Chapter 19: 
**Solubility and Simultaneous Equilibria**

Reference: Chapter 15 in “Chemistry” 6/e by Steven S. Zumdahl & Susan A. Zumdahl

19.1 An insoluble salt is in equilibrium with the solution around it
For solids dissolving to form aqueous solutions

\[ \text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \]

\[ K_{sp} = \]

\[ K_{sp} = \text{solubility product constant} \]

The is the product of the molar concentrations of the dissolved ions of the solute.

- **effect (共同離子效應):** The shift in equilibrium that occurs because of the addition of an ion already involved in the equilibrium reaction.

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

adding \( \text{NaCl}(aq) \) shifts equilibrium position

- \( K_{sp} \) can be used to determine if a precipitation will occur:
  - If the ion product \( K_{sp} \), the solution is *supersaturated* and a precipitate will form.
  - If the ion product \( K_{sp} \), the solution is *saturated* and no precipitate will form.
  - If the ion product \( K_{sp} \), the solution is *unsaturated* and no precipitate will form.

- **Solubility (s) vs. solubility product (\( K_{sp} \))**
  - \( K_{sp} \) is \( s \) is (at a given temperature) (especially with a common ion present)
Precipitation of bismuth sulfide ($\text{Bi}_2\text{S}_3$).

- $K_{sp}$ can be calculated by determining the molar solubility or the number of moles of salt dissolved in one liter of the solution.

Example: The molar solubility of $\text{PbF}_2$ in a 0.10 M $\text{Pb(NO}_3\text{)}_2$ solution at 25°C is $3.1 \times 10^{-4}$ mol L$^{-1}$. What is $K_{sp}$ for $\text{PbF}_2$?

SOLUTION:

$\text{PbF}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{F}^-(aq)$

$K_{sp} = [\text{Pb}^{2+}][\text{F}^-]^2$

\begin{align*}
\text{I} & \quad 0.10 & \quad 0 & \quad (0.10 + x)(2x)^2 \\
\text{C} & \quad +x & \quad +2x \\
\text{E} & \quad 0.10 + x & \quad 2x \\
\end{align*}

but $x$ is the molar solubility so that

$K_{sp} = (0.10 + x)(2x)^2 = (0.10 + 3.1 \times 10^{-4})(2 \times 3.1 \times 10^{-4})^2$

$= 3.9 \times 10^{-8}$ (the value from Table 19.1 is $3.6 \times 10^{-8}$)
• Molar solubility can be calculated from $K_{sp}$.

Example: What is the molar solubility of PbI$_2$ in 0.10 M NaI?

**SOLUTION:**

$$PbI_2(aq) \rightarrow Pb^{2+}(aq) + 2I^-(aq) \quad K_{sp} = [Pb^{2+}][I^-]^2$$

I

$$= 7.9 \times 10^{-9}$$

(from Table 19.1)

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### TABLE 15.4 $K_w$ Values at 25°C for Common Ionic Solids

