Objectives:

- Learning about precipitation reactions
- Learning about the solubility constant expression $K_{sp}$ and how to use it
- Learning about the solubilities of various classes of ionic solids and how to use that knowledge to analyze for the presence of unknown ions in solution
- Nanomaterials synthesis
Synthesis, magnetic and electrical characteristics of poly(2-thiophen-3-yl-malonic acid)/Fe₃O₄ nanocomposite
M. Aydin¹, B. Önal¹,b,c, B. Esat¹,d,e, A. Baykal¹,c,d, E. Karaoglu¹,d, M.S. Toprak¹,c, H. Sözeri¹,f

2.1. Materials

2-Thiophen-3-yl-malonic acid (T3MA), anhydrous iron (III) chloride (98% FeCl₃), ammonium hydroxide (NH₄OH), iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98% iron (II) chloride tetrahydrate (FeCl₂·4H₂O, 98%), concentrated sulfuric acid (H₂SO₄), hydrochloric acid (HCl), sodium hydroxide (NaOH) were all of analytical purity (obtained from Merck and Sigma–Aldrich) and used as-received, without any purification.

2.4. Synthesis of PT3MA/Fe₃O₄ nanocomposite

Stoichiometric amounts of Fe(III) and Fe(II) chloride salts (with a molar ratio of 2:1) and 50 mg of PT3MA were dissolved in 100 ml distilled water under vigorous stirring. Then a 2 M aqueous NaOH solution was added very slowly until the pH was raised to ~11 and a black suspension was formed. This suspension was then refluxed at 90 °C for 12 h, under vigorous stirring and Ar gas. Magnetic particles were separated from the aqueous solution by magnetic decantation, washed with distilled water several times and then dried in an oven overnight.

Types of Solutions

√ Saturated
√ Unsaturated
√ Supersaturated
Solubility Equilibria

• Acid and base equilibria involve homogenous systems
  – Same phase

• Saturated solution
  – The solution is in contact with undissolved solute.
  – Heterogeneous equilibria system

Solution Equilibrium

NaCl(s)
Degrees of Solubility

\[ \text{NaCl}_{(s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \quad \text{soluble} \]

\[ \text{AgCl}_{(s)} \leftrightharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \quad \text{insoluble} \]

\[ \text{Ca(OH)}_2_{(s)} \leftrightharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) \quad \text{slightly soluble} \]

• To write an equilibrium product constant for a heterogeneous system, ignore the concentrations of pure solids or pure liquids.

\[ \text{BaSO}_4_{(s)} \leftrightharpoons \text{Ba}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \]

• The \( K_c \) depends only on the molar conc. of species in solution.

• Solubility-Product constant \( (K_{sp}) \)
\[
\text{BaSO}_4(s) \leftrightharpoons \text{Ba}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)}
\]

• Even though \([\text{BaSO}_4]\) is not included in the \(K_{sp}\), some must be present for the system to be at equilibrium.

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

• \(K_{sp}\) is the equilibrium constant between an ionic solute and its ions in a saturated solution.

• A very small \(K_{sp}\) indicates that only a small amount of solid will dissolve in water.
## Table 16.1: Some Solubility Product Constants (\(K_{sp}\)) at 25 °C

