Chemistry, The Central Science, 11th edition
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Chapter 17
Additional Aspects of Aqueous Equilibria

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The Common-Ion Effect

- Consider a solution of acetic acid:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

- If acetate ion is added to the solution, Le Châtelier says the equilibrium will shift to the left.

The Common-Ion Effect

"The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte."

The Common-Ion Effect

Calculate the fluoride ion concentration and pH of a solution that is 0.20 *M* in HF and 0.10 *M* in HCl.

K_a for HF is 6.8×10^{-4}.

$$K_a = \frac{[H_3O^+]\,[F^-]}{[HF]} = 6.8 \times 10^{-4}$$

The Common-Ion Effect

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Because HCl, a strong acid, is also present, the initial $[H_3O^+]$ is not 0, but rather 0.10 *M*.

	[HF], *M*	$[H_3O^+]$, *M*	$[F^-]$, *M*
Initially	0.20	0.10	0
Change			
At Equilibrium			

The Common-Ion Effect

$$6.8 \times 10^{-4} = \frac{(0.10)\,(x)}{(0.20)}$$

$$\frac{(0.20)\,(6.8 \times 10^{-4})}{(0.10)} = x$$

$$1.4 \times 10^{-3} = x$$

The Common-Ion Effect

- Therefore, $[\mathrm{F}^-] = x = 1.4 \times 10^{-3}$

$$[\mathrm{H_3O^+}] = 0.10 + x = 0.10 + 1.4 \times 10^{-3} = 0.10\ M$$

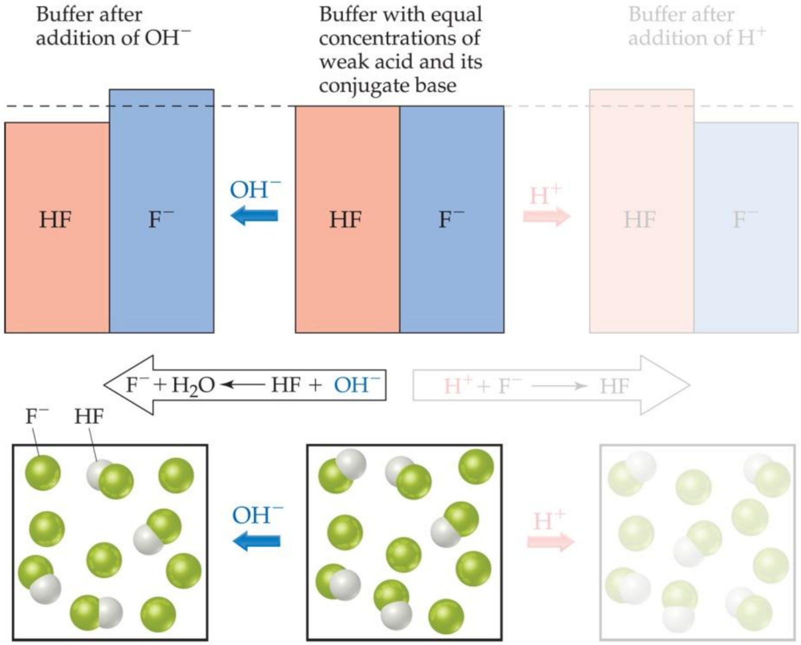