<table>
<thead>
<tr>
<th>Ionic Solid</th>
<th>$K_w$ (at 25°C)</th>
<th>Ionic Solid</th>
<th>$K_w$ (at 25°C)</th>
<th>Ionic Solid</th>
<th>$K_w$ (at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluorides</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>$2.4 \times 10^{-5}$</td>
<td></td>
<td>BiF$_3$</td>
<td>$2.9 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>$6.4 \times 10^{-9}$</td>
<td></td>
<td>AgF$_2$</td>
<td>$9.0 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>PbF$_2$</td>
<td>$4.0 \times 10^{-8}$</td>
<td></td>
<td>PbF$_3$</td>
<td>$2.0 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>SnF$_2$</td>
<td>$7.9 \times 10^{-10}$</td>
<td></td>
<td>SnF$_3$</td>
<td>$1.4 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>$4.0 \times 10^{-11}$</td>
<td></td>
<td>CaF$_3$</td>
<td>$1.0 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td><strong>Carbonates</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>$6.4 \times 10^{-9}$</td>
<td></td>
<td>K$_2$CO$_3$</td>
<td>$1.7 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>$1.6 \times 10^{-5}$</td>
<td></td>
<td>CaCO$_3$</td>
<td>$2.0 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$CO$_3$</td>
<td>$1.3 \times 10^{-2}$</td>
<td></td>
<td>ZnCO$_3$</td>
<td>$2.0 \times 10^{-4}$</td>
<td></td>
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<tr>
<td><strong>Bromides</strong></td>
<td></td>
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<tr>
<td>PbBr$_2$</td>
<td>$4.6 \times 10^{-5}$</td>
<td></td>
<td>K$_2$Br</td>
<td>$1.7 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>AgBr</td>
<td>$5.0 \times 10^{-13}$</td>
<td></td>
<td>Na$_2$Br</td>
<td>$2.0 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>HgBr$_2$</td>
<td>$1.3 \times 10^{22}$</td>
<td></td>
<td>Hg$_2$Br$_2$</td>
<td>$5.0 \times 10^{11}$</td>
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<tr>
<td><strong>Iodides</strong></td>
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<tr>
<td>PbI$_2$</td>
<td>$1.4 \times 10^{-6}$</td>
<td></td>
<td>K$_2$I</td>
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<td></td>
</tr>
<tr>
<td>AgI</td>
<td>$1.5 \times 10^{-16}$</td>
<td></td>
<td>Na$_2$I</td>
<td>$2.0 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>HgI$_2$</td>
<td>$4.5 \times 10^{-20}$</td>
<td></td>
<td>Hg$_2$I$_2$</td>
<td>$1.0 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td><strong>Sulfates</strong></td>
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<tr>
<td>CaSO$_4$</td>
<td>$6.1 \times 10^{-5}$</td>
<td></td>
<td>Ag$_2$SO$_4$</td>
<td>$1.2 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$SO$_4$</td>
<td>$1.2 \times 10^{-5}$</td>
<td></td>
<td>Mg$_2$SO$_4$</td>
<td>$8.9 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>SrSO$_4$</td>
<td>$1.2 \times 10^{-7}$</td>
<td></td>
<td>BaSO$_4$</td>
<td>$1.5 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>PbSO$_4$</td>
<td>$1.5 \times 10^{-5}$</td>
<td></td>
<td>PbSO$_4$</td>
<td>$1.2 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td><strong>Chromates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrCrO$_4$</td>
<td>$3.6 \times 10^{-3}$</td>
<td></td>
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</tr>
</tbody>
</table>

Example 19.1 ~ 19.8
19.2 Solubility equilibria of metal oxides and sulfides involve reactions with water

- Some metal oxides dissolve in water by reacting with $\text{H}_2\text{O}$.  
  例如: 
  - Most water-insoluble metal oxides dissolve in acid.  
    例如: 
  - Water-insoluble metal oxides can form in basic solution.  
    例如: 

Metal sulfides are similar to metal oxides. 
- Some sulfides dissolve by reacting with water  
  例如: $\text{Na}_2\text{S}(s) + \text{H}_2\text{O} \rightarrow 2\text{Na}^+(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$

- Some metal ions are so reactive that they react with $\text{H}_2\text{S}$ directly. These active ions include $\text{Cu}^{2+}$, $\text{Pb}^{2+}$, and $\text{Ni}^{2+}$.  
  例如: $\text{Cu}^{2+}(aq) + \text{H}_2\text{S}(aq) \rightarrow \text{CuS}(s) + 2\text{H}^+(aq)$  
  $K = 1.7 \times 10^{15}$
– The solubility of CuS in water is described by:
\[ \text{CuS}(s) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{S}^{2-}(aq) \]
But the S\(^{2-}\) reacts with water so that
\[ \text{CuS}(s) + \text{H}_2\text{O} \rightleftharpoons \text{Cu}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq) \]
the ion product is now \([\text{Cu}^{2+}][\text{HS}^-][\text{OH}^-]\) and
\[ K_{sp} = [\text{Cu}^{2+}][\text{HS}^-][\text{OH}^-] \]
– Both OH\(^-\) and HS\(^-\) would react (to form H\(_2\)O and H\(_2\)S) in acidic solutions ⇒ a modification to the ion product.
\[ \text{CuS}(s) + 2\text{H}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{H}_2\text{S}(aq) + \text{H}_2\text{O} \]
removing water
\[ \text{CuS}(s) + 2\text{H}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{H}_2\text{S}(aq) \]
which is described by the acid solubility product, \(K_{spa}\)
\[ K_{spa} = \frac{[\text{Cu}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2} \]

• The metal sulfides can be collected into two groups:
  – The **acid-insoluble** sulfides, which dissolve in neither acidic nor basic solution.
  – The **acid-soluble** or base-insoluble sulfides that dissolve in acidic, but not basic, solutions.