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solubility Equilibrium</th>
<th>(K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum hydroxide</td>
<td>(\text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+}(aq) + 3 \text{OH}^{-}(aq))</td>
<td>(1.3 \times 10^{-33})</td>
</tr>
<tr>
<td>Barium carbonate</td>
<td>(\text{BaCO}_3(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{CO}_3^{2-}(aq))</td>
<td>(5.1 \times 10^{-9})</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>(\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq))</td>
<td>(1.1 \times 10^{-10})</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>(\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq))</td>
<td>(2.8 \times 10^{-9})</td>
</tr>
<tr>
<td>Calcium fluoride</td>
<td>(\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq))</td>
<td>(5.3 \times 10^{-3})</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>(\text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq))</td>
<td>(9.1 \times 10^{-6})</td>
</tr>
<tr>
<td>Calcium oxalate</td>
<td>(\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq))</td>
<td>(2.7 \times 10^{-9})</td>
</tr>
<tr>
<td>Chromium(III) hydroxide</td>
<td>(\text{Cr(OH)}_3(s) \rightleftharpoons \text{Cr}^{3+}(aq) + 3 \text{OH}^{-}(aq))</td>
<td>(6.3 \times 10^{-31})</td>
</tr>
<tr>
<td>Copper(II) sulfide</td>
<td>(\text{CuS}(s) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{S}^{2-}(aq))</td>
<td>(8.7 \times 10^{-36})</td>
</tr>
<tr>
<td>Iron(III) hydroxide</td>
<td>(\text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3 \text{OH}^{-}(aq))</td>
<td>(4 \times 10^{-38})</td>
</tr>
<tr>
<td>Lead(II) chloride</td>
<td>(\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{Cl}^{-}(aq))</td>
<td>(1.6 \times 10^{-5})</td>
</tr>
<tr>
<td>Lead(II) chromate</td>
<td>(\text{PbCrO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{CrO}_4^{2-}(aq))</td>
<td>(2.8 \times 10^{-13})</td>
</tr>
<tr>
<td>Lead(II) iodide</td>
<td>(\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{I}^{-}(aq))</td>
<td>(7.1 \times 10^{-9})</td>
</tr>
<tr>
<td>Magnesium carbonate</td>
<td>(\text{MgCO}_3(s) \rightleftharpoons \text{Mg}^{2+}(aq) + \text{CO}_3^{2-}(aq))</td>
<td>(3.5 \times 10^{-8})</td>
</tr>
<tr>
<td>Magnesium fluoride</td>
<td>(\text{MgF}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2 \text{F}^{-}(aq))</td>
<td>(3.7 \times 10^{-8})</td>
</tr>
<tr>
<td>Magnesium hydroxide</td>
<td>(\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2 \text{OH}^{-}(aq))</td>
<td>(1.8 \times 10^{-11})</td>
</tr>
<tr>
<td>Magnesium phosphate</td>
<td>(\text{Mg}_3\text{PO}_4(s) \rightleftharpoons 3 \text{Mg}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq))</td>
<td>(1 \times 10^{-25})</td>
</tr>
<tr>
<td>Mercury(I) chloride</td>
<td>(\text{HgCl}_2(s) \rightleftharpoons \text{Hg}^{2+}(aq) + 2 \text{Cl}^{-}(aq))</td>
<td>(1.3 \times 10^{-18})</td>
</tr>
<tr>
<td>Mercury(II) sulfide</td>
<td>(\text{HgS}(s) \rightleftharpoons \text{Hg}^{2+}(aq) + \text{S}^{2-}(aq))</td>
<td>(2 \times 10^{-53})</td>
</tr>
<tr>
<td>Silver bromide</td>
<td>(\text{AgBr}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Br}^{-}(aq))</td>
<td>(5.0 \times 10^{-13})</td>
</tr>
<tr>
<td>Silver chloride</td>
<td>(\text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq))</td>
<td>(1.8 \times 10^{-10})</td>
</tr>
<tr>
<td>Silver iodide</td>
<td>(\text{AgI}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{I}^{-}(aq))</td>
<td>(8.5 \times 10^{-17})</td>
</tr>
</tbody>
</table>
## Solubility Chart

<table>
<thead>
<tr>
<th>Soluble</th>
<th>Insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I and NH$_4^+$ compounds</td>
<td>carbonates (except Group I, NH$_4^+$ and uranyl compounds)</td>
</tr>
<tr>
<td>nitrates</td>
<td>sulfites (except Group I and NH$_4^+$ compounds)</td>
</tr>
<tr>
<td>acetates (ethanoates) (except Ag$^+$ compounds)</td>
<td>phosphates (except Group I and NH$_4^+$ compounds)</td>
</tr>
<tr>
<td>chlorides, bromides and iodides (except Ag$^+$, Pb$^{2+}$, Cu$^+$ and Hg$^{2+}$)</td>
<td>hydroxides and oxides (except Group I, NH$_4^+$, Ba$^{2+}$, Sr$^{2+}$ and Ti$^4+$)</td>
</tr>
<tr>
<td>sulfates (except Ag$^+$, Pb$^{2+}$, Ba$^{2+}$, Sr$^{2+}$ and Ca$^{2+}$)</td>
<td>sulfides (except Group I, Group II and NH$_4^+$ compounds)</td>
</tr>
</tbody>
</table>

