Solubility and Complex-ion Equilibria

2. Solubility and the Common-Ion Effect
   - a. Explain how the solubility of a salt is affected by another salt that has the same cation or anion. (common ion)
   - b. Calculate the solubility of a slightly soluble salt in a solution of a common ion.

Contents and Concepts

Solubility Equilibria
1. The Solubility Product Constant
2. Solubility and the Common-Ion Effect
3. Precipitation Calculations
4. Effect of pH on Solubility

Complex-Ion Equilibria
5. Complex-Ion Formation
6. Complex Ions and Solubility

An Application of Solubility Equilibria
7. Qualitative Analysis of Metal Ions

Learning Objectives

Solubility Equilibria
1. The Solubility Product Constant
   - a. Define the **solubility product constant**, \( K_{sp} \)
   - b. Write solubility product expressions.
   - c. Define **molar solubility**.
   - d. Calculate \( K_{sp} \) from the solubility (simple example).
   - e. Calculate \( K_{sp} \) from the solubility (more complicated example).
   - f. Calculate the solubility from \( K_{sp} \)

3. Precipitation Calculations
   - a. Define **ion product**.
   - b. State the criterion for precipitation.
   - c. Predict whether precipitation will occur, given ion concentrations.
   - d. Predict whether precipitation will occur, given solution volumes and concentrations.
   - e. Define **fractional precipitation**.
   - f. Explain how two ions can be separated using fractional precipitation.

4. Effect of pH on Solubility
   - a. Explain the qualitative effect of pH on solubility of a slightly soluble salt.
   - b. Determine the qualitative effect of pH on solubility.
   - c. Explain the basis for the sulfide scheme to separate a mixture of metal ions.
Complex-Ion Equilibria

5. Complex-Ion Formation
   a. Define complex ion and ligand.
   b. Define formation constant or stability constant, $K_f$, and dissociation constant, $K_d$.
   c. Calculate the concentration of a metal ion in equilibrium with a complex ion.
   d. Define amphoteric hydroxide.

6. Complex Ions and Solubility
   a. Predict whether a precipitate will form in the presence of the complex ion.
   b. Calculate the solubility of a slightly soluble ionic compound in a solution of the complex ion.

An Application of Solubility Equilibria

7. Qualitative Analysis of Metal Ions
   a. Define qualitative analysis.
   b. Describe the main outline of the sulfide scheme for qualitative analysis.

Solubility Equilibria

- Many natural processes depend on the precipitation or dissolving of a slightly soluble salt.
  - In the next section, we look at the equilibria of slightly soluble, or nearly insoluble, ionic compounds.
  - Their equilibrium constants can be used to answer questions regarding solubility and precipitation.

- When an ionic compound is insoluble or slightly soluble, an equilibrium is established:
  $$MX(s) \rightleftharpoons M^{+}(aq) + X^{-}(aq)$$

- The equilibrium constant for this type of reaction is called the solubility-product constant, $K_{sp}$.

  - For the above reaction,
    $$K_{sp} = [M^{+}][X^{-}]$$

The Solubility Product Constant

- In general, the solubility product constant is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.
  - It equals the product of the equilibrium concentrations of the ions in the compound.
  - Each concentration is raised to a power equal to the number of such ions in the formula of the compound.
  - For example, lead iodide, PbI$_2$, is another slightly soluble salt. Its equilibrium is:
    $$\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{I}^{-}(aq)$$
The expression for the solubility product constant is:

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

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

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

When an excess of a slightly soluble ionic compound is mixed with water, an equilibrium is established between the solid and the ions in the saturated solution.

- For the salt calcium oxalate, CaC₂O₄, you have the following equilibrium.

\[ \text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \]

- The equilibrium constant for this process is called the solubility product constant.

\[ K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] \]

- Write the solubility-product expression for the following salts:
  - a. Hg₂Cl₂
  - b. HgCl₂

  - a. Hg₂Cl₂
    - \[ \text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq}) \]
    - \[ K_{sp} = [\text{Hg}^{2+}][\text{Cl}^-]^2 \]
  - b. HgCl₂
    - \[ \text{HgCl}_2(s) \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq}) \]
    - \[ K_{sp} = [\text{Hg}^{2+}][\text{Cl}^-]^2 \]

- Exactly 0.133 mg of AgBr will dissolve in 1.00 L of water. What is the value of \( K_{sp} \) for AgBr?