- So, $\mathrm{pH} = -\log (0.10)$

  $\mathrm{pH} = 1.00$

Buffers

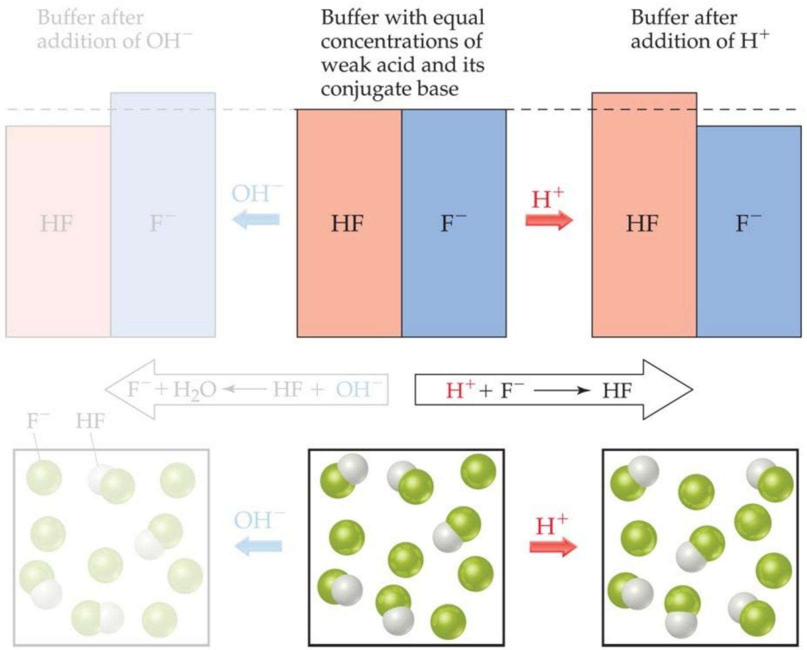
- Buffers are solutions of a weak conjugate acid-base pair.
- They are particularly resistant to pH changes, even when strong acid or base is added.

Buffers



If a small amount of hydroxide is added to an equimolar solution of HF in NaF, for example, the HF reacts with the OH^- to make F^- and water.

Buffers



Similarly, if acid is added, the F^- reacts with it to form HF and water.

Buffer Calculations

Consider the equilibrium constant expression for the dissociation of a generic acid, HA:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Buffer Calculations

Rearranging slightly, this becomes

$$K_a = [H_3O^+]\,\frac{[A^-]}{[HA]}$$

Taking the negative log of both side, we get

$$\underset{\text{p}K_a}{-\log K_a} = \underset{\text{pH}}{-\log [H_3O^+]} + -\log \frac{\overset{\text{base}}{[A^-]}}{\underset{\text{acid}}{[HA]}}$$

Buffer Calculations

- So

$$pK_a = pH - \log \frac{[\text{base}]}{[\text{acid}]}$$

- Rearranging, this becomes

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

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

Henderson–Hasselbalch Equation

What is the pH of a buffer that is 0.12 *M* in lactic acid, $CH_3CH(OH)COOH$, and 0.10 *M* in sodium lactate? K_a for lactic acid is 1.4×10^{-4}.