### Table

<table>
<thead>
<tr>
<th></th>
<th>Bromide</th>
<th>Carbonate</th>
<th>Chloride</th>
<th>Hydroxide</th>
<th>Nitrate</th>
<th>Oxide</th>
<th>Phosphate</th>
<th>Sulfate</th>
<th>Dichromate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aluminium</strong></td>
<td>Br$^-$</td>
<td>S</td>
<td>X</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>S</td>
</tr>
<tr>
<td><strong>Ammonium</strong></td>
<td>NH$_4^+$</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>X</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td>Ca$^{2+}$</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>sS</td>
<td>I</td>
<td>sS</td>
<td>I</td>
</tr>
<tr>
<td><strong>Copper(II)</strong></td>
<td>Cu$^{2+}$</td>
<td>S</td>
<td>X</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>S</td>
</tr>
<tr>
<td><strong>Iron(II)</strong></td>
<td>Fe$^{2+}$</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>S</td>
</tr>
<tr>
<td><strong>Iron(III)</strong></td>
<td>Fe$^{3+}$</td>
<td>S</td>
<td>X</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>sS</td>
<td>I</td>
</tr>
<tr>
<td><strong>Magnesium</strong></td>
<td>Mg$^{2+}$</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>S</td>
<td>I</td>
</tr>
<tr>
<td><strong>Potassium</strong></td>
<td>K$^+$</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td><strong>Silver</strong></td>
<td>Ag$^+$</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>X</td>
<td>I</td>
<td>I</td>
<td>sS</td>
<td>I</td>
</tr>
<tr>
<td><strong>Sodium</strong></td>
<td>Na$^+$</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td><strong>Zinc</strong></td>
<td>Zn$^{2+}$</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>S</td>
</tr>
</tbody>
</table>

### Key:
- S: soluble
- I: insoluble
- sS: slightly soluble
- X: other
Rules for Writing $K_{sp}$

- $K_{sp}$ is equal to the product of the concentration of the ions in the equilibrium, each raised to the power of its coefficient in the equation.

The Solubility Product Constant

$K_{sp}$

Example:

$$\text{AgBr}_\text{(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Br}^-\text{(aq)}$$

$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$
Example:
Ca(OH)_2(s) ⇌ Ca^{2+}(aq) + 2OH^-(aq)

\[ K_{sp} = [Ca^{2+}][OH^-]^2 \]

Example:
Ag_2CrO_4(s) ⇌ 2Ag^+(aq) + CrO_4^{2-}(aq)

\[ K_{sp} = [Ag^+]^2[CrO_4^{2-}] \]

Your Turn

- Give the \( K_{sp} \) expressions for
  a) Barium carbonate
  b) Silver sulfate
  c) Calcium flouride
Solubility and $K_{sp}$

Solubility = grams of solute
liter of solution

Molar = moles of solute
solubility liter of saturated solution

$K_{sp}$ is the equilibrium constant between the ionic solid and saturated solution.

• The solubility of a substance can change as concentrations of other solutes change.
  – Mg(OH)$_2$ solubility is dependent on pH as well as concentration of Mg$^{2+}$

• $K_{sp}$ has only one value at any specific temperature.
Calculating $K_{sp}$ from Solubility Data

Step 1: Use data to determine molar solubility.

Step 2: Use molar solubility and stoichiometry of dissociation to determine concentrations of cations and anions.

Step 3: Write equilibrium expression, calculate $K_{sp}$.

