the pH of a buffer.
- The pH at the equivalence point is determined using the  $K_b$  of the conjugate base of the weak acid.
- The pH after equivalence is dominated by the excess strong base.
  - The basicity from the conjugate base anion is negligible.

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## Titration Curve of a Weak Acid with a Strong Base



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## Titrating Weak Acid with a Strong Base

- The initial pH is that of the weak acid solution.
  - Calculate like a weak acid equilibrium problem as in Chapter 16.
- Before the equivalence point, the solution becomes a buffer.
  - Calculate mol  $\text{HA}_{\text{init}}$  and mol  $\text{A}^-_{\text{init}}$  using reaction stoichiometry.
  - Calculate pH with Henderson–Hasselbalch using mol  $\text{HA}_{\text{init}}$  and mol  $\text{A}^-_{\text{init}}$ .
- Half-neutralization pH =  $\text{p}K_a$

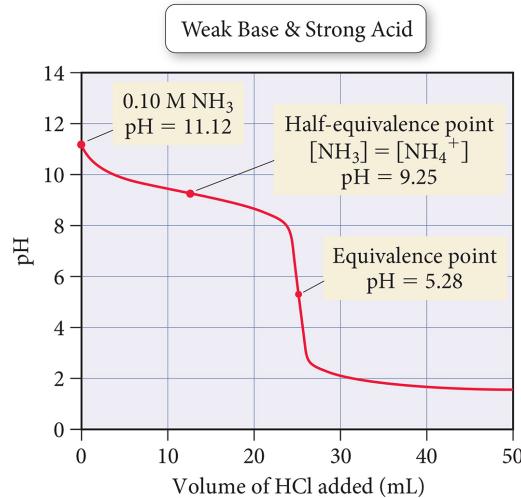
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## Titrating Weak Acid with a Strong Base

- At the equivalence point, the mole HA = mol base, so the resulting solution has only the conjugate base anion in it before equilibrium is established.
  - Mol A<sup>-</sup> = original mole HA
    - Calculate the volume of added base as you did in Chapter 4.
  - [A<sup>-</sup>]<sub>init</sub> = mol A<sup>-</sup>/total liters
  - Calculate like a weak base equilibrium problem as in Chapter 16.
- Beyond equivalence point, the OH<sup>-</sup> is in excess.
  - [OH<sup>-</sup>] = excess mol MOH /total liters
  - [H<sub>3</sub>O<sup>+</sup>][OH<sup>-</sup>] = 1 × 10<sup>-14</sup>

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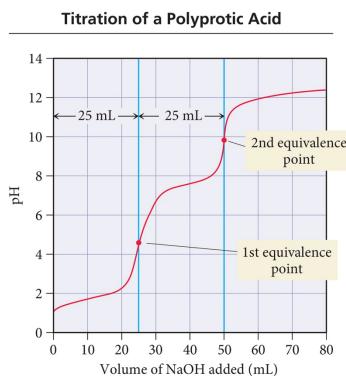
## Titration Curve of a Weak Base with a Strong Acid



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## Titration of a Polyprotic Acid

- If  $K_{a1} \gg K_{a2}$ , there will be two equivalence points in the titration.
  - The closer the  $K_a$  values are to each other, the less distinguishable the equivalence points are.