Henderson–Hasselbalch Equation

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

$$= -\log\,(1.4 \times 10^{-4}) + \log\,\frac{(0.10)}{(0.12)}$$

$$= 3.85 + (-0.08)$$

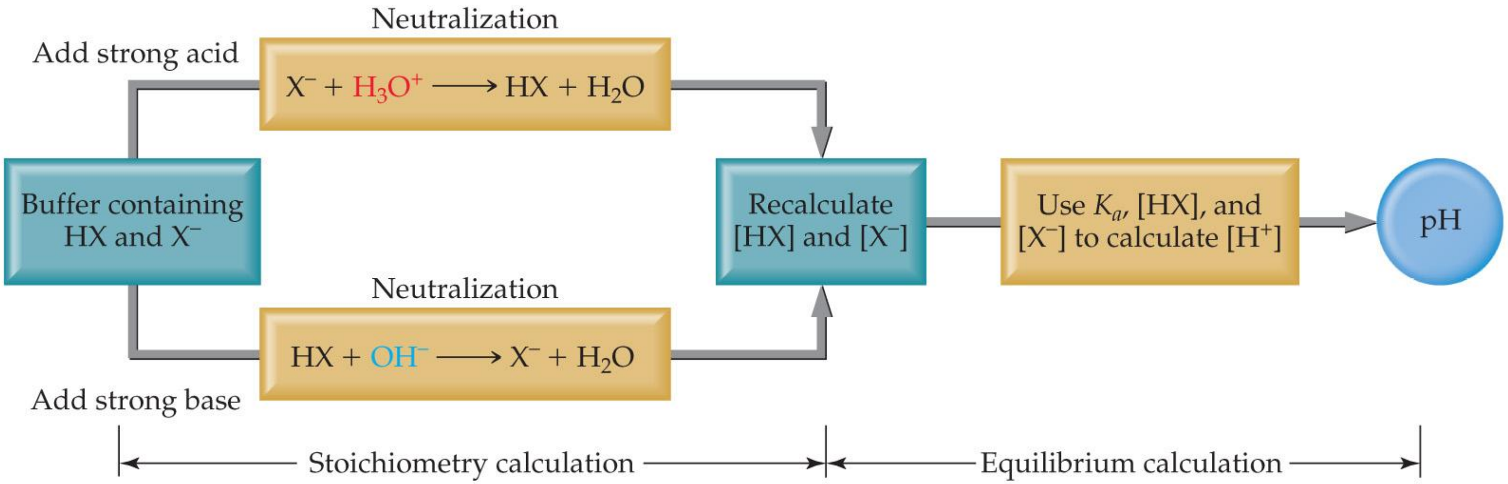
$$= 3.77$$

pH Range

- The pH range is the range of pH values over which a buffer system works effectively.
- It is best to choose an acid with a pK_a close to the desired pH.

When Strong Acids or Bases Are Added to a Buffer…

…it is safe to assume that all of the strong acid or base is consumed in the reaction.



Add strong acid

Neutralization

$X^- + H_3O^+ \longrightarrow HX + H_2O$

Buffer containing HX and X^-

Recalculate [HX] and $[X^-]$

Use K_a, [HX], and $[X^-]$ to calculate $[H^+]$

pH

Neutralization

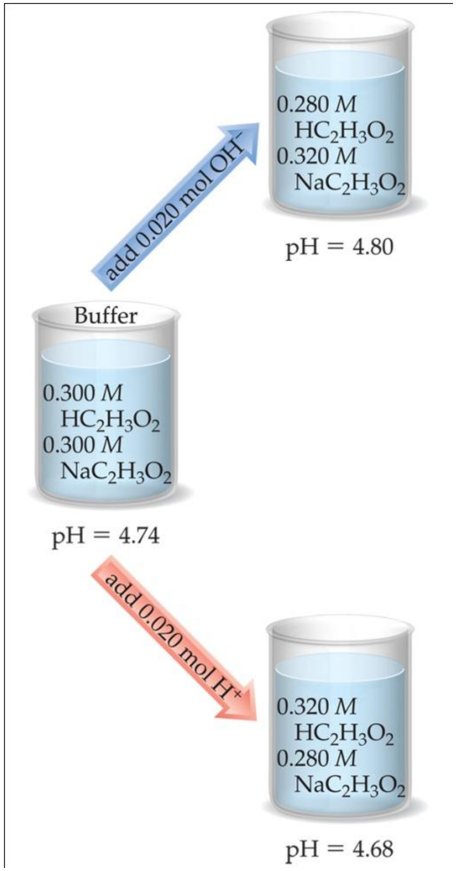
$HX + OH^- \longrightarrow X^- + H_2O$

Add strong base

Stoichiometry calculation

Equilibrium calculation

Addition of Strong Acid or Base to a Buffer



1. Determine how the neutralization reaction affects the amounts of the weak acid and its conjugate base in solution.
2. Use the Henderson–Hasselbalch equation to determine the new pH of the solution.

Aqueous Equilibria

Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol $HC_2H_3O_2$ and 0.300 mol $NaC_2H_3O_2$ to enough water to make 1.00 L of solution. The pH of the buffer is 4.74. Calculate the pH of this solution after 0.020 mol of NaOH is added.

Calculating pH Changes in Buffers

Before the reaction, since

$$\text{mol } HC_2H_3O_2 = \text{mol } C_2H_3O_2^-$$

$$pH = pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Calculating pH Changes in Buffers

The 0.020 mol NaOH will react with 0.020 mol of the acetic acid:

$$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O(l)$$

	$HC_2H_3O_2$	$C_2H_3O_2^-$	OH^-
Before reaction	0.300 mol	0.300 mol	0.020 mol
After reaction	[illegible]	[illegible]	[illegible]

Calculating pH Changes in Buffers

Now use the Henderson–Hasselbalch equation to calculate the new pH:

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

$$= 4.74 + 0.06$$

$$= 4.80$$

Solubility Products

Consider the equilibrium that exists in a saturated solution of $BaSO_4$ in water:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Solubility Products