A saturated solution of AgCl in contact with undissolved solid is prepared at 25°C. The concentration of Ag⁺ ions in the solution is found to be $1.35 \times 10^{-5}$ M. Assuming that AgCl dissociates completely in water and that there are no other simultaneous equilibria involving the Ag⁺ or Cl⁻ ions in the solution, calculate $K_{sp}$ for this compound.
Your Turn

• The molar solubility of silver sulfate is $1.5 \times 10^{-2}$ mol/L. Calculate the solubility product of the salt.

Calculating solubility from $K_{sp}$

Step 1: Use equilibrium expression & $K_{sp}$ value to determine concentrations of cations and anions.

Step 2: Use ion concentrations to determine molar solubility.

Step 3: Convert molar solubility to solubility (grams solute/liter).
Calculate the solubility of copper (II) hydroxide in g/L.

\[ K_{sp} = 2.2 \times 10^{-20} \]

Molar mass Cu(OH)_2 = 97.57 g/mol

\[
\begin{array}{c|c|c}
\text{Cu(OH)}_2 & \text{Cu}^{2+} & 2\text{OH}^- \\
\hline
\text{Initial} & 0.00 & 0.00 \\
\text{Change} & +x & +2x \\
\text{Equil.} & x & 2x \\
\end{array}
\]

\[ K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 \]
\[ 2.2 \times 10^{-20} = (x)(2x)^2 \]

\[
x^3 = \frac{2.2\times10^{-20}}{4}
\]
\[ x = 1.8\times10^{-7} \text{ M} \]

Solubility Cu(OH)_2 = \[
\frac{1.8\times10^{-7} \text{ mol}}{L} \times \frac{97.57 \text{ g}}{\text{mol}}
\]
= 1.8\times10^{-5} \text{ g/L}
Solubility Factors

1) Common-ion effect

2) pH

3) Complex ion formation

4) Amphoterism

Common-ion effect & Solubility

• In general, the solubility of a slightly soluble salt is decreased by the presence of a second solute that supplies a common ion.

• $K_{sp}$ is unchanged by additional solutes.
The common ion effect decreases the solubility of the salt.

$$\text{AgBr(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq})$$

Adding $\text{Ag}^+$, shift left
Adding $\text{Br}^-$, shift left

- The $K_{sp}$ for manganese(II) hydroxide is $1.6 \times 10^{-13}$. Calculate the molar solubility of manganese (II) hydroxide in a solution that contains 0.020 M NaOH.

$$\text{Mn(OH)}_2(\text{s}) \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$$
\[ \text{Mn(OH)}_2(s) \rightleftharpoons \text{Mn}^{2+}(aq) + 2\text{OH}^-(aq) \]

<table>
<thead>
<tr>
<th>Initial</th>
<th>_____</th>
<th>0.00</th>
<th>0.020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td><em>-x</em>_</td>
<td>+x</td>
<td>2x</td>
</tr>
<tr>
<td>Equil.</td>
<td>_____</td>
<td>+ x</td>
<td>0.020+2x</td>
</tr>
</tbody>
</table>

\[
K_{sp} = [\text{Mn}^{2+}][\text{OH}^-]^2
\]

\[
1.6 \times 10^{-13} = (x)(0.020 + x)^2
\]

- The solubility of Mn(OH)_2 is very small compared to the 0.020M NaOH

\[
1.6 \times 10^{-13} = (x)(4.0 \times 10^{-4})
\]

\[
x = 4.0 \times 10^{-10} M
\]
Calculate the solubility of silver chloride (g/L) in a 6.5 x 10^{-3} M silver nitrate solution.

$$K_{sp} \text{AgCl}=1.6 \times 10^{-10}$$

$$\text{AgNO}_3(s) \rightarrow \text{Ag}^{+}(aq) + \text{NO}_3^{-}(aq)$$

$$6.5 \times 10^{-3} \quad 6.5 \times 10^{-3}$$

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq)$$

The **Common Ion Effect** on Solubility

The solubility of MgF$_2$ in pure water is 2.6 x 10^{-4} mol/L. What happens to the solubility if we dissolve the MgF$_2$ in a solution of NaF, instead of pure water?
Explaining the Common Ion Effect

*The presence of a common ion in a solution will lower the solubility of a salt.*

- LeChatelier’s Principle:
  
  The addition of the common ion will shift the solubility equilibrium backwards. This means that there is more solid salt in the solution and therefore the solubility is lower!