Titration of 25.0 mL of 0.100 M  $\text{H}_2\text{SO}_3$  with 0.100 M NaOH

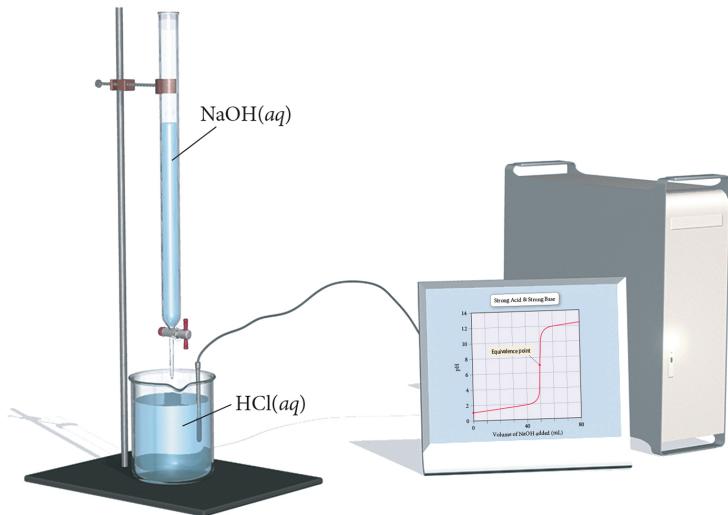
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## Monitoring pH during a Titration

- The general method for monitoring the pH during the course of a titration is to measure the conductivity of the solution due to the  $[\text{H}_3\text{O}^+]$ .
  - Using a probe that specifically measures just  $\text{H}_3\text{O}^+$
- The **endpoint** of the titration is reached when the indicator changes color.

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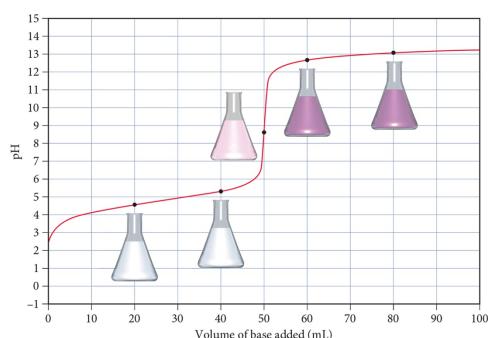
## Monitoring pH during a Titration



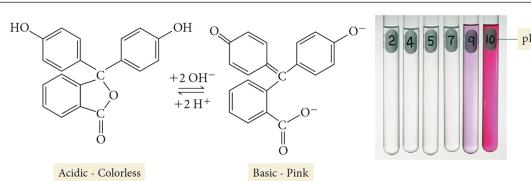
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## Phenolphthalein

Using an Indicator



Phenolphthalein, a Common Indicator



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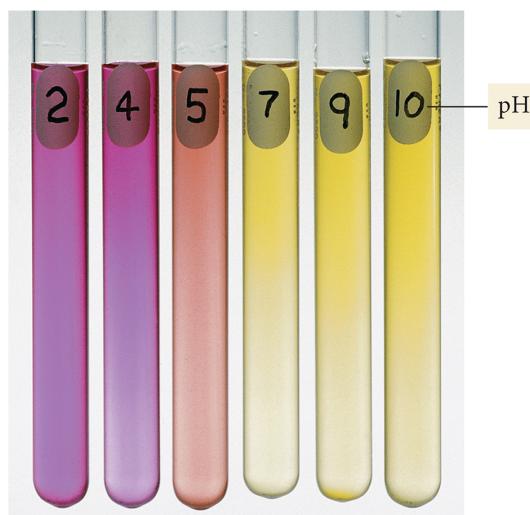
## Indicators

- Many dyes change color depending on the pH of the solution.
- These dyes are weak acids, establishing an equilibrium with the H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> in the solution.
$$\text{HIn}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{In}^-(aq) + \text{H}_3\text{O}^+(aq)$$
- The color of the solution depends on the relative concentrations of In<sup>-</sup>:HIn.
  - When In<sup>-</sup>:HIn ≈ 1, the color will be a mix of the colors of In<sup>-</sup> and HIn.
  - When In<sup>-</sup>:HIn > 10, the color will be a mix of the colors of In<sup>-</sup>.
  - When In<sup>-</sup>:HIn < 0.1, the color will be a mix of the colors of HIn.