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**Table 19.2**  Metal Ions Separable by Selective Precipitation of Sulfides*  

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Sulfide</th>
<th>(K_{spa})</th>
<th>(K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acid-Insoluble Sulfides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>HgS (black form)</td>
<td>(2 \times 10^{-32})</td>
<td>(2 \times 10^{-32})</td>
</tr>
<tr>
<td>Ag(^{+})</td>
<td>AgS</td>
<td>(6 \times 10^{-38})</td>
<td>(6 \times 10^{-38})</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>CuS</td>
<td>(6 \times 10^{-34})</td>
<td>(6 \times 10^{-34})</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>CdS</td>
<td>(3 \times 10^{-27})</td>
<td>(3 \times 10^{-27})</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>PbS</td>
<td>(3 \times 10^{-28})</td>
<td>(3 \times 10^{-28})</td>
</tr>
<tr>
<td>Sn(^{4+})</td>
<td>SnS</td>
<td>(1 \times 10^{-5})</td>
<td>(1 \times 10^{-5})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Sulfide</th>
<th>(K_{spa})</th>
<th>(K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base-Insoluble Sulfides (Acid-Soluble Sulfides)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>(\alpha)-ZnS</td>
<td>(3 \times 10^{-4})</td>
<td>(3 \times 10^{-4})</td>
</tr>
<tr>
<td></td>
<td>(\beta)-ZnS</td>
<td>(3 \times 10^{-2})</td>
<td>(3 \times 10^{-2})</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>CuS</td>
<td>(5 \times 10^{-11})</td>
<td>(5 \times 10^{-11})</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>NiS</td>
<td>(4 \times 10^{-1})</td>
<td>(4 \times 10^{-1})</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>FeS</td>
<td>(6 \times 10^{-1})</td>
<td>(6 \times 10^{-1})</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>MnS (pink form)</td>
<td>(3 \times 10^{-11})</td>
<td>(3 \times 10^{-11})</td>
</tr>
<tr>
<td>MnS (green form)</td>
<td>(3 \times 10^{-1})</td>
<td>(3 \times 10^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 15.11:** The separation of Cu$^{2+}$ and Hg$^{2+}$ from Ni$^{2+}$ and Mn$^{2+}$ using H$_2$S.

**19.3** Metal ions can be separated by selective precipitation
Selective precipitation means causing one metal ion to precipitate while holding the other in solution.

Selective precipitation by control of pH applies to any system where the anion comes from a weak acid.

Consider the solubility of metal carbonates

- The amount of $[\text{CO}_3^{2-}]$ depends on $[\text{H}^+]$:

  \[ H_2\text{CO}_3(aq) \rightleftharpoons H\text{CO}_3^-(aq) + H^+(aq) \quad K_{a_1} = 4.3 \times 10^{-7} \]
  \[ H\text{CO}_3^-(aq) \rightleftharpoons \text{CO}_3^{2-}(aq) + H^+(aq) \quad K_{a_2} = 4.7 \times 10^{-11} \]

- Thus, the $[\text{CO}_3^{2-}]$:
  - as pH increases (because $[\text{H}^+] \downarrow$)
  - as pH decreases (because $[\text{H}^+] \uparrow$)

**Example 19.10**

Example: Over what range of pH is it possible to selectively precipitate Cu$^{2+}$ and Ni$^{2+}$ as their sulfides from a solution initially 0.010 M in both ions? ([H$_2$S] = 0.1 M in a saturated solution.)

**ANALYSIS:** Cu$^{2+}$ is an acid-insoluble sulfide ($K_{spa} = 6 \times 10^{-16}$) and Ni$^{2+}$ is a base-insoluble sulfide ($K_{spa} = 4 \times 10^1$). Thus NiS will dissolve in acidic solution while CuS will not. The pH limits for the precipitation of both sulfides in saturates H$_2$S must be calculated.
SOLUTION:
Consider CuS first
\[ CuS(s) + 2H^+ (aq) \rightarrow Cu^{2+} (aq) + H_2S(aq) \quad K_{spa} = \frac{[Cu^{2+}][H_2S]}{[H^+]^2} \]

The Cu\(^{2+}\) will stay in solution only if \([H^+]\) is above
\[ [H^+] = \sqrt{\frac{[Cu^{2+}][H_2S]}{K_{spa}}} = \sqrt{\frac{(0.010)(0.1)}{6 \times 10^{-16}}} = 1 \times 10^6 \text{ M} \]

this \([H^+]\) could never be reached so Cu\(^{2+}\) precipitates no matter how acidic the solution is.