Solubility & pH

- The solubility of almost any ionic compound is affected if the solution is made sufficiently acidic or basic.

- The solubility of slightly soluble salts containing basic anions increases as $[H^+]$ (pH↓). 

11/09/14
pH Can Change Solubility

\[
\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{+2}_{(aq)} + 2\text{OH}^{-}_{(aq)}
\]

High pH, shift left  Low pH, shift right

At 25°C the molar solubility of \( \text{Mg(OH)}_2 \) in pure water is \( 1.4 \times 10^{-4} \) M. Calculate its molar solubility in a buffer medium whose pH is:

\( \text{K}_{\text{sp}} = 1.2 \times 10^{-11} \)

a.) 12.00  b.) 11.00
• Calculate the concentration of aqueous ammonia necessary to initiate the precipitation of iron(II) hydroxide from a 0.0030 M solution of FeCl₂.
  • $K_{sp}$ of Fe(OH)₂ = 1.6 x 10⁻¹⁴
  • $K_b$ of NH₃ = 1.8 x 10⁻⁵

\[ \text{NH}_3(aq) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

\[ \text{Fe}^{2+}(aq) + 2 \text{OH}^-(aq) \rightleftharpoons \text{Fe(OH)}_2(s) \]

**Formation of Complex Ions**

• Metal ions have the ability to act as Lewis acids (electron pair acceptors) toward water molecules, which act as Lewis bases.
  • Lewis bases other than water also interact with metal ions (particularly transition metals)
\[ K_f = \frac{[\text{Cu}^{2+}] [\text{NH}_3]^4}{[\text{Cu}^{2+}] [\text{NH}_3]^4} = 5.0 \times 10^{13} \]

- a complex ion is formed by Lewis acid-Lewis base reaction;
  metal ion is the Lewis acid
  the neutral molecule or ion that acts as the Lewis base is called a **Ligand**
- the number of ligands attached to the metal ion is called the **coordination number**
- the bond between the Lewis acid and Lewis base is covalent
- a complex ion is characterized by the formation constant \( K_f \)
### Some typical complex ions

<table>
<thead>
<tr>
<th>Complex ion</th>
<th>$K_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+$</td>
<td>$1.5 \times 10^7$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cu(CN)}_4^{2-}$</td>
<td>$1.0 \times 10^{25}$</td>
</tr>
<tr>
<td>$\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons \text{Co(NH}_3)_6^{3+}$</td>
<td>$5.0 \times 10^{31}$</td>
</tr>
</tbody>
</table>

### Some typical coordination numbers

<table>
<thead>
<tr>
<th>Coordination numbers</th>
<th>Coordination numbers</th>
<th>Coordination numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}^+$ 2</td>
<td>$\text{Mn}^{2+}$ 4,6</td>
<td>$\text{Co}^{3+}$ 6</td>
</tr>
<tr>
<td>$\text{Cu}^+$ 2,4</td>
<td>$\text{Fe}^{2+}$ 6</td>
<td>$\text{Cr}^{3+}$ 6</td>
</tr>
<tr>
<td>$\text{Au}^+$ 2,4</td>
<td>$\text{Co}^{2+}$ 4,6</td>
<td>$\text{Au}^{3+}$ 4</td>
</tr>
<tr>
<td></td>
<td>$\text{Ni}^{2+}$ 4,6</td>
<td>$\text{Sc}^{3+}$ 6</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}$ 4,6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Zn}^{2+}$ 4,6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Some common ligands

- H$_2$O
- SCN$^-$
- CO
- CN$^-$
- NO
- F$^-$
- NH$_3$
- F$^-$
- CH$_3$NH$_2$
- Cl$^-$
- Br$^-$
AgCl  \( K_{sp} = 1.8 \times 10^{-10} \)