Solubility equilibrium:

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

Solubility-product constant expression:

\[ K_{sp} = [\text{Ag}^+][\text{Br}^-] \]

The solubility is given as 0.133 mg/1.00 L, but \( K_{sp} \) uses molarity:

\[
\frac{0.133 \times 10^{-3} \text{ g}}{1.00 \text{ L}} \times \frac{1 \text{ mol}}{187.772 \text{ g}} = 7.083 \times 10^{-7} \text{ M}
\]

<table>
<thead>
<tr>
<th></th>
<th>AgBr(s) \rightleftharpoons Ag⁺(aq) + Br⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>+x</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>x</td>
</tr>
</tbody>
</table>

\[ [\text{Ag}^+] = [\text{Br}^-] = x = 7.083 \times 10^{-7} \text{ M} \]

\[ K_{sp} = (7.083 \times 10^{-7})^2 \]

\[ K_{sp} = 5.02 \times 10^{-13} \]
Calculating $K_{sp}$ from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC$_2$O$_4$, contains 0.0061-g of the salt at 25°C. Calculate the $K_{sp}$ for this salt at 25°C.

  - We must first convert the solubility of calcium oxalate from 0.0061 g/liter to moles per liter.

$$M_{CaC_2O_4} = \frac{(0.0061 \text{ g CaC}_2\text{O}_4)}{1 \text{ mol CaC}_2\text{O}_4} \times \frac{128 \text{ g CaC}_2\text{O}_4}{1} = 4.8 \times 10^{-5} \text{ mol CaC}_2\text{O}_4/L$$

- When $4.8 \times 10^{-5}$ mol of solid dissolve it forms $4.8 \times 10^{-5}$ mol of each ion.

$$\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{C}_2\text{O}_4^{2-}(aq)$$

<table>
<thead>
<tr>
<th>Starting</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>+4.8 x 10^{-5}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.8 x 10^{-5}</td>
</tr>
</tbody>
</table>

- You can now substitute into the equilibrium-constant expression.

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (4.8 \times 10^{-5})(4.8 \times 10^{-5}) = 2.3 \times 10^{-9}$$

What is the solubility of Ca(OH)$_2$?

Calculating $K_{sp}$ from the Solubility

- By experiment, it is found that $1.2 \times 10^{-3}$ mol of lead(II) iodide, PbI$_2$, dissolves in 1.0 L of water at 25°C. What is the $K_{sp}$ at this temperature?

  - Note that in this example, you find that $1.2 \times 10^{-3}$ mol of the solid dissolves to give $1.2 \times 10^{-3}$ mol Pb$^{2+}$ and $2 \times (1.2 \times 10^{-3})$ mol of I$^-$.

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

<table>
<thead>
<tr>
<th>Starting</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+1.2 x 10^{-3}</td>
<td>+2 x (1.2 x 10^{-3})</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.2 x 10^{-3}</td>
</tr>
</tbody>
</table>

- Substituting into the equilibrium-constant expression:

$$K_{sp} = \frac{[\text{Pb}^{2+}][\text{I}^-]^2}{1} = (1.2 \times 10^{-3})(2 \times (1.2 \times 10^{-3}))^2 = 6.9 \times 10^{-9}$$

Table 17.1 lists the solubility product constants for various ionic compounds.

- If the solubility product constant is known, the solubility of the compound can be calculated.
An experimenter finds that the solubility of barium fluoride is 1.1 g in 1.00 L of water at 25°C. What is the value of $K_{sp}$ for barium fluoride, $\text{BaF}_2$, at this temperature?

**Solubility equilibrium:**

\[ \text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{F}^-(aq) \]

**Solubility-product constant expression:**

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

The solubility is given as 1.1 g/1.00 L, but $K_{sp}$ uses molarity:

\[ x = \frac{1.1 \text{ g}}{1.00 \text{ L}} \times \frac{1 \text{ mol}}{175.32 \text{ g}} = 6.27 \times 10^{-3} \text{ M} \]

<table>
<thead>
<tr>
<th>BaF$_2$(s) $\rightleftharpoons$ Ba$^{2+}$(aq) + 2F$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Change</td>
</tr>
<tr>
<td>Equilibrium</td>
</tr>
</tbody>
</table>

\[ [\text{Ba}^{2+}] = x = 6.27 \times 10^{-3} \text{ M} \]

\[ [\text{F}^-] = 2x = 2(6.27 \times 10^{-3}) = 1.25 \times 10^{-2} \text{ M} \]

\[ K_{sp} = (6.27 \times 10^{-3})(1.25 \times 10^{-2})^2 \]

\[ K_{sp} = 9.8 \times 10^{-7} \]

- When $K_{sp}$ is known, we can find the molar solubility.

