CHAPTER 8 – EQUILIBRIA CONTAINING METAL IONS

Introduction

Several different equilibria must be considered when dealing with aqueous metal ions:

- Metal ions are Lewis acids, so they are involved in acid-base equilibria.
- As Lewis acids, they can react with other Lewis bases to form complex ions.
- Many metal ions form sparingly soluble salts, so solubility equilibria must also be considered.

In this chapter, all three of these types of equilibria are considered.

8.1 Acid-Base Equilibria

Introduction

While metal ions rarely have protons to donate as required by the Brønsted acid definition, they can accept electron pairs to form covalent bonds, which makes them acidic by the Lewis definition. Thus, an aqueous solution of iron(III) nitrate is acidic even though it contains no protons.

Objectives

- Explain the acidity of metal ions and write the acid-dissociation reaction associated with the acidity.

8.1-1. Metal Ions as Acids

Metal ions form acidic solutions because the positive charge on the metal ion weakens the O–H bonds of the bound water molecules.

Fe(NO₃)₃ is a strong electrolyte that dissociates completely into Fe³⁺ and NO₃⁻ ions. The small, highly charged iron(III) ion interacts with the surrounding water molecules in a Lewis acid-base reaction to produce Fe(H₂O)₆³⁺, the octahedral ion in Figure 8.1. Ions, such as Fe(H₂O)₆³⁺, that consist of a metal ion bound to several molecules or anions are called complex ions, and the bound molecules or anions are referred to as ligands. The positive charge of the central metal ion withdraws electron density from the O–H bonds, which weakens them and makes the water ligands stronger acids.

![Figure 8.1: Acidity of Metal Ions](image)

Thus, the acidity of Fe³⁺ ions arises from the following reaction:

\[ \text{Fe(H}_2\text{O)}\text{₆}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(H}_2\text{O)}\text{₆(OH)}^{2+} + \text{H}_3\text{O}^{1+} \]

\[ K = 6 \times 10^{-3} \]
which is the reaction of a weak acid with water, so the equilibrium constant is the $K_a$ of the weak acid $\text{Fe(H}_2\text{O)}_6^{3+}$. Note that $\text{Fe(H}_2\text{O)}_6^{3+}$ is a stronger acid than acetic acid ($K_a = 1.8 \times 10^{-5}$). The $K_a$ values of several hydrated metal ions are listed in the table.

<table>
<thead>
<tr>
<th>Hydrated Metal Ion</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe(H}_2\text{O)}_6^{3+}$</td>
<td>$6 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\text{Al(H}_2\text{O)}_6^{3+}$</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{Cu(H}_2\text{O)}_6^{2+}$</td>
<td>$3 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{Zn(H}_2\text{O)}_6^{2+}$</td>
<td>$1 \times 10^{-9}$</td>
</tr>
<tr>
<td>$\text{Ni(H}_2\text{O)}_6^{2+}$</td>
<td>$1 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Table 8.1: Acid Dissociation Constants of Hydrated Metal Ions

8.2 Dissolution and the Solubility Product Constant

Introduction

Calcium carbonate (also known as limestone) is a slightly soluble salt that is responsible for scale in containers of hard water. In addition, caves and the unusual structures in them called stalactites and stalagmites are the result of dissociation and subsequent precipitation of calcium carbonate. This important dissociation process is represented in the following equilibrium:

$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad K = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

This type of process, the equilibrium between a solid and its ions in solution, is an important one and forms the topic of this section.

Objectives

- Write the dissociation reaction of a slightly soluble salt.
- Write the expression for the solubility product constant, $K_{sp}$, of a given salt.
- Calculate the solubility of an ionic compound given its $K_{sp}$ value, and vice versa.
- Calculate the solubility of an ionic compound in the presence of one of its ions.

8.2-1. The Solubility Product

The equilibrium between a solid and its solution is an important one. Indeed, it is so important that the equilibrium is given a special symbol and name: the solubility product constant ($K_{sp}$). Consider the equilibrium between solid silver chloride and its solution: $\text{AgCl} \rightleftharpoons \text{Ag}^{1+} + \text{Cl}^{-}$. The activity of the solid is unity, so the form of the equilibrium constant, $K_{sp}$, for the reaction is $K_{sp} = [\text{Ag}^{1+}][\text{Cl}^{-}]$. It is called the solubility product constant because it is simply a product of concentrations that indicates the solubility of the solid.