Now consider Ni\(^{2+}\)
\[ NiS(s) + 2H^+ (aq) \rightarrow Ni^{2+} (aq) + H_2S(aq) \quad K_{spa} = \frac{[Ni^{2+}][H_2S]}{[H^+]^2} \]

The Ni\(^{2+}\) precipitate from solution when \([H^+]\) is below
\[ [H^+] = \sqrt{\frac{[Ni^{2+}][H_2S]}{K_{spa}}} = \sqrt{\frac{(0.010)(0.1)}{4 \times 10^4}} = 0.005 \text{ M} \]
or a pH > 2.3

Thus, if we maintain the pH of the solution of 0.010 M Cu\(^{2+}\) and 0.010 M Ni\(^{2+}\) at pH ≤ 2.3, as we make the solution saturated in H\(_2\)S, virtually all the Cu\(^{2+}\) will precipitate as CuS, but all the Ni\(^{2+}\) will stay in solution.
19.4 Complex ions participate in equilibria in aqueous solutions
• **Complex Ion (錯合離子):** A charged species consisting of a metal ion (Lewis acids) surrounded by ligands (Lewis bases).

  例如: \( Cu^{2+} + 4H_2O \rightarrow Cu(H_2O)_4^{2+} \)

• **Coordination compounds (配位化合物):** Compounds that contain complex ions are called and the complex itself is sometimes called a **coordination complex**.

• **Coordination Number (配位數):** Number of ligands attached to a metal ion. (Most common are ...)

• **Formation (Stability) Constants:** The equilibrium constants characterizing the stepwise addition of ligands to metal ions. The inverse of the formation constant is called the **instability constant,** \( K_{inst} \).

  例如:

  \[
  Cu(NH_3)_4^{2+} (aq) \rightarrow Cu^{2+} (aq) + 4NH_3 (aq)
  \]

  \[
  K_{form} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.1 \times 10^{13}
  \]

  \[
  K_{inst} = \frac{1}{K_{form}} = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 9.1 \times 10^{-14}
  \]
• The solubility of a slightly soluble salt increases when one of its ions can be changed into soluble complex ion.

(Left) Aqueous ammonia is added to silver chloride (white). (Right) Silver chloride, insoluble in water, dissolves to form Ag(NH$_3$)$_2^+$ (aq) and Cl$^-$ (aq).

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

$$
2\text{H}^+(aq) + \text{Ag(NH}_3)_2^+(aq) + \text{Cl}^-(aq) \rightarrow 2\text{NH}_4^+(aq) + \text{AgCl(s)}
$$

• Example: Calculate the solubility of silver chloride in 0.10 M NH$_3$.

**SOLUTION:**

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

\[ K_{sp} = [\text{Ag}^+ ][\text{Cl}^-] = 1.8 \times 10^{-10} \]

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

\[ K_{\text{form}} = \frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+ ][\text{NH}_3]^2} = 1.6 \times 10^7 \text{, combining} \]

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

\[ K_c = K_{sp} K_{\text{form}} = \frac{[\text{Ag(NH}_3)_2^+ ][\text{Cl}^-]}{[\text{NH}_3]^2} = 2.9 \times 10^{-3} \]
\[ AgCl(s) + 2NH_3(aq) \xrightleftharpoons{\text{c}} \rightarrow Ag(NH_3)_2^+ + Cl^-(aq) \]

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>C</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>0.10</td>
<td>-2x</td>
<td>0.10-2x</td>
</tr>
<tr>
<td>( x )</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_c = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = \frac{x^2}{(0.10-x)^2} = 2.9 \times 10^{-3}
\]

\[
\frac{x}{0.10-x} = \sqrt{K_c} = 0.054 \text{ or } x = 5.1 \times 10^{-3} M
\]

The solubility of AgCl in pure water is \( \sqrt{K_{sp}} = 1.3 \times 10^{-5} M \) thus, the solubility is a factor of

\[
\frac{5.1 \times 10^{-3}}{1.3 \times 10^{-5}} = 392 \text{ times larger in } 0.10 M \text{ NH}_3
\]

**Example 19.11**

**Fig. 15.13:** The separation of the Group I ions in the classic scheme of qualitative analysis.