Calomel, whose chemical name is mercury(I) chloride, $\text{Hg}_2\text{Cl}_2$, was once used in medicine (as a laxative and diuretic). It has a $K_{sp}$ equal to $1.3 \times 10^{-18}$. What is the solubility of $\text{Hg}_2\text{Cl}_2$ in grams per liter?

**Solubility equilibrium:**

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

**Solubility-product constant expression:**

\[ K_{sp} = [\text{Hg}^{2+}][\text{Cl}]^2 \]

The molar solubility is $6.9 \times 10^{-7}$ M, but we also need the solubility in g/L:

\[
\frac{6.88 \times 10^{-7} \text{ mol/L} \times 472.086 \text{ g/mol}}{1 \text{ mol}} = 3.2 \times 10^{-4} \text{ g/L} = 0.32 \text{ mg/L}
\]
Calculating the Solubility from $K_{sp}$

- The mineral fluorite is calcium fluoride, $\text{CaF}_2$.
- Calculate the solubility (in grams per liter) of calcium fluoride in water from the $K_{sp}$ ($3.4 \times 10^{-11}$).
  - Let $x$ be the molar solubility of $\text{CaF}_2$.

\[
\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)
\]

<table>
<thead>
<tr>
<th>Starting</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>+2x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>x</td>
<td>2x</td>
</tr>
</tbody>
</table>

You substitute into the equilibrium-constant equation

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

\[
(x)(2x)^2 = 3.4 \times 10^{-11}
\]

\[
x^3 = 3.4 \times 10^{-11}
\]

- You now solve for $x$.

\[
x = \sqrt[3]{\frac{3.4 \times 10^{-11}}{4}} = 2.0 \times 10^{-4}
\]

- Convert to g/L ($\text{CaF}_2$ 78.1 g/mol).

\[
\text{solubility} = \frac{2.0 \times 10^{-4} \text{ mol/L} \times 78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2} = 1.6 \times 10^{-2} \text{ g CaF}_2 / \text{L}
\]

Quick Quiz

- 1. The solubility product constant for $\text{CaCO}_3$ is $3.8 \times 10^{-9}$. Calculate the mass of calcium carbonate that will dissolve in 1 liter of water.

- 2. The solubility product constant for $\text{Fe(OH)}_3$ is $2.5 \times 10^{-39}$. Calculate the moles of iron that will dissolve in 1 liter of water.

Solubility and the Common-Ion Effect

- In this section we will look at calculating solubilities in the presence of other ions.
  - The importance of the $K_{sp}$ becomes apparent when you consider the solubility of one salt in the solution of another having the same cation.

  - For example, suppose you wish to know the solubility of calcium oxalate in a solution of calcium chloride.
    - Each salt contributes the same cation ($\text{Ca}^{2+}$)
    - The effect is to make calcium oxalate less soluble than it would be in pure water.
• What effect does the presence of a common ion have on solubility?

• Given: \( \text{MX}(s) \rightleftharpoons \text{M}^+(aq) + \text{X}^-(aq) \)

• Qualitatively, we can use Le Châtelier’s principle to predict that the reaction will shift in the reverse direction when \( \text{M}^+ \) or \( \text{X}^- \) is added, reducing the solubility.

• In the next problem, we will explore this situation quantitatively.

The molar solubility is given by \( x \):

\[
x = 9.0 \times 10^{-9} \text{ M}
\]

• Let’s compare this result to the solubility of AgCl in water:
  - \( K_{sp} = x^2 \)
  - \( 1.8 \times 10^{-10} = x^2 \)
  - \( x = 1.3 \times 10^{-5} \text{ M} \)

• The solubility was reduced by a factor of about 1400!

A Problem To Consider

• What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The \( K_{sp} \) for calcium oxalate is \( 2.3 \times 10^{-9} \).

  – Note that before the calcium oxalate dissolves, there is already 0.15 M \( \text{Ca}^{2+} \) in the solution.

\[
\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq)
\]

<table>
<thead>
<tr>
<th>Starting</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>+x</td>
<td>0.15+x</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Starting} & : 0.15 \\
\text{Change} & : +x \\
\text{Equilibrium} & : 0.15+x
\end{align*}
\]

You substitute into the equilibrium-constant equation

\[
[\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}] = K_{sp} \\
(0.15 + x)(x) = 2.3 \times 10^{-9}
\]

Now rearrange this equation to give

\[
x = \frac{2.3 \times 10^{-9}}{0.15} \approx 2.3 \times 10^{-9}
\]

• We expect \( x \) to be negligible compared to 0.15.

• What is the molar solubility of silver chloride in 1.0 L of solution that contains \( 2.0 \times 10^{-2} \) mol of HCl?