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## Methyl Red

### Indicator Color Change: Methyl Red



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## Monitoring a Titration with an Indicator

- For most titrations, the titration curve shows a very large change in pH for very small additions of titrant near the equivalence point.
- An indicator can therefore be used to determine the endpoint of the titration if it changes color within the same range as the rapid change in pH.
  - $pK_a$  of  $\text{HIn} \approx \text{pH}$  at equivalence point

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## Acid–Base Indicators

TABLE 17.1 Ranges of Color Changes for Several Acid–Base Indicators



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## Solubility Equilibria

- All ionic compounds dissolve in water to some degree.
  - However, many compounds have such low solubility in water that we classify them as insoluble.
- We can apply the concepts of equilibrium to salts dissolving, and use the equilibrium constant for the process to measure relative solubilities in water.

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## Solubility Product

- The equilibrium constant for the dissociation of a solid salt into its aqueous ions is called the **solubility product**,  $K_{sp}$ .
- The dissociation reaction for AgCl is
$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq).$$
- And its solubility product constant is
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-].$$

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## Solubility Product Constants

**TABLE 17.2 Selected Solubility Product Constants ( $K_{sp}$ ) at 25 °C**

Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$
Barium fluoride	$\text{BaF}_2$	$2.45 \times 10^{-5}$	Lead(II) chloride	$\text{PbCl}_2$	$1.17 \times 10^{-5}$
Barium sulfate	$\text{BaSO}_4$	$1.07 \times 10^{-10}$	Lead(II) bromide	$\text{PbBr}_2$	$4.67 \times 10^{-6}$
Calcium carbonate	$\text{CaCO}_3$	$4.96 \times 10^{-9}$	Lead(II) sulfate	$\text{PbSO}_4$	$1.82 \times 10^{-8}$
Calcium fluoride	$\text{CaF}_2$	$1.46 \times 10^{-10}$	Lead(II) sulfide*	$\text{PbS}$	$9.04 \times 10^{-29}$
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	$4.68 \times 10^{-6}$	Magnesium carbonate	$\text{MgCO}_3$	$6.82 \times 10^{-6}$
Calcium sulfate	$\text{CaSO}_4$	$7.10 \times 10^{-5}$	Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	$2.06 \times 10^{-13}$
Copper(II) sulfide*	$\text{CuS}$	$1.27 \times 10^{-36}$	Silver chloride	$\text{AgCl}$	$1.77 \times 10^{-10}$
Iron(II) carbonate	$\text{FeCO}_3$	$3.07 \times 10^{-11}$	Silver chromate	$\text{Ag}_2\text{CrO}_4$	$1.12 \times 10^{-12}$
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	$4.87 \times 10^{-17}$	Silver bromide	$\text{AgBr}$	$5.35 \times 10^{-13}$
Iron(II) sulfide*	$\text{FeS}$	$3.72 \times 10^{-19}$	Silver iodide	$\text{AgI}$	$8.51 \times 10^{-17}$

\*Sulfide equilibrium is of the type:  $\text{MS}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{M}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$

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## Molar Solubility

- **Solubility** is the amount of solute that will dissolve in a given amount of solution at a particular temperature.
- The **molar solubility** is the number of moles of solute that will dissolve in a liter of solution.
  - The molarity of the dissolved solute in a saturated solution

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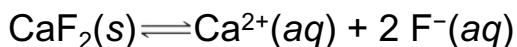
## K<sub>sp</sub> and Relative Solubility

- Molar solubility is related to K<sub>sp</sub>.
- But you cannot always compare solubilities of compounds by comparing their K<sub>sp</sub> values.
- To compare K<sub>sp</sub> values, the compounds must have the same dissociation stoichiometry.

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## The Effect of Common Ion on Solubility

- Addition of a soluble salt that contains one of the ions of the “insoluble” salt decreases the solubility of the “insoluble” salt.
- For example, addition of NaF to the solubility equilibrium of solid CaF<sub>2</sub> decreases the solubility of PbCl<sub>2</sub>.

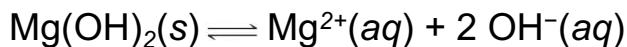


Addition of F<sup>-</sup> shifts the equilibrium to the left.