Most slightly soluble salts contain basic anions, which are involved in both acid-base equilibria with water and salt dissolution equilibria with metal ions. This can lead to a complicated set of equilibria in the case of fairly strong bases such as $\text{CO}_3^{2-}$ and $\text{PO}_4^{3-}$. Consequently, our discussions of solubility in water centers on the solubility of neutral or only weakly basic anions, such as $\text{Cl}^{-}$ and $\text{SO}_4^{2-}$. The reaction table for the dissociation of $\text{Ag}_2\text{SO}_4$ in water has the following form:

$$\text{Ag}_2\text{SO}_4(s) = 2 \text{Ag}^{1+} + \text{SO}_4^{2-} \quad K_{sp} = 1.4 \times 10^{-5}$$

<table>
<thead>
<tr>
<th>initial</th>
<th>$\Delta$</th>
<th>equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}_2\text{SO}_4$</td>
<td>$+2x$</td>
<td>$2x$</td>
</tr>
<tr>
<td>enough</td>
<td>$0$</td>
<td>$x$</td>
</tr>
<tr>
<td>$M$</td>
<td>$M$</td>
<td>$M$</td>
</tr>
</tbody>
</table>

where $x$ is the molar solubility of silver sulfate. The activity of a solid is unity, so it does not enter into the equilibrium constant expression. Consequently, the amount of solid is irrelevant so long as there is enough of the solid initially to assure that there is some solid present at equilibrium. The $K_{sp}$ expression is
\[ K_{sp} = 1.4 \times 10^{-5} = [Ag^{1+}]^2[SO_4^{2-}] = (2x)^2(x) = 4x^3 \]

Solving the above expression for \( x \), we obtain the molar solubility of silver sulfate and the ion concentrations in a saturated solution in terms of the solubility product constant.

\[ x = \frac{\sqrt[3]{K_{sp}}}{4} = [SO_4^{2-}] = \frac{1}{2}[Ag^{1+}] \]

Substituting \( 1.4 \times 10^{-5} = K_{sp} \), we obtain the following:

- molar solubility of silver sulfate; \( x = 0.015 \) M
- \([SO_4^{2-}] = x = 0.015 \) M
- \([Ag^{1+}] = 2x = 0.030 \) M

We can check our calculation by substituting concentrations back into the \( K_{sp} \) expression:

\[ K_{sp} = [Ag^{1+}]^2[SO_4^{2-}] = (0.030)^2(0.015) = 1.4e-05 \]

\( K_{sp} \) values can be found in Selected Solubility Product Constants in the Resources.

### 8.2-2. \( K_{sp} \) from Solubility Exercise

#### EXERCISE 8.1:
What is the \( K_{sp} \) of MgF_2 (\( M_m = 62.3 \) g/mol) if its solubility is 7.6 mg/100. mL?

The molar solubility of MgF_2 = \( \) M

\([Mg^{2+}] = \) M \hspace{1cm} \([F^{-}] = \) M \hspace{1cm} \( K = \) 

### 8.2-3. \( K_{sp} \) from pH Exercise

#### EXERCISE 8.2:
What is the \( K_{sp} \) of Fe(OH)_2 if the pH of a saturated solution is 9.07? Watch out for rounding errors!

\([OH^{-}] = \) M \hspace{1cm} \([Fe^{2+}] = \) M \hspace{1cm} \( K = \) 

### 8.2-4. Solubility from \( K_{sp} \) Exercise

#### EXERCISE 8.3:
The \( K_{sp} \) of AgI is 8.3e−17. What is its molar solubility?

Molar solubility = \( \) M

### 8.2-5. \( K_{sp} \) and Strong Bases

Let us now determine the solubility of the salt of Ag_3PO_4; \( K_{sp} = 2.6 \times 10^{-18} \).
The reaction table for the dissolution has the following form:

\[
\text{Ag}_3\text{PO}_4(s) \rightleftharpoons 3\text{Ag}^{1+} + \text{PO}_4^{3-}
\]

<table>
<thead>
<tr>
<th>initial</th>
<th></th>
<th>Δ</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>enough</td>
<td>0</td>
<td>+3x</td>
<td>+x</td>
</tr>
<tr>
<td>equilibrium</td>
<td>3x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

\[K_{sp} = [\text{Ag}^{1+}]^3[\text{PO}_4^{3-}] = (3x)^3(x) = 27x^4\]

Solving \(27x^4 = 2.6 \times 10^{-18}\) for \(x\), we obtain a solubility of \(1.8 \times 10^{-5}\) \(M\).