First, using Table 17.1, we find that the \( K_{sp} \) for AgCl at 25°C is \( 1.8 \times 10^{-10} \).

Next, we construct the ICE chart with the initial \( [\text{Cl}^-] = 0.020 \text{ M} \). We then solve for \( x \), the molar solubility.

\[
\begin{array}{c|c|c}
\text{AgCl(s)} & \text{Ag}^+(aq) + \text{Cl}^-(aq) \\
\hline
\text{Initial} & 0 & 0.020 \\
\text{Change} & +x & +x \\
\text{Equilibrium} & x & 0.020 + x
\end{array}
\]

\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} = x(0.020 + x)
\]

We make the following simplifying assumption:

\[
0.020 + x = 0.020. \\
1.8 \times 10^{-10} = 0.020x
\]
Now rearrange this equation to give

\[ x = \frac{2.3 \times 10^{-9}}{0.15 + x} \]

\[ x = 1.5 \times 10^{-8} \]

Therefore, the molar solubility of calcium oxalate in 0.15 M CaCl\(_2\) is 1.5 \times 10^{-8} M.

In pure water, the molarity was 4.8 \times 10^5 M, which is over 3000 times greater.

When a problem gives the amounts and concentrations of two samples that are then mixed, the first step in solving the problem is to calculate the new initial concentrations.

- Exactly 0.400 L of 0.50 M Pb\(^{2+}\) and 1.60 L of 2.50 \times 10^{-2} M Cl\(^-\) are mixed together to form 2.00 L of solution.

- Calculate \(Q_c\) and predict whether PbCl\(_2\) will precipitate. \(K_{sp}\) for PbCl\(_2\) is 1.6 \times 10^{-5}.

Precipitation Calculations

- Precipitation is merely another way of looking at solubility equilibrium.
  - Rather than considering how much of a substance will dissolve, we ask:
  - Will precipitation occur for a given starting ion concentration?

\[
\begin{align*}
\text{PbCl}_2(s) &\rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \\
K_{sp} &= [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.6 \times 10^{-8} \\
Q_c &= (0.100)(0.0200)^2 = 4.00 \times 10^{-5}
\end{align*}
\]

\[ K_{sp} < Q_c \]

- A precipitate will form.

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the reaction quotient, \(Q_c\).
  - To predict the direction of reaction, you compare \(Q_c\) with \(K_{sp}\) (Chapter 10 and 14)
  - The reaction quotient has the same form as the \(K_{sp}\) expression, but the concentrations of products are starting values.
  - Consider the following equilibrium.

\[
\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)
\]

- We can use the reaction quotient, \(Q_c\), to determine whether precipitation will occur.
  - One form of kidney stones is calcium phosphate, Ca\(_3\)(PO\(_4\))\(_2\), which has a \(K_{sp}\) of 1.0 \times 10^{-26}. A sample of urine contains 1.0 \times 10^{-3} M Ca\(^{2+}\) and 1.0 \times 10^{-8} M PO\(_4^{3-}\) ion.
  - Calculate \(Q_c\) and predict whether Ca\(_3\)(PO\(_4\))\(_2\) will precipitate.
\[ \text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \]

\[ K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 \]

\[ K_{sp} = 1.0 \times 10^{-26} \]

\[ Q_c = (1.0 \times 10^{-3})^3 (1.0 \times 10^{-8})^2 \]

\[ Q_c = 1.0 \times 10^{-25} \]

\[ K_{sp} < Q_c \]

A precipitate will form.

\[ K_{sp} = 1.0 \times 10^{-26} \]

\[ Q_c = 2.5 \times 10^{-10} < K_{sp} \]

**Fractional Precipitation**

- Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth. (page 744)

- For example, when you slowly add potassium chromate, \( \text{K}_2\text{CrO}_4 \), to a solution containing \( \text{Ba}^{2+} \) and \( \text{Sr}^{2+} \), barium chromate precipitates first.

**Predicting Whether Precipitation Will Occur**

- The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is \( 1.0 \times 10^{-7} \) M, do you expect calcium oxalate to precipitate? \( K_{sp} \) for calcium oxalate is \( 2.3 \times 10^{-9} \).

- The ion product quotient, \( Q_c \), is:

\[ Q_c = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] \]

\[ Q_c = (0.0025) \times (1.0 \times 10^{-7}) \]

\[ Q_c = 2.5 \times 10^{-10} \]

This value is smaller than the \( K_{sp} \), so you do not expect precipitation to occur.

\[ Q_c = 2.5 \times 10^{-10} < K_{sp} \]

**Fractional Precipitation**

- Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.