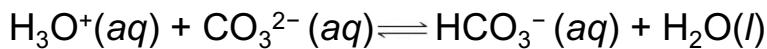
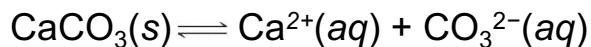
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## The Effect of pH on Solubility

- For insoluble ionic hydroxides, the higher the pH, the lower the solubility of the ionic hydroxide.
  - And the lower the pH, the higher the solubility
  - Higher pH = increased  $[\text{OH}^-]$



- For insoluble ionic compounds that contain anions of weak acids, the lower the pH, the higher the solubility.



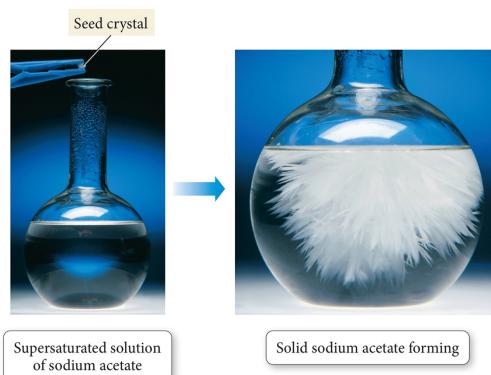
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## Precipitation

- Precipitation will occur when the concentrations of the ions exceed the solubility of the ionic compound.
- If we compare the reaction quotient,  $Q$ , for the current solution concentrations to the value of  $K_{\text{sp}}$ , we can determine if precipitation will occur.
  - $Q = K_{\text{sp}}$ , the solution is saturated, no precipitation.
  - $Q < K_{\text{sp}}$ , the solution is unsaturated, no precipitation.
  - $Q > K_{\text{sp}}$ , the solution would be above saturation, the salt above saturation will precipitate.
- Some solutions with  $Q > K_{\text{sp}}$  will not precipitate unless disturbed; these are called **supersaturated solutions**.

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## Precipitation



Precipitation occurs if  $Q > K_{sp}$ .

A supersaturated solution will precipitate if a seed crystal is added.

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## Selective Precipitation

- A solution containing several different cations can often be separated by addition of a reagent that will form an insoluble salt with one of the ions but not the others (**selective precipitation**).
- A successful reagent can precipitate with more than one of the cations, as long as their  $K_{sp}$  values are significantly different.

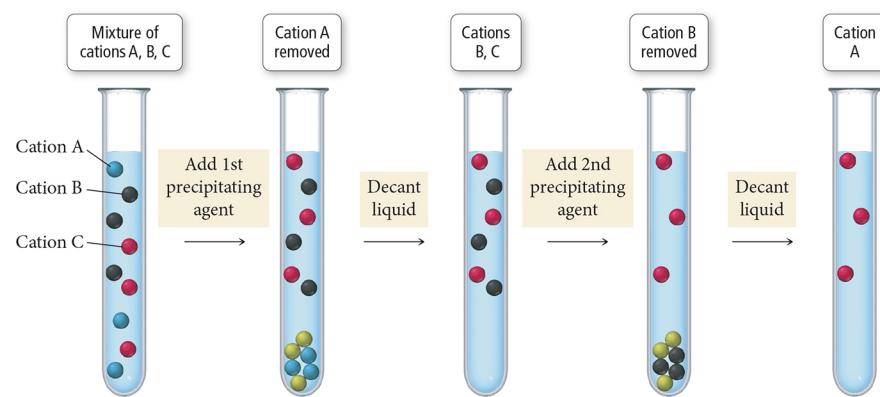
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## Qualitative Analysis

- An analytical scheme that utilizes selective precipitation to identify the ions present in a solution is called **qualitative analysis**.
  - Wet chemistry
- A sample containing several ions is subjected to the addition of several precipitating agents.
- Addition of each reagent causes one of the ions present to precipitate out.