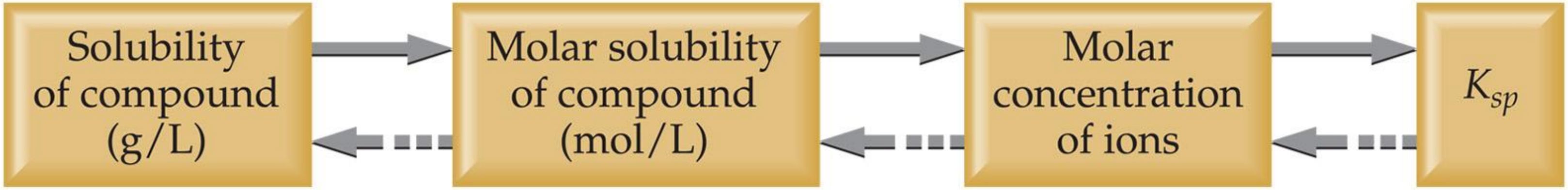
The equilibrium constant expression for this equilibrium is

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

where the equilibrium constant, K_{sp}, is called the solubility product.

Solubility Products

- K_{sp} is *not* the same as solubility.
- Solubility is generally expressed as the mass of solute dissolved in 1 L (g/L) or 100 mL (g/mL) of solution, or in mol/L (*M*).



Solubility of compound (g/L)

Molar solubility of compound (mol/L)

Molar concentration of ions

K_{sp}

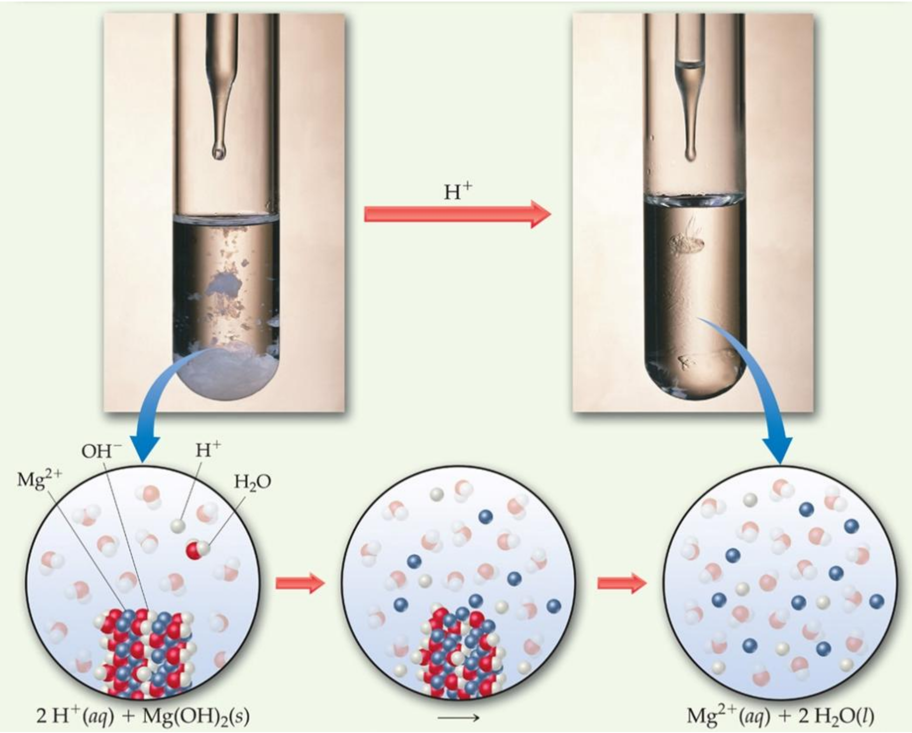
Factors Affecting Solubility

- The Common-Ion Effect
  - If one of the ions in a solution equilibrium is already dissolved in the solution, the equilibrium will shift to the left and the solubility of the salt will decrease.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