- The solubility of an insoluble salt can be manipulated by adding a species that reacts with either the cation or the anion.

- Effect of pH on Solubility

- When a salt contains the conjugate base of a weak acid, the pH will affect the solubility of the salt.

**Fractional Precipitation**

- 0.1 M \( \text{Ba}^{2+} \) and 0.1 M \( \text{Sr}^{2+} \)

\[ [\text{Ba}^{2+}][\text{CrO}_4^{2-}] = K_{sp} = 1.2 \times 10^{-10} \]

\[ [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = K_{sp} = 3.5 \times 10^{-5} \]

\[ [\text{CrO}_4^{2-}] = 3.5 \times 10^{-4} \]

Calculate the percent \( \text{Ba}^{2+} \) remaining when \( \text{Sr}^{2+} \) begins to precipitate.
\[
[Ba^{2+}][CrO_4^{2-}] = 1.2 \times 10^{-10}
\]
\[
[Ba^{2+}][3.5 \times 10^{-4}] = 1.2 \times 10^{-10}
\]
\[
[Ba^{2+}] = \frac{[1.2 \times 10^{-10}]}{[3.5 \times 10^{-4}]} = 3.4 \times 10^{-7}
\]
\%
\[
Ba^{2+} = \frac{3.4 \times 10^{-7}}{0.1} \times 100 = 3.4 \times 10^{-6}
\]

After most of the \(Ba^{2+}\) ion has precipitated, strontium chromate begins to precipitate.

Fractional Precipitation

- **Fractional precipitation** is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.
  - After most of the \(Ba^{2+}\) ion has precipitated, strontium chromate begins to precipitate.
  - It is therefore possible to separate \(Ba^{2+}\) from \(Sr^{2+}\) by **fractional precipitation** using \(K_2CrO_4\).

If you add a dilute acidic solution to a mixture containing magnesium oxalate and calcium oxalate, which of the two compounds is more likely to dissolve?

- \(K_{sp}\) for \(MgC_2O_4\) is \(8.5 \times 10^{-5}\).
- \(K_{sp}\) for \(BaC_2O_4\) is \(1.5 \times 10^{-8}\).
- \(MgC_2O_4\) is more soluble.
  - If a dilute acidic solution is added, it will increase the solubility of both salts. \(MgC_2O_4\) is still more soluble.

We will qualitatively explore the situation involving a generic salt, \(MX\), where \(X\) is the conjugate base of a weak acid.

- \(MX(s) \rightarrow M^{+}(aq) + X^{-}(aq)\)
- As the acid concentration increases, \(X^{-}\) reacts with the \(H_3O^{+}\), forming \(HX\) and reducing the \(X^{-}\) concentration. As a result, more \(MX\) dissolves, increasing the solubility.

It is possible to use these differences to separate compounds.

- This is common practice when the goal is to separate sulfides from one another.
- The qualitative analysis scheme for the separation of metal ions uses sulfide solubility to separate \(Co^{2+}\), \(Fe^{3+}\), \(Mn^{2+}\), \(Ni^{2+}\), and \(Zn^{2+}\) (Analytical Group III).
Effect of pH on Solubility

- Sometimes it is necessary to account for other reactions aqueous ions might undergo.
  - For example, if the anion is the conjugate base of a weak acid, it will react with $H_3O^+$.
  - You should expect the solubility to be affected by pH.

- Consider the following equilibrium.
  \[
  CaC_2O_4(s) \xrightleftharpoons{H_2O} Ca^{2+}(aq) + C_2O_4^{2-}(aq)
  \]
  - Because the oxalate ion is conjugate to a weak acid ($HC_2O_4^-$), it will react with $H_3O^+$.
  \[
  C_2O_4^{2-}(aq) + H_3O^+(aq) \xrightarrow{H_2O} HC_2O_4^-(aq) + H_2O(l)
  \]
  - According to Le Chatelier’s principle, as $C_2O_4^{2-}$ ion is removed by the reaction with $H_3O^+$, more calcium oxalate dissolves.
  - Therefore, you expect calcium oxalate to be more soluble in acidic solution (low pH) than in pure water.

