19.3 Equilibria of Slightly Soluble Ionic Compounds
- Slightly soluble ionic solids reach equilibrium with their saturated solutions at very low concentrations of the dissolved solute
- The dissolved portion of the ionic solid is assumed to be completely dissociated to ions (not always the case)

The Solubility-Product Constant ($K_{sp}$)
- For an ionic solid, $M_{p}A_{q}$, in equilibrium with its saturated solution, the equilibrium constant of the dissolution process is called solubility-product
  $$M_{p}A_{q}(s) \leftrightarrow pM^{m+} + qA^{n-}$$
  $$K_{sp} = [M^{m+}]^{p}[A^{n-}]^{q}$$

- $K_{sp}$ is a measure of the extent to which the solubility equilibrium proceeds to the right
  $$\uparrow K_{sp} \iff \uparrow \text{Solubility}$$
- $K_{sp}$ depends on temperature

Calculations Involving $K_{sp}$
- Molar solubility ($s$) – the molarity of the saturated solution (mol/L)
  - The solubility is often expressed in g/L or grams/100 mL of solution → can be easily converted to mol/L
  - $K_{sp}$ can be experimentally determined by measuring the molar solubility, $s$
  - $s$ can be calculated if $K_{sp}$ is known

Example: Write the solubility-product expression for Al(OH)$_3$.
  → The subscripts in the formula become powers in the solubility-product expression
  $$\Rightarrow K_{sp} = [Al^{3+}][OH^{-}]^{3}$$

Sulfides are slightly different since $S^{2-}$ acts as a strong base in water and converts entirely to OH$^{-}$

Example: Ag$_2$S
  $$\text{Ag}_2\text{S}(s) \leftrightarrow 2\text{Ag}^{+} + \text{S}^{2-}$$
  $$\text{S}^{2-} + \text{H}_2\text{O}(l) \rightarrow \text{HS}^{-} + \text{OH}^{-}$$
  $$\text{Ag}_2\text{S}(s) + \text{H}_2\text{O}(l) \leftrightarrow 2\text{Ag}^{+} + \text{HS}^{-} + \text{OH}^{-}$$
  $$\Rightarrow K_{sp} = [\text{Ag}^{+}]^{2}[\text{HS}^{-}][\text{OH}^{-}]$$

Example: The solubility of Pb(IO$_3$)$_2$ is 0.022 g/L at 25°C. Calculate $K_{sp}$ of Pb(IO$_3$)$_2$.
  → Convert the solubility to molar solubility, $s$
    $$s = \frac{0.022 \text{ g Pb(IO}_3\text{)}_2}{557 \text{ g Pb(IO}_3\text{)}_2} \times \frac{1 \text{ mol Pb(IO}_3\text{)}_2}{\text{L}} = 3.9 \times 10^{-5} \text{ mol/L}$$
  → Express $K_{sp}$ through the molar solubility, $s$
    $$\text{Pb(IO}_3\text{)}_2(s) \leftrightarrow \text{Pb}^{2+} + 2\text{IO}_3^{-}$$
    $$1 \text{ mol Pb(IO}_3\text{)}_2 \rightarrow 1 \text{ mol Pb}^{2+}$$
    $$1 \text{ mol Pb(IO}_3\text{)}_2 \rightarrow 2 \text{ mol IO}_3^{-}$$
    $$\Rightarrow [\text{Pb}^{2+}] = s \text{ and } [\text{IO}_3^{-}] = 2s$$
    $$\Rightarrow K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^{-}]^{2} = s(2s)^{2} = 4s^{3}$$
    $$\Rightarrow K_{sp} = 4 \times (3.9 \times 10^{-5})^{3} = 2.5 \times 10^{-13}$$
Example: The $K_{sp}$ of Ag$_2$SO$_4$ is $1.4 \times 10^{-5}$ at 24°C. Calculate the molar solubility of Ag$_2$SO$_4$.