However, the measured solubility is \(1.5 \times 10^{-4}\). Thus, the actual solubility is over eight times greater than that determined with \(K_{sp}\). The \(K_{sp}\) is correct, and it is still obeyed. However, \(\text{PO}_4^{3-}\) is a fairly strong base, so some of the \(\text{PO}_4^{3-}\) that is produced by the dissolution reacts with water to produce \(\text{HPO}_4^{2-}\) and \(\text{OH}^{1-}\). Therefore, \(K_{sp} = [\text{Ag}^{1+}]^3[\text{PO}_4^{3-}]\) is still valid, but the loss of \(\text{PO}_4^{3-}\) in the reaction with water means that the equality \(3[\text{Ag}^{1+}] = [\text{PO}_4^{3-}]\) is no longer valid. This is why we restrict our discussion of solubility to neutral or weakly basic salts only. We treat the solubility of \(\text{Ag}_3\text{PO}_4\) in more detail in Section 8.4.

### 8.2-6. Cation:Anion Ratios in \(K_{sp}\)

The preceding examples demonstrate that the form of the \(K_{sp}\) expression in terms of the molar solubility of the salt \((x)\) depends only upon the cation:anion ratio in the salt. The \(K_{sp}\) expressions for the common ratios are given below.

<table>
<thead>
<tr>
<th>Cation:Anion Ratio</th>
<th>(K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>(x^2)</td>
</tr>
<tr>
<td>1:2 or 2:1</td>
<td>(4x^3)</td>
</tr>
<tr>
<td>1:3 or 3:1</td>
<td>(27x^4)</td>
</tr>
<tr>
<td>2:3 or 3:2</td>
<td>(108x^5)</td>
</tr>
</tbody>
</table>

Table 8.2: \(K_{sp}\) expressions in terms of molar solubilities \((x)\) for salts with common cation:anion ratios

The relative solubilities of salts with the same cation:anion ratios can be obtained by simply looking at the magnitudes of their \(K_{sp}\)'s. However, when the ratios are different, you must determine the value of \(x\).

### 8.2-7. Determining Relative Solubilities Exercise

**EXERCISE 8.4:**

List the following salts in order of increasing solubility.

<table>
<thead>
<tr>
<th>Salt</th>
<th>(K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCl(_2)</td>
<td>(1.7e-5)</td>
</tr>
<tr>
<td>AgCl</td>
<td>(1.2e-10)</td>
</tr>
<tr>
<td>TlCl</td>
<td>(1.9e-4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Least soluble salt: PbCl(_2)</th>
<th>Intermediate salt: PbCl(_2)</th>
<th>Most soluble salt: PbCl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>AgCl</td>
<td>AgCl</td>
</tr>
<tr>
<td>TlCl</td>
<td>TlCl</td>
<td>TlCl</td>
</tr>
</tbody>
</table>
8.2-8. Predicting the More Soluble Salt Exercise

**EXERCISE 8.5:**
Indicate the more soluble compound in each pair.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSO$_4$</td>
<td>$K_{sp} = 2 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>$K_{sp} = 2 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>BaCrO$_4$</td>
<td>$K_{sp} = 2 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$CrO$_4$</td>
<td>$K_{sp} = 2 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>$K_{sp} = 4 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>PbF$_2$</td>
<td>$K_{sp} = 2 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Ag$_3$PO$_4$</td>
<td>$K_{sp} = 5 \times 10^{-24}$</td>
<td></td>
</tr>
<tr>
<td>Mg$_3$(PO$_4$)$_2$</td>
<td>$K_{sp} = 5 \times 10^{-24}$</td>
<td></td>
</tr>
</tbody>
</table>

8.2-9. Common-Ion Effect

Consider the dissolution of Ag$_2$SO$_4$(s) in 1.0 M Na$_2$SO$_4$.

\[
\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^{1+} + \text{SO}_4^{2-} \quad K_{sp} = 1.4 \times 10^{-5}
\]

<table>
<thead>
<tr>
<th>Condition</th>
<th>Ag$^{1+}$</th>
<th>SO$_4^{2-}$</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0</td>
<td>1.0</td>
<td>$K_{sp}$</td>
</tr>
<tr>
<td>equilibrium</td>
<td>2$x$</td>
<td>0.10 + $x$</td>
<td>$K_{sp}$</td>
</tr>
</tbody>
</table>

\[K_{sp} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}] = (2x)^2(1.0 + x)\]

which would involve solving a cubic equation. However, in the beginning of this section, we determined that the solubility of Ag$_2$SO$_4$ in water was 0.015 M, and the presence of the common ion (sulfate) will decrease the dissociation, so $x < 0.015$. If we assume that $x$ is negligible in the addition ($1.0 + x \sim 1.0$), we can simplify the expression

\[K_{sp} = (2x)^2(1.0)\]

which is solved for $x$ as follows:

\[x = \sqrt{\frac{K_{sp}}{4(1.0)}} = \sqrt{\frac{1.4 \times 10^{-5}}{4.0}} = 1.9 \times 10^{-3} \ M\]

Thus, the solubility drops from 0.015 M in water down to 0.0019 M (an 88% drop) in 1.0 M Na$_2$SO$_4$ due to the presence of the common ion.