Separation of Metal Ions by Sulfide Precipitation

- Many metal sulfides are insoluble in water but dissolve in acidic solution.
  - Qualitative analysis uses this change in solubility of the metal sulfides with pH to separate a mixture of metal ions.
  - By adjusting the pH in an aqueous solution of $H_2S$, you adjust the sulfide concentration to precipitate the least soluble metal sulfide first.
  - Qualitative analysis is covered in Section 17.7.

\[
H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)
\]
\[
HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)
\]

\[
K_{a1} = \frac{[HS^-][H_3O^+]}{[H_2S]}
\]
\[
K_{a2} = \frac{[S^{2-}][H_3O^+]}{[HS^-]}
\]

\[
K_{a1} \times K_{a2} = \frac{[H_3O^+]}{[H_2S]} \times \frac{[S^{2-}][H_3O^+]}{[HS^-]} = 1.3 \times 10^{-20}
\]

\[
[H_3O^+] = \frac{0.10}{1.3 \times 10^{-21}} = 7.6 \times 10^{10}
\]
• Complex-Ion Formation
  • Some cations form soluble complex ions. Their formation increases the solubility of a salt containing those cations.

  Metal ions that form complex ions include $\text{Ag}^+$, $\text{Cd}^{2+}$, $\text{Cu}^{2+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Ni}^{2+}$, and $\text{Zn}^{2+}$.

  Complexing agents, called ligands, are Lewis bases. They include $\text{CN}^-$, $\text{NH}_3$, $\text{S}_2\text{O}_3^{2-}$, and $\text{OH}^-$.

  In each case, an equilibrium is established, called the complex-ion formation equilibrium.

Complex-Ion Equilibria

  Many metal ions, especially transition metals, form coordinate covalent bonds with molecules or anions having a lone pair of electrons.

  This type of bond formation is essentially a Lewis acid-base reaction.

  For example, the silver ion, $\text{Ag}^+$, can react with ammonia to form the $\text{Ag(NH}_3)_2^+$ ion.

  $$\text{Ag}^+ + 2(\text{NH}_3) \rightarrow (\text{H}_3\text{N}:\text{Ag}:\text{NH}_3)^+$$

Complex-Ion Equilibria

  A complex ion is an ion formed from a metal ion with a Lewis base attached to it by a coordinate covalent bond.

  A complex is defined as a compound containing complex ions.

  A ligand is a Lewis base (an electron pair donor) that bonds to a metal ion to form a complex ion.

Complex-Ion Formation

  The aqueous silver ion forms a complex ion with ammonia in steps.

  $$\text{Ag}^+(aq) + \text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)$$

  $$\text{Ag(NH}_3)_2^+(aq) + \text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_3^+(aq)$$

  When you add these equations, you get the overall equation for the formation of $\text{Ag(NH}_3)_2^+$.

  $$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)$$
Complex-Ion Formation

- The formation constant, $K_f$, is the equilibrium constant for the formation of a complex ion from the aqueous metal ion and the ligands.
  - The formation constant for $\text{Ag(NH}_3\text{)}_2^{+}$ is:
    $$K_f = \frac{[\text{Ag(NH}_3\text{)}_2^{+}]}{[\text{Ag}^{+}][\text{NH}_3]^2}$$
  - The value of $K_f$ for $\text{Ag(NH}_3\text{)}_2^{+}$ is $1.7 \times 10^7$.

- The large value means that the complex ion is quite stable.
  - When a large amount of NH$_3$ is added to a solution of Ag$^+$, you expect most of the Ag$^+$ ion to react to form the complex ion.
  - Table 17.2 lists formation constants of some complex ions.

Equilibrium Calculations with $K_f$

- What is the concentration of Ag$^+$ (aq) ion in 0.010 M AgNO$_3$ that is also 1.00 M NH$_3$? The $K_f$ for $\text{Ag(NH}_3\text{)}_2^{+}$ is $1.7 \times 10^7$.
  - In 1.0 L of solution, you initially have 0.010 mol Ag$^+$ (aq) from AgNO$_3$.
  - This reacts to give 0.010 mol Ag$($NH$_3$)$_2$$^{+}$, leaving ($1.00 - (2 \times 0.010)$) = 0.98 mol NH$_3$.
  - You now look at the dissociation of Ag$($NH$_3$)$_2$$^{+}$.

- The following table summarizes.