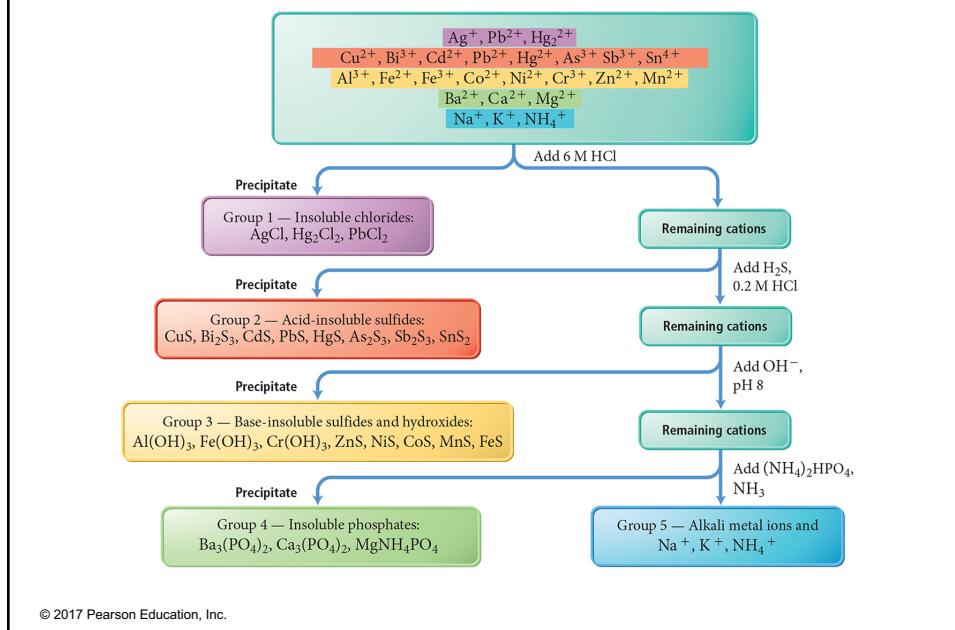
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## Qualitative Analysis



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## A General Qualitative Analysis Scheme



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### Group 1

- Group 1 cations are  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}_2^{2+}$ .
- All of these cations form compounds with  $\text{Cl}^-$  that are insoluble in water.
  - As long as the concentration is large enough
- Precipitated by the addition of HCl

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## Group 2

- Group 2 cations are  $\text{Cu}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ , and  $\text{Sn}^{4+}$ .
- All these cations form compounds with  $\text{HS}^-$  and  $\text{S}^{2-}$  that are insoluble in water at low pH.
- Precipitated by the addition of  $\text{H}_2\text{S}$  in  $\text{HCl}$



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## Group 3

- Group 3 cations are  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$  precipitated as sulfides, as well as  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  precipitated as hydroxides.
- All of these cations form compounds with  $\text{S}^{2-}$  that are insoluble in water at high pH.
- Precipitated by the addition of  $\text{H}_2\text{S}$  in  $\text{NaOH}$ .

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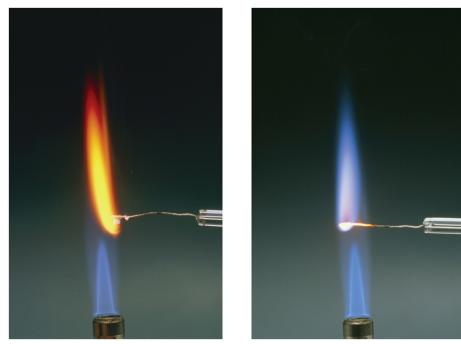
## Group 4

- Group 4 cations are  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Ba^{2+}$ .
- These cations form compounds with  $PO_4^{3-}$  that are insoluble in water at high pH.
- Precipitated by the addition of  $(NH_4)_2HPO_4$

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## Group 5

- Group 5 cations are  $Na^+$ ,  $K^+$ , and  $NH_4^+$ .
- All of these cations form compounds that are soluble in water; they do not precipitate.
- They are identified by the color of their flame.