8.2-10. Common-Ion Solubility from pH Exercise

**EXERCISE 8.6:**
Determine the solubility of Sn(OH)$_2$ in solutions buffered at the following pHs.

\[K_{sp} = \underline{\underline{\underline{}}}\]

pH = 9.00

The concentration of the common ion: \[[\text{OH}^-] = \underline{\underline{\underline{}}} \ M\]

solubility \[\underline{\underline{\underline{}}} \ M\]

pH = 2.00

The concentration of the common ion: \[[\text{OH}^-] = \underline{\underline{\underline{}}} \ M\]

solubility \[\underline{\underline{\underline{}}} \ M\]
EXERCISE 8.7:

\[ K_{sp} = 1.8 \times 10^{-10} \text{ for AgCl. Determine the solubility of AgCl in the following:} \]

-  
  \[
    \begin{array}{c}
    \text{water} \\
    0.10 \text{ M NaCl}
    \end{array}
  \]

solubility = \text{___________ M} \\
solubility = \text{___________ M}

8.3 Precipitation and Separation of Ions

Introduction

Our discussions thus far have focused on the amount of a slightly soluble salt that dissolves, but now we consider the reverse process; i.e., does a precipitate form under a given set of concentrations? We do this by considering the dissociation reaction from the reverse direction; that is, we examine the formation (precipitation) of the salt.

Objectives

- Predict whether a precipitation will occur given the concentrations of the ions and the \( K_{sp} \) of the salt.
- Determine the appropriate anion concentration to achieve maximum separation of two ions by the selective precipitation of one.

8.3-1. The Ion Product

Does a solid form under a given set of conditions, or what minimum concentration of one of the ions is required to produce a precipitate? These are two questions we will answer in this section. For example, consider a mixture that contains some solid \( \text{Ag}_2\text{SO}_4(s) \) suspended in a solution that is 0.01 M in \( \text{Ag}^{1+} \) and 0.10 M in \( \text{SO}_4^{2-} \). Under these conditions, does the solid dissolve or does it precipitate out of solution? To answer this question, we examine the direction in which the following reaction is proceeding under these conditions.

\[
\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^{1+} + \text{SO}_4^{2-} \quad K_{sp} = 1.4 \times 10^{-5}
\]

The direction in which a reaction proceeds depends upon the relative values of the reaction quotient, \( Q \), and the equilibrium constant \( K \). The reaction quotient for dissociation is used so frequently that it is given a special name and symbol: the \textbf{ion product}, \( Q_{ip} \).

- Precipitation occurs (reaction proceeds \( \leftarrow \)) if \( Q_{ip} > K_{sp} \)
- The salt dissolves (reaction proceeds \( \rightarrow \)) if \( Q_{ip} < K_{sp} \)

In this case, \( Q_{ip} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}] = (0.01)^2(0.10) = 1 \times 10^{-5} \) and \( K_{sp} = 1.4 \times 10^{-5} \). \( K_{sp} > Q_{ip} \), so some salt can still dissolve and no precipitate would form.
8.3-2. Identifying Precipitating Hydroxides Exercise

**EXERCISE 8.8:**
An acidic solution is made 0.01 M in Cu$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, and Sn$^{2+}$. The pH of the solution is then adjusted by adding NaOH. Select all hydroxides that precipitate at each of the following pHs.

**pH = 4**

\[ Q_{ip} = \] ____________

- only Sn(OH)$_2$
- Sn(OH)$_2$ and Cu(OH)$_2$
- Sn(OH)$_2$, Cu(OH)$_2$, and Fe(OH)$_2$
- All four hydroxides precipitate.

**pH = 6**

\[ Q_{ip} = \] ____________

- only Sn(OH)$_2$
- Sn(OH)$_2$ and Cu(OH)$_2$
- Sn(OH)$_2$, Cu(OH)$_2$, and Fe(OH)$_2$
- All four hydroxides precipitate.

**pH = 8**

\[ Q_{ip} = \] ____________

- only Sn(OH)$_2$
- Sn(OH)$_2$ and Cu(OH)$_2$
- Sn(OH)$_2$, Cu(OH)$_2$, and Fe(OH)$_2$
- All four hydroxides precipitate.