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>$K_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(CN)$_2$$^{−}$</td>
<td>$5.6 \times 10^{38}$</td>
</tr>
<tr>
<td>Ag(NH$_3$)$_2$$^{−}$</td>
<td>$1.7 \times 10^{24}$</td>
</tr>
<tr>
<td>Ag(S$_2$O$_3$)$_2$$^{−}$</td>
<td>$2.9 \times 10^{13}$</td>
</tr>
<tr>
<td>Cd(NH$_3$)$_4$$^{2+}$</td>
<td>$1.0 \times 10^{7}$</td>
</tr>
<tr>
<td>Cu(NH$_3$)$_4$$^{2+}$</td>
<td>$1.0 \times 10^{8}$</td>
</tr>
<tr>
<td>Cu(NH$_3$)$_4$$^{2+}$</td>
<td>$4.8 \times 10^{8}$</td>
</tr>
<tr>
<td>Fe(CN)$_6$$^{3−}$</td>
<td>$1.0 \times 10^{15}$</td>
</tr>
<tr>
<td>Fe(CN)$_6$$^{3−}$</td>
<td>$9.1 \times 10^{14}$</td>
</tr>
<tr>
<td>Ni(CN)$_6$$^{3−}$</td>
<td>$1.0 \times 10^{13}$</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_6$$^{3+}$</td>
<td>$5.6 \times 10^{8}$</td>
</tr>
<tr>
<td>Zn(NH$_3$)$_4$$^{2+}$</td>
<td>$2.9 \times 10^{8}$</td>
</tr>
<tr>
<td>Zn(OH)$_2$$^{−}$</td>
<td>$2.8 \times 10^{3}$</td>
</tr>
</tbody>
</table>

- The dissociation constant equation is:
  $$K_d = \frac{[\text{Ag}^{+}][\text{NH}_3]^2}{[\text{Ag(NH}_3\text{)}_2^{+}]} = \frac{1}{K_f}$$

Complex-Ion Formation

- The dissociation constant, $K_d$, is the reciprocal, or inverse, value of $K_f$.
  - The equation for the dissociation of $\text{Ag(NH}_3\text{)}_2^{+}$ is
    $$\text{Ag(NH}_3\text{)}_2^{+} (\text{aq}) \rightleftharpoons \text{Ag}^{+} (\text{aq}) + 2\text{NH}_3 (\text{aq})$$
  - The equilibrium constant equation is
    $$K_d = \frac{1}{K_f} = \frac{[\text{Ag}^{+}][\text{NH}_3]^2}{[\text{Ag(NH}_3\text{)}_2^{+}]}$$

Formation constants are shown to the right.

Note that all the values are quite large, which means that the equilibrium favors the complex ion.
Substituting into this equation gives:

\[(x)(0.98+2x)^2 = \frac{1}{(0.010-x)^7}\]

If we assume \(x\) is small compared with 0.010 and 0.98, then

\[(x)(0.98)^2 \approx 5.9 \times 10^{-8}\]

and

\[x \approx 5.9 \times 10^{-8} \times \frac{(0.010)}{(0.98)} = 6.1 \times 10^{-10}\]

The silver ion concentration is \(6.1 \times 10^{-10}\) M.

Silver chloride usually does not precipitate in solutions of 1.00 M NH₃. However, silver bromide has a smaller \(K_{sp}\) than silver chloride.

Will silver bromide precipitate from a solution containing 0.010 M AgNO₃, 0.010 M NaBr, and 1.00 M NH₃?

Calculate the \(Q_c\) value and compare it with silver bromide’s \(K_{sp}\) of \(5.0 \times 10^{-13}\).

We’ll begin with the complex-ion formation, and then find the concentration of Ag⁺ in solution. Finally, we’ll find the value of \(Q_c\) for AgBr and compare it to \(K_{sp}\).

1.00 L of solution contains 0.010 mol Ag⁺ and 1.00 mol NH₃.

<table>
<thead>
<tr>
<th></th>
<th>Ag⁺(aq)</th>
<th>2NH₃(aq)</th>
<th>Ag(NH₃)₂⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.010</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-0.010</td>
<td>-2(0.010)</td>
<td>+0.010</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0</td>
<td>0.98</td>
<td>0.010</td>
</tr>
</tbody>
</table>

\([\text{Ag(NH₃)₂⁺(aq)}] = 0.0010 \text{ M}; [\text{NH₃}] = 0.980 \text{ M}\)

\[\begin{array}{ccc}
\text{Ag(NH₃)₂⁺(aq)} & \text{Ag⁺(aq)} & + 2\text{NH₃(aq)} \\
\text{Initial} & 0.010 & 0 & 0.980 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.010 - x & x & 0.980 \\
\end{array}\]

\[K_{sp} = \frac{[\text{Ag⁺}][\text{Br}^-]^2}{[\text{Ag(NH₃)₂⁺}]} = \frac{1}{1.7 \times 10^7} = 5.9 \times 10^{-8}\]

\[5.9 \times 10^{-8} = \frac{x(0.980 + x)^2}{(0.010 - x)}\]

We can assume that 0.980 + \(x\) = 0.980 and 0.010 - \(x\) = 0.010.

\[5.9 \times 10^{-8} = \frac{x(0.980)^2}{0.010}\]

\[5.9 \times 10^{-8} = 96.0x\]

\[x = 6.1 \times 10^{-10} \text{ M}\]

The assumptions are valid.