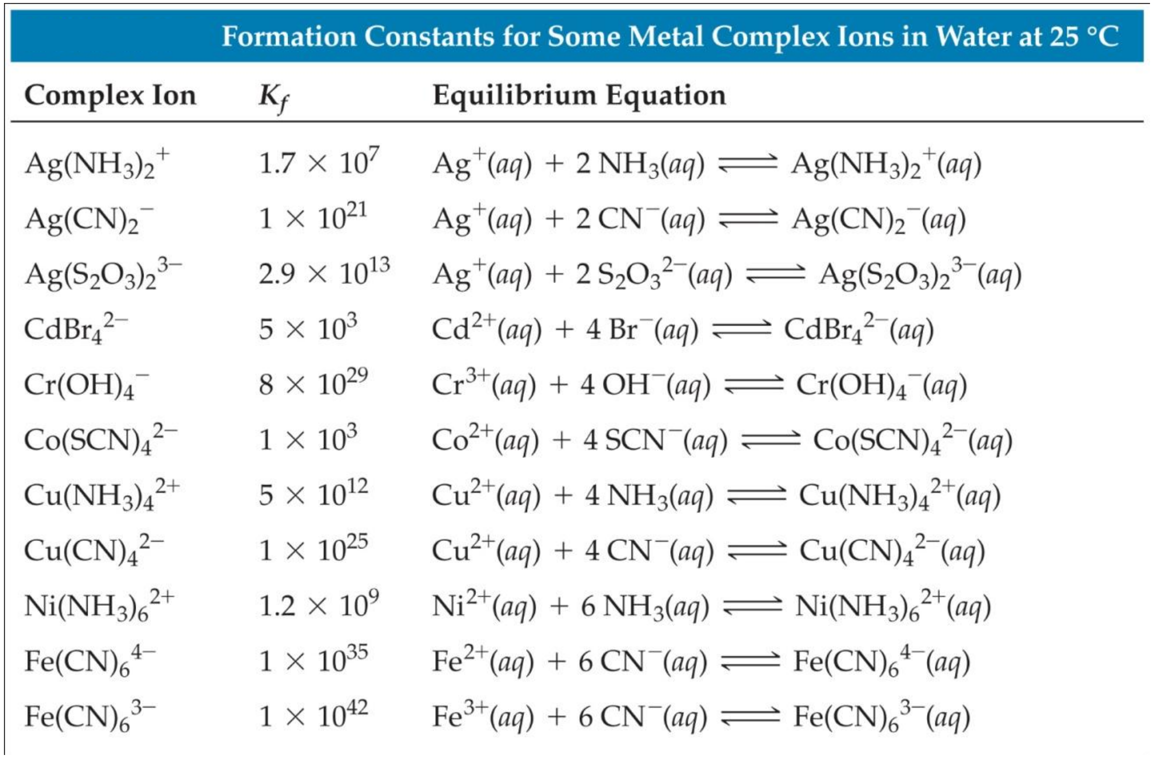
Factors Affecting Solubility

- pH
  - If a substance has a basic anion, it will be more soluble in an acidic solution.
  - Substances with acidic cations are more soluble in basic solutions.