8.3-3. Identifying Precipitating Chlorides Exercise

**EXERCISE 8.9:**
Identify any precipitates that result when 5.0 mL of 0.010 M HCl is added to 20. mL of a solution in which [Tl$^{1+}$] = 0.15 M and [Pb$^{2+}$] = 0.20 M. 

\[ K_{sp} \text{ of TlCl} = 1.9 \times 10^{-4} \]

\[ K_{sp} \text{ of PbCl}_2 = 1.7 \times 10^{-5} \]

Concentrations after mixing:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^{-}$</td>
<td>[ [\text{Cl}^{-}] = ] ____________ M</td>
</tr>
<tr>
<td>Tl$^{1+}$</td>
<td>[ [\text{Tl}^{1+}] = ] ____________ M</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>[ [\text{Pb}^{2+}] = ] ____________ M</td>
</tr>
</tbody>
</table>

The precipitate is ____________.

- TlCl
- PbCl$_2$

8.3-4. Determining a Required Concentration

Precipitation occurs when the ion-product exceeds the solubility product, so the concentration of one reactant that is required to initiate precipitation can be determined if the concentration of the other reactant and the $K_{sp}$ are known. To determine the minimum concentration required, we solve the $K_{sp}$ expression for the unknown concentration, which is the maximum concentration at which no precipitation occurs. Thus, the calculation indicates both the minimum concentration required for precipitation or the maximum concentration allowed with no precipitation.
8.3-5. Determining pH at which Precipitate Forms Exercise

**EXERCISE 8.10:**

At what pH does Mg(OH)\(_2\) (\(K_{sp} = 1.8 \times 10^{-11}\)) begin to precipitate from a solution that is 0.01 \(M\) in Mg\(^{2+}\)?

Use the given Mg\(^{2+}\) concentration to determine the hydroxide ion concentration at which \(Q_{sp} = K_{sp}\).

\[
[OH^-] = \text{__________} M
\]

Convert the hydroxide ion concentration into a pOH.

\[
pOH = \text{__________}
\]

Convert the pOH into a pH.

\[
pH = \text{__________}
\]

8.3-6. Separations

Chemists frequently need to separate a mixture into its components. In the case of aqueous mixtures of ions, this can often be accomplished by selectively precipitating the ions from the solution. We demonstrate the method by separating Sn\(^{2+}\) and Mg\(^{2+}\) ions from a solution by selectively precipitating the less soluble hydroxide by adjusting the pH to a value that results in the precipitation of only one ion.

The \(K_{sp}\) of Sn(OH)\(_2\) is much less than that of Mg(OH)\(_2\), so we will choose to precipitate Sn(OH)\(_2\) and leave Mg\(^{2+}\) ions in solution. We could determine the pH at which Sn(OH)\(_2\) begins to precipitate, and adjust the pH to a slightly higher value to precipitate Sn(OH)\(_2\). However, Sn\(^{2+}\) ions will remain in solution with the following concentration:

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

In an optimum separation, the remaining Sn\(^{2+}\) concentration in solution should be at a minimum. To minimize the Sn\(^{2+}\) concentration, the hydroxide ion concentration should be as high as possible without precipitating any Mg\(^{2+}\) ions. Thus, we determine the hydroxide ion concentration at which Mg(OH)\(_2\) begins to precipitate and adjust the pH of the solution to just below that value. See the example in Exercise 8.11.

8.3-7. Optimum Separation Exercise

**EXERCISE 8.11:**

A solution is 0.010 \(M\) each in Sn\(^{2+}\) and Fe\(^{2+}\). At what pH would optimum separation be achieved?

\(K_{sp} = 8.0e-16\) for Fe(OH)\(_2\) and \(1.4e-28\) for Sn(OH)\(_2\).

Which metal ion should be precipitated? Which of the following would be the best pH to use for the separation?

- Sn\(^{2+}\)  
- Fe\(^{2+}\)  

6  
7  
8  
9  
10  
11
What are the concentrations of the metal ions in solution after precipitation?

\[ [\text{Fe}^{2+}] = \text{M} \quad \text{[Sn}^{2+}] = \text{M} \]

Note that the precipitated hydroxide could be redissolved in an acidic solution, so the solution of two metal ions could be separated into two solutions that each contain only one metal ion.

8.3-8. Reaction Table Exercise

**EXERCISE: 8.12**

Determine the mass of \( \text{Ag}_2\text{CrO}_4 \) \((K_{sp} = 1.1 \times 10^{-12}, M_m = 331.7 \text{ g/mol})\) that is formed and the concentrations of \( \text{Ag}^{1+} \) and \( \text{CrO}_4^{2-} \) in the resulting solution when 50. mL of 0.10 \( M \) \( \text{K}_2\text{CrO}_4 \) and 50. mL of 0.10 \( M \) \( \text{AgNO}_3 \) are mixed.

The equilibrium constant for the precipitation is \( \sim 1 \times 10^{12} \) (the reciprocal of \( K_{sp} \) because the reaction is the reverse of the dissociation reaction), so essentially all of the limiting reactant disappears.