→ Express $K_{sp}$ through the molar solubility, $s$

\[ \text{Ag}_2\text{SO}_4(s) \leftrightarrow 2\text{Ag}^+ + \text{SO}_4^{2-} \]

⇒ $[\text{Ag}^+] = 2s$ and $[\text{SO}_4^{2-}] = s$

⇒ $K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2s)^2s = 4s^3$

⇒ $s^3 = K_{sp}/4$ ⇒ $s = (K_{sp}/4)^{1/3}$

⇒ $s = (1.4 \times 10^{-5}/4)^{1/3} = 1.5 \times 10^{-2}$ M

Note: The problem can be solved using an ice table:

<table>
<thead>
<tr>
<th>i</th>
<th>excess</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>-$s$</td>
<td>+2$s$</td>
<td>+$s$</td>
</tr>
<tr>
<td>e</td>
<td>excess</td>
<td>2$s$</td>
<td>$s$</td>
</tr>
</tbody>
</table>

$K_{sp}$ can be used as a guide in comparing molar solubilities of different ionic compounds (works only if the compounds have the same number of ions in the formula)

$\uparrow K_{sp} \iff \uparrow s$

Table 19.3 Relationship Between $K_{sp}$ and Solubility at 25°C

<table>
<thead>
<tr>
<th>No. of ions</th>
<th>Formula</th>
<th>Cation:Anion</th>
<th>$K_{sp}$</th>
<th>Solubility (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>MgCO$_3$</td>
<td>1:1</td>
<td>$3.5 \times 10^{-8}$</td>
<td>$1.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>PbSO$_4$</td>
<td>1:1</td>
<td>$1.6 \times 10^{-8}$</td>
<td>$1.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>BaCrO$_4$</td>
<td>1:1</td>
<td>$2.1 \times 10^{-10}$</td>
<td>$1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>Ca(OH)$_2$</td>
<td>1:2</td>
<td>$6.5 \times 10^{-6}$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>BaF$_2$</td>
<td>1:2</td>
<td>$1.5 \times 10^{-6}$</td>
<td>$7.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>CaF$_2$</td>
<td>1:2</td>
<td>$3.2 \times 10^{-11}$</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>Ag$_2$CrO$_4$</td>
<td>2:1</td>
<td>$2.6 \times 10^{-12}$</td>
<td>$8.7 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The Common Ion Effect

➢ For a slightly soluble ionic solid, MA

\[ \text{MA}(s) \leftrightarrow \text{M}^{n^+} + \text{A}^{n^-} \]

$K_{sp} = [\text{M}^{n^+}][\text{A}^{n^-}]$

– If $\text{M}^{n^+}$ is added by means of the soluble salt (MB), the equilibrium shifts to the left toward formation of more MA(s)

– MA and MB have a common ion ($\text{M}^{n^+}$)

– Similarly, if $\text{A}^{n^-}$ is added to the solution, the equilibrium also shifts to the left toward formation of more MA(s)

⇒ The molar solubility decreases in the presence of common ions

Example: At a given temperature, $K_{sp}$ of AgBr is $7.7 \times 10^{-13}$. Estimate the solubility of AgBr in:

a) Pure H$_2$O  

b) 0.10 M CaBr$_2$ solution

a) In pure H$_2$O

→ Express $K_{sp}$ through the molar solubility, $s$

\[ \text{AgBr(s)} \leftrightarrow \text{Ag}^+ + \text{Br}^- \]

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<td>excess</td>
<td>$s$</td>
<td>$s$</td>
</tr>
</tbody>
</table>

⇒ $[\text{Ag}^+] = s$ and $[\text{Br}^-] = s$

⇒ $K_{sp} = [\text{Ag}^+]\text{[Br}^-] = s^2$

⇒ $s = (K_{sp})^{1/2} = (7.7 \times 10^{-13})^{1/2} = 8.8 \times 10^{-7}$ M
b) In 0.10 M CaBr₂ solution