Sodium

Potassium

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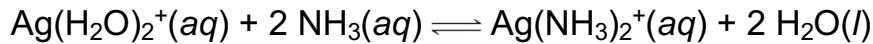
## Complex Ion Formation

- Transition metals tend to be good Lewis acids.
  - They often bond to one or more H<sub>2</sub>O molecules to form a hydrated ion.
    - H<sub>2</sub>O is the Lewis base, donating electron pairs to form coordinate covalent bonds.
- $$\text{Ag}^+(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ag}(\text{H}_2\text{O})_2^+(\text{aq})$$
- Ions that form by combining a cation with several anions or neutral molecules are called **complex ions**.
    - For example, Ag(H<sub>2</sub>O)<sub>2</sub><sup>+</sup>
  - The ions or molecules that act as Lewis bases are called **ligands**.
    - For example, H<sub>2</sub>O

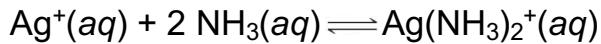
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## Complex Ion Equilibria

- If a ligand is added to a solution that forms a stronger bond than the current ligand, it will replace the current ligand.



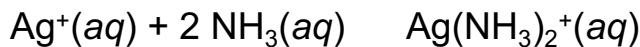
- Generally, H<sub>2</sub>O is not included, because its complex ion is always present in aqueous solution.



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## Formation Constant

- The reaction between an ion and ligands to form a complex ion is called a **complex ion formation reaction**.



- The equilibrium constant for the formation reaction is called the **formation constant,  $K_f$** .

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

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## Formation Constants

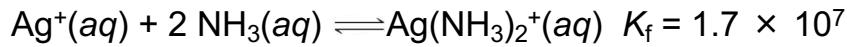
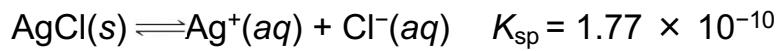
**TABLE 17.3** Formation Constants of Selected Complex Ions in Water at 25 °C

Complex Ion	$K_f$	Complex Ion	$K_f$
$\text{Ag}(\text{CN})_2^-$	$1 \times 10^{21}$	$\text{Cu}(\text{NH}_3)_2^{2+}$	$1.7 \times 10^{13}$
$\text{Ag}(\text{NH}_3)_2^+$	$1.7 \times 10^7$	$\text{Fe}(\text{CN})_6^{4-}$	$1.5 \times 10^{35}$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	$2.8 \times 10^{13}$	$\text{Fe}(\text{CN})_6^{3-}$	$2 \times 10^{43}$
$\text{AlF}_6^{3-}$	$7 \times 10^{19}$	$\text{Hg}(\text{CN})_4^{2-}$	$1.8 \times 10^{41}$
$\text{Al(OH)}_4^-$	$3 \times 10^{33}$	$\text{HgCl}_4^{2-}$	$1.1 \times 10^{16}$
$\text{CdBr}_4^{2-}$	$5.5 \times 10^3$	$\text{HgI}_4^{2-}$	$2 \times 10^{30}$
$\text{CdI}_4^{2-}$	$2 \times 10^6$	$\text{Ni}(\text{NH}_3)_6^{2+}$	$2.0 \times 10^8$
$\text{Cd}(\text{CN})_4^{2-}$	$3 \times 10^{18}$	$\text{Pb}(\text{OH})_3^-$	$8 \times 10^{13}$
$\text{Co}(\text{NH}_3)_6^{3+}$	$2.3 \times 10^{33}$	$\text{Sn}(\text{OH})_3^-$	$3 \times 10^{25}$
$\text{Co}(\text{OH})_4^{2-}$	$5 \times 10^9$	$\text{Zn}(\text{CN})_4^{2-}$	$2.1 \times 10^{19}$
$\text{Co}(\text{SCN})_4^{2-}$	$1 \times 10^3$	$\text{Zn}(\text{NH}_3)_4^{2+}$	$2.8 \times 10^9$
$\text{Cr}(\text{OH})_4^-$	$8.0 \times 10^{29}$	$\text{Zn}(\text{OH})_4^{2-}$	$2 \times 10^{15}$
$\text{Cu}(\text{CN})_4^{2-}$	$1.0 \times 10^{25}$		