Fill in the reaction table in millimoles.

<table>
<thead>
<tr>
<th></th>
<th>2 ( \text{Ag}^{1+} )</th>
<th>+</th>
<th>( \text{CrO}_4^{2-} )</th>
<th>⇒</th>
<th>( \text{Ag}_2\text{CrO}_4(s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

mass (in grams) of \( \text{Ag}_2\text{CrO}_4 \) that precipitates = \( \text{g} \)

\[ [\text{CrO}_4^{2-}] = \text{M} \]

The stoichiometry of Chapter 1 can be used for all entries except the limiting reactant because the limiting reactant concentration cannot be zero if the \( K_{sp} \) is to be satisfied. Finding the concentration of the limiting reactant is the same as finding the solubility of the salt in the presence of a common ion (the excess reactant). Use the \( K_{sp} \) expression and the \([\text{CrO}_4^{2-}]\) determined above to find the limiting reactant concentration, which will be small but not zero.

\[ [\text{Ag}^{1+}] = \text{M} \]
EXERCISE 8.13:
What is the concentration of lead ions in a solution formed by mixing 24 mL of 0.10 \( M \) \( \text{Pb(NO}_3\text{)}_2 \) and 50. mL of 0.12 \( M \) \( \text{KF} \)?

Be sure to include coefficients with the substances in the balanced equation.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pb(NO}_3\text{)}_2 )</td>
<td>( \text{KF} )</td>
<td>( \text{Pb}^{2+} )</td>
</tr>
</tbody>
</table>

\[ [\text{F}^-] = \frac{\text{initial}}{\text{equilibrium}} \ M \]
\[ [\text{Pb}^{2+}] = \frac{\text{initial}}{\text{equilibrium}} \ M \]

8.4 Complex Ions

Introduction

Complex ions are ions in which a central metal ion is surrounded by molecular or anionic ligands. For example, the \([\text{Fe(H}_2\text{O)}_6]^3+\) ion discussed in Section 8.1 is a complex ion. The ligands and the metal are in equilibrium in much the same way that the protons and anion of a polyprotic acid are in equilibrium. That is, there is a series of equilibria in which the ligands are added or removed one at a time. However, in our treatment of complex-ion equilibria, we will consider only the overall process in which all of the ligands are added or removed in one step.

Objectives

- Write the formation reaction for a given complex ion.
- Write the formation constant expression for a given complex ion.

8.4-1. The Formation and Dissociation Constants

The equilibrium constant governing the one-step formation of a complex ion from its metal ion and ligands is called the formation constant, \( K_f \). Table 8.3 contains the formation constants at 25 °C for some common complex ions.

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>( K_f )</th>
<th>( K_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ag(NH}_3\text{)}_2^{1+} )</td>
<td>1.7e07</td>
<td>5.9e−08</td>
</tr>
<tr>
<td>( \text{Ag(CN)}_2^{1−} )</td>
<td>3.0e20</td>
<td>3.3e−21</td>
</tr>
<tr>
<td>( \text{Cu(NH}_3\text{)}_4^{2+} )</td>
<td>4.8e12</td>
<td>2.1e−13</td>
</tr>
<tr>
<td>( \text{Fe(CN)}_6^{4−} )</td>
<td>1.0e35</td>
<td>1.0e−35</td>
</tr>
<tr>
<td>( \text{Fe(CN)}_6^{3−} )</td>
<td>1.0e42</td>
<td>1.0e−42</td>
</tr>
<tr>
<td>( \text{Ni(NH}_3\text{)}_6^{2+} )</td>
<td>5.6e08</td>
<td>1.8e−09</td>
</tr>
<tr>
<td>( \text{Zn(OH)}_2^{2−} )</td>
<td>2.8e15</td>
<td>3.6e−16</td>
</tr>
</tbody>
</table>

Table 8.3: Formation and Dissociation Constants at 25 °C

As an example, consider formation of the complex ion \( \text{Ag(NH}_3\text{)}_2^{1+} \).
\[
\text{Ag}^{1+} + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^{1+}
\]

The equilibrium constant for the reaction is the formation constant of the \( \text{Ag(NH}_3)_2^{1+} \) ion.

\[
K_f = \frac{[\text{Ag(NH}_3)_2^{1+}]}{[\text{Ag}^{1+}][\text{NH}_3]^2} = 1.7 \times 10^7
\]

Biochemists prefer the reverse of the formation reaction, so the **dissociation constant**, \( K_d \), is also common. However, the \( K_d \) of an ion is merely the reciprocal of its \( K_f \). Table 8.3 shows both the dissociation and formation constants of selected complex ions.