- In the presence of aqueous ammonia AgCl will dissolve.

\[
\text{AgCl(s)} \leftrightarrow \text{Ag}^+ (aq) + \text{Cl}^- (aq)
\]

\[
\text{Ag}^+ (aq) + 2 \text{NH}_3(aq) \leftrightarrow \text{Ag(NH}_3)_2^+ (aq)
\]

\[
\text{AgCl(s)} + 2\text{NH}_3(aq) \leftrightarrow \text{Ag(NH}_3)_2^+ (aq) + \text{Cl}^- (aq)
\]

Presence of \( \text{NH}_3 \) drives the top reaction to the right (\( \uparrow \) solubility of AgCl).

---

**Complex Ions**

an ion made up of the metal ion with one or more molecules or ions (Lewis bases) bonded to it.

**Examples:**

\[
\text{Ag(NH}_3)_2^+
\]

\[
\text{Cu(CN)}_4^{2-}
\]
• The stability of a complex ion in aqueous solution is dependent upon the size of the equilibrium constant for its formation \((K_f)\).

\[
\text{Ag}^+_{(aq)} + 2 \text{NH}_3_{(aq)} \rightleftharpoons \text{Ag(NH}_3)_2^+_{(aq)}
\]

\[
K_f = \frac{[\text{Ag(NH}_3)_2^+]^2}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7
\]

**Stable or Unstable?**

\[
\text{Ag}^+_{(aq)} + 2\text{CN}^-_{(aq)} \rightleftharpoons \text{Ag(CN)}_2^-_{(aq)}
\]

\[
K_f = \frac{[\text{Ag(CN)}_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 1.0 \times 10^{21}
\]

The larger the \(K_f\) the more stable the ion.
The formation of a complex ion has a strong affect on the solubility of a metal salt.

\[
\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)
\]

Adding CN\(^-\) shift right

\[
\text{Ag}^+(aq) + 2\text{CN}^- \rightleftharpoons \text{Ag(CN)}_2^-(aq)
\]

\[
\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq) \quad K_{sp}
\]

\[
\text{Ag}^+(aq) + 2\text{CN}^- \rightleftharpoons \text{Ag(CN)}_2^-(aq) \quad K_f
\]

\[
\text{AgI}(s) + 2\text{CN}^- \rightleftharpoons \text{I}^-(aq) + \text{Ag(CN)}_2^-(aq)
\]

\[
K = K_{sp}K_f
\]

\[
= (8.3 \times 10^{-17})(1.0 \times 10^{21})
\]

\[
= 8.3 \times 10^4
\]

Solubility has increased!
A 0.20 mole quantity of CuSO$_4$ is added to a liter of 1.20 M NH$_3$ solution. What is the concentration of Cu$^{2+}$ ions at equilibrium?

$K_f$ for Cu(NH$_3$)$_4^{2+}$ = 5.0 x 10$^{13}$

$$
\text{Cu}^{2+}_{(aq)} + 4\text{NH}_3_{(aq)} \rightleftharpoons \text{Cu(NH}_3)_4^{2+} \text{ (aq)}
$$

$K_f$ is very large.
Assume that all of the Cu$^{2+}$ added ends up as complex.

NH$_3$ consumed is 4(0.20mol) = 0.80 mol

[ NH$_3$ ] at equilibrium is 1.20-0.80, or 0.40M

[Cu(NH$_3$)$_4^{2+}$] at equilibrium is 0.20M
\[ K_f = \frac{[Cu(NH_3)^{+2}_4]}{[Cu^{2+}][NH_3]} = 5.0 \times 10^{13} \]

\[ \frac{0.20}{x(0.40)^4} = 5.0 \times 10^{13} \]

\[ X = [Cu^{2+}] = 1.6 \times 10^{-13} \text{ M} \]