\([\text{Ag⁺}] = 6.1 \times 10^{-10} \text{ M}\)

Next we’ll use the solubility equilibrium to find \(Q_c\).

\[Q_c = [\text{Ag⁺}] [\text{Br}^-]\]

\[Q_c = (6.1 \times 10^{-10})(0.010)\]

\[Q_c = 6.1 \times 10^{-12}\]

\[K_{sp} = 5.0 \times 10^{-13}\]

\[K_{sp} < Q_c\]

The precipitate forms.
• Calculate the molar solubility of AgBr in 1.0 M NH₃ at 25°C.

We will first combine the two equilibria and find the combined equilibrium constant.

\[
\begin{align*}
\text{AgBr(s)} & \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq); \ K_{sp} \\
\text{Ag}^+(aq) + 2\text{NH}_3(aq) & \rightleftharpoons \text{Ag(NH}_3)_2^+(aq); \ K_f \\
\text{AgBr(s)} + 2\text{NH}_3(aq) & \rightleftharpoons \text{Br}^-(aq) + 2\text{NH}_3(aq)
\end{align*}
\]

\[K = K_{sp} \cdot K_f = (5.0 \times 10^{-13})(1.7 \times 10^7) = 8.5 \times 10^{-6}\]

• Now, we’ll use the combined equilibrium to find the solubility of AgBr in 1.0 M NH₃.

<table>
<thead>
<tr>
<th></th>
<th>AgBr(s)</th>
<th>2NH₃(aq)</th>
<th>Br(aq)</th>
<th>Ag(NH₃)₂⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-2x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.0 − 2x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\[K = \frac{[\text{Br}^-][\text{Ag(NH}_3)_2^{+}]}{[\text{NH}_3]^2}\]

\[8.5 \times 10^{-6} = \frac{x^2}{(1.0 − 2x)^2}\]

• The right side of the equation is a perfect square.

\[2.9 \times 10^{-3} = \frac{x}{(1.0 − 2x)}\]

\[0.0029 - 0.0058x = x\]

\[0.0029 = 1.0058x\]

\[x = 2.9 \times 10^{-3}\]

• The molar solubility of AgBr in 1.0 M NH₃ is • \[2.9 \times 10^{-3}\ M.\]

• The combination of solubility and complex-ion equilibria can be applied to separate metal ions.

• Cations can be separated into groups according to their precipitation properties.

• In each major step, one group of cations precipitates out. After separating the precipitate, the remaining solution is treated with the next reagent, precipitating the next group of cations.

Amphoteric Hydroxides

• An amphoteric hydroxide is a metal hydroxide that reacts with both acids and bases.

  – For example, zinc hydroxide, Zn(OH)₂, reacts with a strong acid and the metal hydroxide dissolves.

\[\text{Zn(OH)}_2(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + 4\text{H}_2\text{O}(l)\]

  – With a base however, Zn(OH)₂ reacts to form the complex ion Zn(OH)₄²⁻.

\[\text{Zn(OH)}_2(s) + 2\text{OH}^-(aq) \rightarrow \text{Zn(OH)}_4^{2-}(aq)\]

• When a strong base is slowly added to a solution of ZnCl₂, a white precipitate of Zn(OH)₂ first forms.

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

  – But as more base is added, the white precipitate dissolves, forming the complex ion Zn(OH)₄²⁻. See Figure 17.

  – Other common amphoteric hydroxides are those of aluminum, chromium(III), lead(II), tin(II), and tin(IV).
Qualitative Analysis

- **Qualitative analysis** involves the determination of the identity of substances present in a mixture.
  - In the qualitative analysis scheme for metal ions, a cation is usually detected by the **presence of a characteristic precipitate**.
  - Figure 18.8 summarizes how metal ions in an aqueous solution are separated into five analytical groups.

Demonstration of the amphoteric behavior of zinc hydroxide

\[
\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}
\]
Operational Skills

- Writing solubility product expressions
- Calculating $K_{sp}$ from the solubility, or vice versa.
- Calculating the solubility of a slightly soluble salt in a solution of a common ion.
- Predicting whether precipitation will occur
- Determining the qualitative effect of pH on solubility
- Calculating the concentration of a metal ion in equilibrium with a complex ion
- Predicting whether a precipitate will form in the presence of the complex ion
- Calculating the solubility of a slightly soluble ionic compound in a solution of the complex ion