**8.4-2. Exercise**

**EXERCISE 8.14:**

What is the concentration of free \( \text{Cu}^{2+} \) in a 0.26 \( M \) solution of \( \text{Cu(NH}_3)_4^{2+} \) \( (K_d = 2.1 \times 10^{-13}) \)?

Use \( x \) for the amount of \( \text{Cu(NH}_3)_4^{2+} \) that reacts and determine the equilibrium line for the reaction table.

<table>
<thead>
<tr>
<th></th>
<th>( \text{Cu(NH}_3)_4^{2+} )</th>
<th>( \text{Cu}^{2+} )</th>
<th>+</th>
<th>( 4\text{NH}_3 )</th>
<th>( M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Assume that \( x \) is negligible compared to the initial concentration of \( \text{Cu(NH}_3)_4^{2+} \) to set up the equilibrium constant expression and solve for \( x \) ([\( \text{Cu}^{2+} \)]).

\[ [\text{Cu}^{2+}] = \ \text{M} \]

**8.4-3. Separations with Sulfide Ion**

Metal sulfides are very insoluble, so many metals can be separated by adjusting the sulfide ion concentration in solution. Recall from Section 7.4 that the two \( K_a \) equilibria of \( \text{H}_2\text{S} \) can be combined to eliminate \( \text{HS}^{-} \) ion as follows:

\[
\text{H}_2\text{S} + 2\text{H}_2\text{O} \rightleftharpoons \text{S}^{2-} + 2\text{H}_3\text{O}^{1+} \quad K_{12} = \frac{[\text{S}^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_2\text{S}]} = K_1 K_2 = 1.3 \times 10^{-20}
\]

If \( [\text{H}_2\text{S}] \) is known, \( K_{12} \) allows us to determine the pH required for a given \( [\text{S}^{2-}] \) or to determine \( [\text{S}^{2-}] \) from a given pH. \( \text{H}_2\text{S} \) is a gas, and its solubility in water at 25 °C is 0.10 \( M \); thus, a solution with a desired sulfide ion concentration can be prepared by buffering a solution to a predetermined pH and then saturating it with \( \text{H}_2\text{S} \). Both \( [\text{H}_2\text{S}] \) and pH are known, so the sulfide ion concentration can be determined. However, as was also shown in Section 7.4, above pH = 5, the \( \text{H}_2\text{S} \) concentration can no longer be assumed to be 0.10 \( M \) because the \( \text{HS}^{-} \) concentration can no longer be ignored.
8.4-4. Sulfide Separation Exercise

EXERCISE 8.15:
To what pH should a solution that is 0.010 M in each Fe$^{2+}$ and Mn$^{2+}$ be saturated with H$_2$S to achieve an optimum separation of ions?

- $K_{sp}(\text{MnS}) = 5.6 \times 10^{-16}$
- $K_{sp}(\text{FeS}) = 6.3 \times 10^{-18}$

The optimum separation is accomplished at the highest pH that does not precipitate the more soluble sulfide, so first determine the highest [S$^{2-}$] allowed without precipitating the more soluble sulfide.

$[S^{2-}] = \text{___________ M}$

Use the $K_{12}$ expression in the previous section to determine the [H$_3$O$^{+}$] required to deliver the above sulfide ion concentration.

$[\text{H}_3\text{O}^+] = \text{___________ M}$

The optimum separation pH to the nearest 0.1 pH units is

pH = \text{___________}

Assume the pH is adjusted to exactly the above pH; i.e., if the above answer is 4.2, assume a pH of 4.20 and calculate the ion concentrations at this pH.

$[S^{2-}] = \text{___________ M}$ \hspace{1cm} $[\text{Mn}^{2+}] = \text{___________ M}$ \hspace{1cm} $[\text{Fe}^{2+}] = \text{___________ M}$

Is this a good separation?
Yes \hspace{1cm} No

8.5 Competing or Simultaneous Equilibria

Introduction
As we have seen, metal ions can be involved in acid-base, solubility, and complex ion equilibria. Thus, several components of a solution containing a metal ion may compete with one another for the metal ion. These competing or simultaneous equilibria are the topic of this section.

Objectives
- Calculate the solubility of a slightly soluble salt in the presence of a substance that forms a complex ion with the metal.
- Write the reaction for the dissociation of a basic salt in acid.
- Determine the equilibrium constant for the dissociation of a basic salt in acid.

8.5-1. Silver Chloride Dissolves in Ammonia

Ag$^{1+}$ ions react with both chloride ions and ammonia molecules, so two competing equilibria are established when AgCl is placed in an aqueous solution of NH$_3$ as both NH$_3$ and Cl$^{-}$ compete for Ag$^{1+}$.