- Calculate the molar solubility of silver chloride in a 1.0 M NH₃ solution.
- \( K_{sp} \ AgCl = 1.6 \times 10^{-10} \)
- \( K_f \ Ag(NH_3)_2^+ = 1.5 \times 10^7 \)

\[ \text{AgCl}_{(s)} \leftrightarrow \text{Ag}^{+}_{(aq)} + \text{Cl}^-_{(aq)} \]

\[ \text{Ag}^{+}_{(aq)} + 2\text{NH}_3(aq) \leftrightarrow \text{Ag(NH}_3)_2^+ \]
Overall Equation

\[
\text{AgCl}_\text{(s)} + 2\text{NH}_3\text{(aq)} \rightleftharpoons \text{Ag(NH}_3\text{)}_2^+\text{(aq)} + \text{Cl}^-\text{(aq)}
\]

\[
K_{sp} = \frac{[\text{Ag}^+] [\text{Cl}^-]}{[\text{Ag(NH}_3\text{)}_2^+] [\text{NH}_3]} = 1.6 \times 10^{-10}
\]

\[
K_f = \frac{[\text{Ag}^+] [\text{NH}_3]}{[\text{Ag(NH}_3\text{)}_2^+]} = 1.5 \times 10^7
\]

\[
K = K_{sp} (K_f) = \frac{[\text{Ag}^+] [\text{Cl}^-]}{[\text{Ag(NH}_3\text{)}_2^+]} = \frac{[\text{Ag}^+] [\text{NH}_3]}{[\text{Ag(NH}_3\text{)}_2^+]}
\]

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Initial} & 1.0 & 0.0 & 0.0 \\
\hline
\text{Change} & -2x & +x & +x \\
\hline
\text{Equil.} & 1.0-2x & x & x \\
\hline
\end{array}
\]

\[
K = \frac{x^2}{(1.0 - 2x)^2} = 2.4 \times 10^{-3}
\]

0.049 mol of AgCl dis. in 1L of 1MNH\textsubscript{3}
Mixing Solutions - Will a Precipitate Form?

If 15 mL of 0.024-M lead nitrate is mixed with 30 mL of 0.030-M potassium chromate - will a precipitate form?

$$\text{Pb(NO}_3\text{)}_2 \text{ (aq)} + \text{K}_2\text{CrO}_4 \text{ (aq)} \rightleftharpoons \text{PbCrO}_4 \text{ (s)} + 2 \text{KNO}_3 \text{ (aq)}$$

Precipitation & Separation

**Ion Product (Q)** - the value obtained from the equilibrium expression using initial concentrations.

For $\text{BaSO}_4$:

$$Q = [\text{Ba}^{+2}][\text{SO}_4^{2-}]$$
Reaction quotient (Q) can be used to determine the direction a reaction will proceed in order to reach equilibrium.

**Compare Q to $K_{sp}$**

- $Q = K_{sp}$: saturated
- $Q < K_{sp}$: unsaturated
- $Q > K_{sp}$: supersaturated

Exactly 200.0mL of 0.0040M BaCl$_2$ are added to 600.0mL of 0.0080M K$_2$SO$_4$. Will a precipitate form?

$K_{sp}$ BaSO$_4$ = $1.1 \times 10^{-10}$

According to solubility rules the only precipitate that might form is BaSO$_4$.

$$\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightleftharpoons \text{BaSO}_4(s)$$
\[ \text{Ba}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{BaSO}_4(s) \]

a) How many moles of \( \text{Ba}^{+2} \) are present in original?

b) Concentration of \( \text{Ba}^{2+} \) in final solution?

c) Moles of \( \text{SO}_4^{2-} \) in original?

d) Concentration of \( \text{SO}_4^{2-} \) in final volume?

A) \( 1.0 \times 10^{-3} \) M \( \text{Ba}^{2+} \)

B) \( 6.0 \times 10^{-3} \) M \( \text{SO}_4^{2-} \)

\[ Q = [\text{Ba}][\text{SO}_4] \]

\[ Q = 1.0 \times 10^{-3}(6.0 \times 10^{-3}) = 6.0 \times 10^{-6} \]

Ksp \( \text{BaSO}_4 = 1.1 \times 10^{-10} \)

\[ Q > K_{sp} \] therefore \( \text{BaSO}_4 \) will precipitate.
Ions in a solution can be separated from each other on the basis of the different solubilities of their salts.