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## The Effect of Complex Ion Formation on Solubility

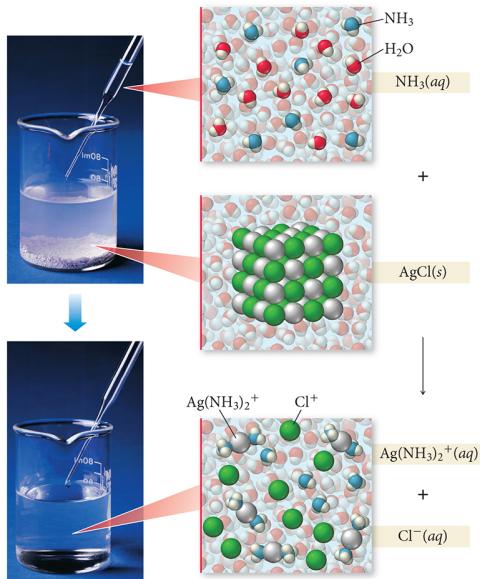
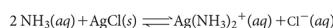
- The solubility of an ionic compound that contains a metal cation that forms a complex ion increases in the presence of aqueous ligands.



- Adding  $\text{NH}_3$  to a solution in equilibrium with  $\text{AgCl}$  increases the solubility of  $\text{Ag}^+$ .

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### Complex Ion Formation



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## Solubility of Amphoteric Metal Hydroxides

- Many metal hydroxides are insoluble.
- All metal hydroxides become more soluble in acidic solution.
  - Shifting the equilibrium to the right by removing OH<sup>-</sup>
- Some metal hydroxides also act as acids, becoming more soluble in basic solution.
  - Amphoteric
- Some cations that form amphoteric hydroxides include Al<sup>3+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, and Sn<sup>2+</sup>.

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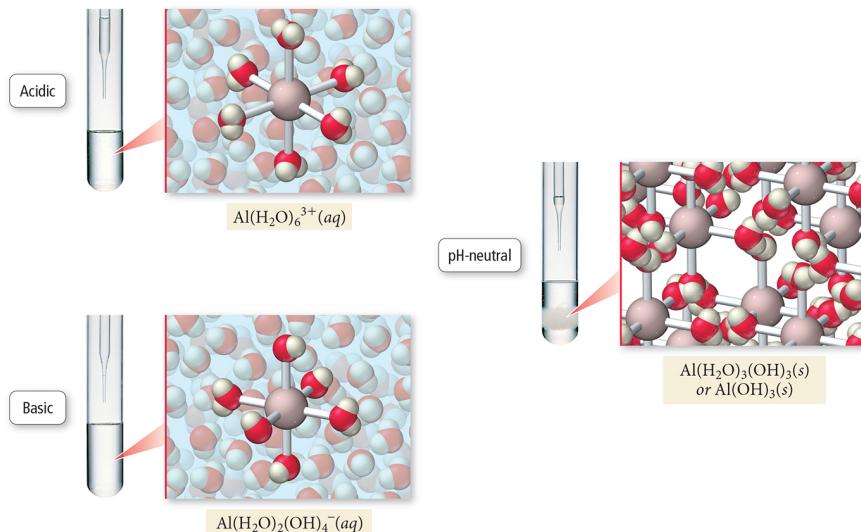
## Al<sup>3+</sup>

- Al<sup>3+</sup> is hydrated in water to form an acidic solution.  
 $\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- Addition of OH<sup>-</sup> drives the equilibrium to the right and continues to remove H<sup>+</sup> from the molecules.  
 $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 $\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(\text{s}) + \text{H}_2\text{O}(\text{l})$

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## Solubility of an Amphoteric Hydroxide

pH-Dependent Solubility of an Amphoteric Hydroxide



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