Factors Affecting Solubility

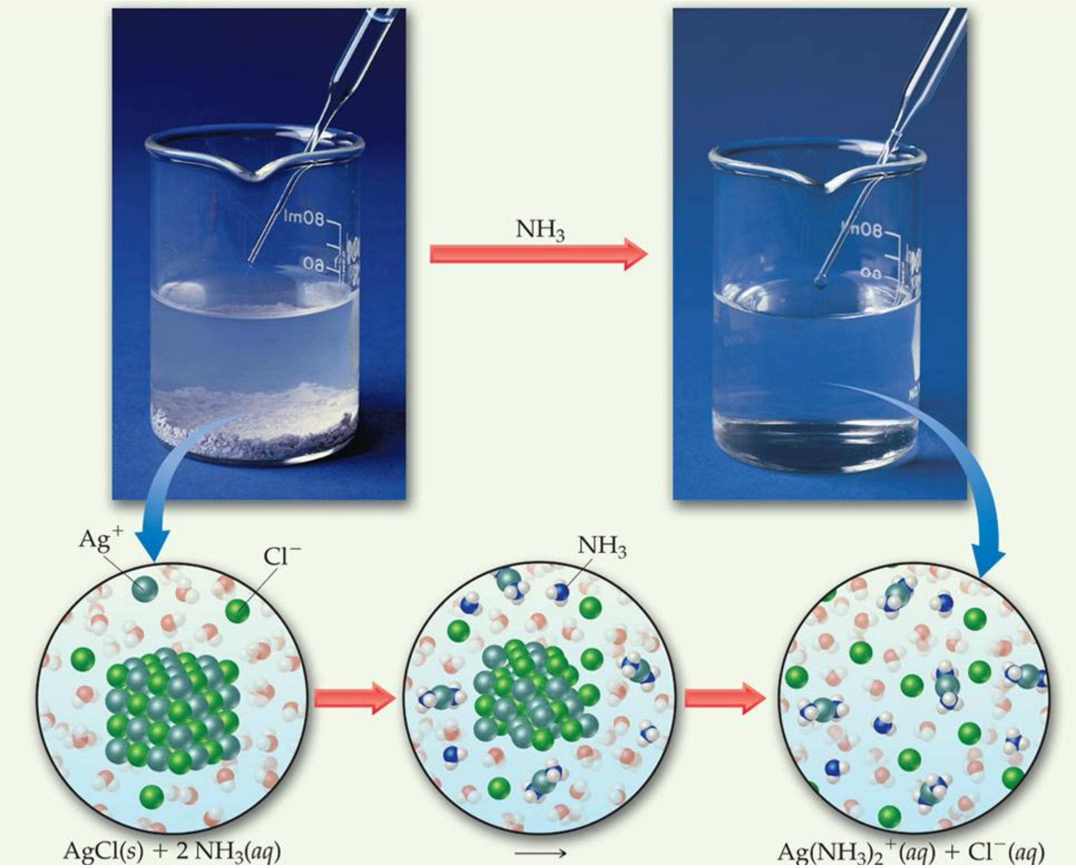
- Complex Ions
  - Metal ions can act as Lewis acids and form complex ions with Lewis bases in the solvent.



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

Complex Ion	K_f	Equilibrium Equation
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2\,S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4\,OH^-(aq) \rightleftharpoons Cr(OH)_4^-(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4\,SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4\,CN^-(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$
$Ni(NH_3)_6^{2+}$	1.2×10^9	$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^{3+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq)$

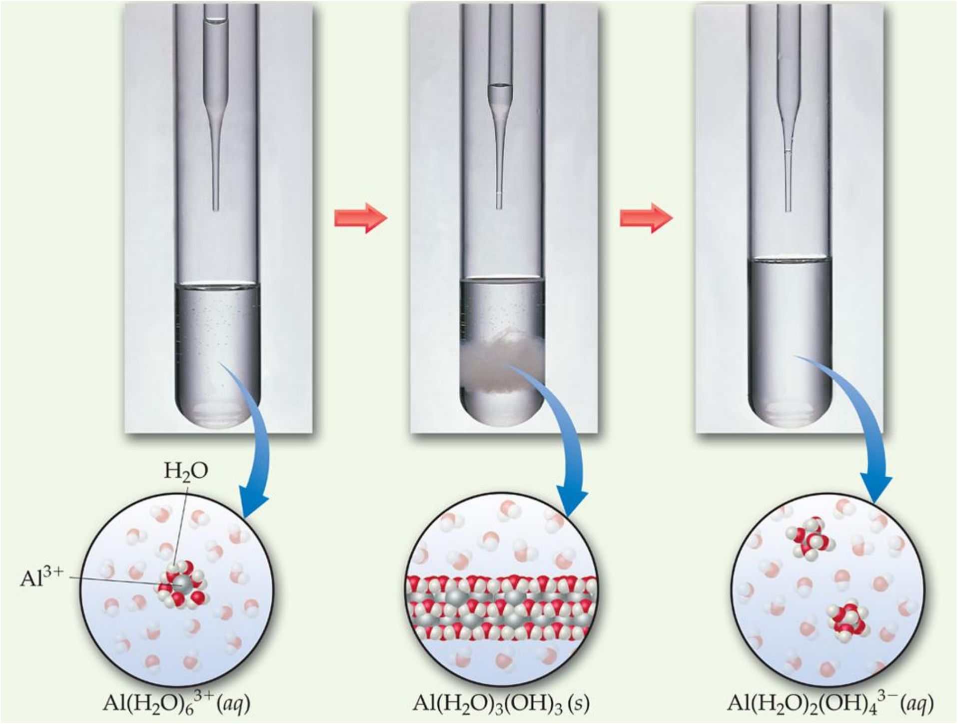
Factors Affecting Solubility



- Complex Ions
  - The formation of these complex ions increases the solubility of these salts.