- Add HCl to a solution containing Ag\(^+\) and Cu\(^{2+}\) and only the AgCl precipitates out.

What could be added to separate these ions from the solution?

Ca(OH)\(_2\), \(K_{sp} = 8.0 \times 10^{-6}\)
Mg(OH)\(_2\), \(K_{sp} = 1.2 \times 10^{-11}\)
\[ K_{sp} = [Ca^{+2}][OH^-]^2 \quad K_{sp} = [Mg^{+2}][OH^-]^2 \]

\[ [OH^-]^2 = \frac{K_{sp}}{[Ca^{+2}]} \quad [OH^-]^2 = \frac{K_{sp}}{[Mg^{+2}]} \]

If the Ca\(^{2+}\) and Mg\(^{2+}\) concentrations are known, you can calculate the OH\(^-\) concentration above which the salt will precipitate.

Silver nitrate is slowly added to a solution that is 0.020M in Cl\(^-\) ions and 0.020M Br\(^-\) ions. Calculate the concentration of Ag\(^+\) ions (in mol/L) needed to:

\[ K_{sp \: AgBr} = 7.7 \times 10^{-13} \quad K_{sp \: AgCl} = 1.6 \times 10^{-10} \]

a) The precipitation of AgBr.

b) The precipitation of AgCl.
Determining the *types of ions* present in a solution.

**Qualitative Analysis of Metallic Elements**

- Scheme that is in common use divides *common cations* into 5 groups.

- The order of addition of reagents is important, the most selective separations are carried out first.
1) **Insoluble Chlorides**
   a. Ag\(^+\), Hg\(^{2+}\), and Pb\(^{2+}\)
   b. Add dilute HCl only these ppt.

2) **Acid insoluble sulfides (b/c excess H\(^+\))**
   a. After any insoluble chlorides have been removed, treat solution with H\(_2\)S.
   b. Only the most insoluble sulfides ppt. b/c only small amts HS\(^-\) and S\(^{2-}\) available
   c. (Le Chat: H\(_2\)S ⇌ HS\(^-\) + H\(^+\) ⇌ S\(^{2-}\) + 2H\(^+\))
   d. CuS, Bi\(_2\)S\(_3\), CdS, PbS, HgS, As\(_2\)S\(_3\), Sb\(_2\)S\(_3\), SnS\(_2\)

3.) **Base insoluble Sulfides and hydroxides.**
   a.) Filter and remove any insoluble sulfides.
   b.) Make slightly basic add small amts of OH\(^-\), then add (NH\(_4\))\(_2\)S.(more S\(^{2-}\) avail.)
      \[K_{sp} \text{ values are exceeded, ppt occurs}\]
      Zn\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\)
      Al\(^{3+}\), Cr\(^{3+}\), Fe\(^{3+}\) (form insol. OH)
4) **Insoluble phosphates**

a) Addition of (NH$_4$)$_2$HPO$_4$ to the solution precipitates the group 2A metals (Mg, Ca, Sr, and Ba).

5) **Formation of complex ions:**

Add excess conc. NH$_3$ or CN$^-$ or OH$^-$ to see if ppt redissolves.

i.e. Excess NH$_3$ will cause AgCl to redissolve.

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**Qualitative Inorganic Analysis**

• Acid-base chemistry, precipitation reactions, oxidation-reduction, and complex-ion formation all come into sharp focus in an area of analytical chemistry called classical qualitative inorganic analysis.

• “Qualitative” signifies that the interest is in determining what is present, not how much is present.

• Although classical qualitative analysis is not as widely used today as instrumental methods, it is still a good vehicle for applying all the basic concepts of equilibria in aqueous solutions.
Summary:

- Precipitation reactions
- Solubility constant expression $K_{sp}$ and its use
- Solubility of various classes of ionic solids and how to use that knowledge to analyze for the presence of unknown ions in solution
- Nanomaterials synthesis