0.10 M CaBr₂ → 0.20 M Br⁻ (Br⁻ is the common ion)

→ Express \( K_{sp} \) through the molar solubility, \( s \)

\[
\begin{array}{c|c|c}
\text{AgBr(s)} & \text{Ag}^+ & \text{Br}^- \\
\hline
\text{i excess} & 0 & 0.20 \\
\text{c excess} & +s & +s \\
\text{e excess} & s & 0.20 + s \\
\end{array}
\]

\( \Rightarrow K_{sp} = [\text{Ag}^+][\text{Br}^-] = s(0.20 + s) \)

→ Assume \( s << 0.20 \) ⇒ \( K_{sp} = s(0.20) \)

\( \Rightarrow s = \frac{K_{sp}}{0.20} = \frac{7.7 \times 10^{-13}}{0.20} = 3.8 \times 10^{-12} \text{ M} \)

→ Check assumption → OK

⇒ The solubility is much lower in 0.1 M CaBr₂

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The Effect of \( pH \) on Solubility

➢ The solubility of some ionic solids in water is greatly affected by the \( pH \)

- Metal hydroxides (Fe(OH)₃, Mg(OH)₂, …) – the anion (OH⁻) reacts with added H₃O⁺

⇒ The solubility can be improved by adding acids

Example: Mg(OH)₂

Mg(OH)₂(s) ⇌ Mg²⁺ + 2OH⁻

→ If acid (H₃O⁺) is added:

\( \Rightarrow \) H₃O⁺ consumes OH⁻ (H₃O⁺ + OH⁻ → 2H₂O)

→ The equilibrium shifts to the right and the solubility increases

Prediciting Precipitation – \( Q_{sp} \) versus \( K_{sp} \)

➢ The reaction quotient of the dissolution process (\( Q_{sp} \)) is defined in the same way as \( K_{sp} \) and at equilibrium \( Q_{sp} = K_{sp} \)

➢ To predict precipitation, compare \( Q_{sp} \) to \( K_{sp} \)

→ If \( Q_{sp} > K_{sp} \), precipitation occurs

→ If \( Q_{sp} < K_{sp} \), dissolution occurs (no precipitation)

→ If \( Q_{sp} = K_{sp} \), no change occurs

Example: Does a precipitate form after mixing of 200. mL 1.0×10⁻⁴ M AgNO₃ with 900. mL 1.0×10⁻⁶ KCl?

(\( K_{sp} = 1.8 \times 10^{-10} \) for AgCl)
\[ \text{AgNO}_3(aq) + \text{KCl}(aq) \rightarrow \text{AgCl}(s) + \text{KNO}_3(aq) \]

→ Net ionic equation: \( \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s) \)

→ Reverse: \( \text{AgCl}(s) \rightarrow \text{Ag}^+ + \text{Cl}^- \)

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

\[ V_{tot} = 0.200 + 0.900 = 1.100 \text{ L} \]

→ Initial concentrations after mixing:

\[
\begin{align*}
[\text{Ag}^+] &= \frac{1.0 \times 10^{-4} \text{ mol}}{1.100 \text{ L}} \times 0.200 \text{ L} = 1.8 \times 10^{-5} \text{ mol/L} \\
[\text{Cl}^-] &= \frac{1.0 \times 10^{-6} \text{ mol}}{1.100 \text{ L}} \times 0.900 \text{ L} = 8.2 \times 10^{-7} \text{ mol/L}
\end{align*}
\]

→ Calculate \( Q_{sp} \):

\[ Q_{sp} = [\text{Ag}^+][\text{Cl}^-] = (1.8 \times 10^{-5}) \times (8.2 \times 10^{-7}) \]

\[ Q_{sp} = 1.5 \times 10^{-11} \]

\[ K_{sp} = 1.8 \times 10^{-10} \]

\[ Q_{sp} < K_{sp} \]

⇒ No precipitation occurs