Factors Affecting Solubility

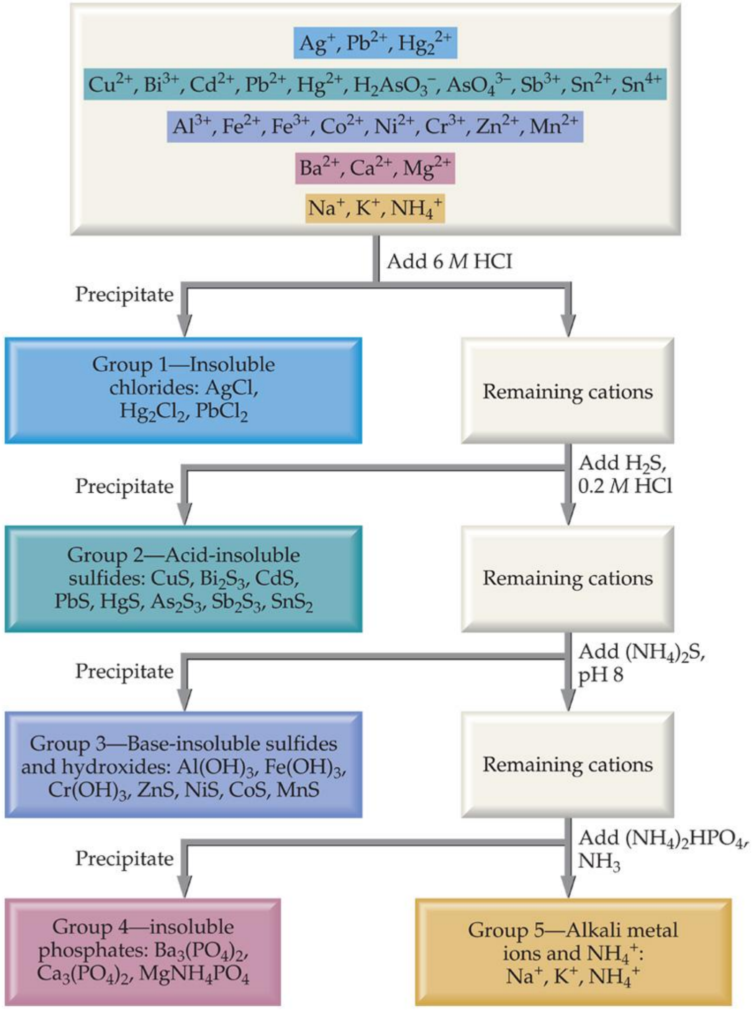
- Amphoterism
  - Amphoteric metal oxides and hydroxides are soluble in strong acid or base, because they can act either as acids or bases.
  - Examples of such cations are Al^{3+}, Zn^{2+}, and Sn^{2+}.



Will a Precipitate Form?

- In a solution,
  - If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.
  - If $Q < K_{sp}$, more solid can dissolve until $Q = K_{sp}$.
  - If $Q > K_{sp}$, the salt will precipitate until $Q = K_{sp}$.

Selective Precipitation of Ions



Ag^+, Pb^{2+}, Hg_2^{2+}

Cu^{2+}, Bi^{3+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, $H_2AsO_3^-$, AsO_4^{3-}, Sb^{3+}, Sn^{2+}, Sn^{4+}

Al^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}

Ba^{2+}, Ca^{2+}, Mg^{2+}

Na^+, K^+, NH_4^+

Add 6 *M* HCl

Precipitate

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

Remaining cations

Add H_2S, 0.2 *M* HCl

Precipitate

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

Remaining cations

Add $(NH_4)_2S$, pH 8

Precipitate

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

Remaining cations

Add $(NH_4)_2HPO_4$, NH_3

Precipitate

Group 4—insoluble phosphates: $Ba_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$

Group 5—Alkali metal ions and NH_4^+: Na^+, K^+, NH_4^+

One can use differences in solubilities of salts to separate ions in a mixture.