AgCl(s) $\rightleftharpoons$ Ag$^{1+}$ + Cl$^{-}$ \hspace{1cm} $K_{sp} = 1.8 \times 10^{-10}$ \hspace{1cm} (Reaction 1)

Ag$^{1+}$ + 2 NH$_3$ $\rightleftharpoons$ Ag(NH$_3$)$_2$$^{1+}$ \hspace{1cm} $K_f = 1.7 \times 10^7$ \hspace{1cm} (Reaction 2)
To determine how much AgCl would dissolve in NH\(_3\), we add *Reaction 1* and *Reaction 2* to obtain *Reaction 3*, which represents the dissolution of AgCl in NH\(_3\). The equilibrium constant for the reaction would then be the product of the equilibrium constants of the summed chemical equations.

\[
2 \text{NH}_3 + \text{AgCl}(s) \rightleftharpoons \text{Ag(NH}_3)_2^{1+} + \text{Cl}^{1-} \quad \text{(Reaction 3)}
\]

\[
K = K_{sp}K_f = (1.8 \times 10^{-10})(1.7 \times 10^7) = 3.1 \times 10^{-3}
\]

\[
k = 3.1 \times 10^{-3} = \frac{[\text{Ag(NH}_3)_2^{1+}][\text{Cl}^{1-}]}{[\text{NH}_3]^2}
\]

*Reaction 1* describes the solubility of AgCl in water, while *Reaction 3* describes its solubility in aqueous NH\(_3\). We examine the solubility of AgCl in NH\(_3\) in the following exercise.

### 8.5-2. AgCl in NH\(_3\) Exercise

**EXERCISE 8.16:**

What is the solubility of AgCl in 1.0 M NH\(_3\)?

Use \(x\) as the solubility of AgCl (\(x\) mol/L of AgCl dissolve) to fill in the reaction table. Note that AgCl is a solid, so there are no entries under it. \((K = 3.1 \times 10^{-3} \text{ for the reaction below.})\)

<table>
<thead>
<tr>
<th></th>
<th>2 \text{NH}_3</th>
<th>+</th>
<th>\text{AgCl}(s)</th>
<th>⇌</th>
<th>\text{Ag(NH}_3)_2^{1+}</th>
<th>+</th>
<th>\text{Cl}^{1-}</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Set up the equilibrium constant expression using the equilibrium line entries. Take the square root of both sides and solve for \(x\), the molar solubility.

\[
\text{solubility of AgCl} = \rule{1in}{0.15cm} \text{M}
\]

### 8.5-3. Acids and Bases Dissolve One Another

The solubility of AgCl is \(4 \times 10^3\) times greater in 1 M ammonia than in water. In fact, it is a general principle that an insoluble salt can be dissolved by placing it into a solution of a Lewis base (OH\(^{-}\), CN\(^{-}\), or NH\(_3\)) with which the metal forms a complex ion. However, the metal goes into solution predominantly as the complex ion, not as the free metal ion. Dissolving an insoluble salt by forming a complex ion is a Lewis acid-base reaction. Ag\(^{1+}\) is a Lewis acid and Cl\(^{-}\) and NH\(_3\) are bases that can compete for the Lewis acid. In cases where the anion is a weak base, the insoluble salt can be dissolved by placing it in strong acid. For example, CN\(^{-}\) is a base and Ag\(^{1+}\) and H\(_3\)O\(^{1+}\) are acids that can compete for the base. An example of this type is considered in the following exercise.

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EXERCISE 8.17:

F\(^{1-}\) ion is a weak base that can react with acids. In this exercise, we use the solubility of CaF\(_2\) in a strong acid to examine the competition between H\(_3\)O\(^{1+}\) and Ca\(^{2+}\) for the F\(^{1-}\) ion.

What is the equilibrium constant for the dissociation of CaF\(_2\) in strong acid?

\[
\text{CaF}_2(s) + 2 \text{H}_3\text{O}^{1+} \rightleftharpoons \text{Ca}^{2+} + 2 \text{HF} + 2 \text{H}_2\text{O}
\]

1. The chemical equation for the \(K_{sp}\) of CaF\(_2\) is the following.

\[
\text{CaF}_2 \rightleftharpoons \underbrace{+} \text{Ca}^{2+} + \underbrace{-}\text{HF} + \underbrace{+}\text{H}_2\text{O}
\]

2. By what number should the above be multiplied? Use a negative sign to indicate that the direction of the reaction must be reversed from the defined direction.

multiply CaF\(_2\) dissociation by ____________

3. The equilibrium constant for the reaction produced in Step 2: \(K = \) ____________

4. The chemical equation for the \(K_a\) of HF is the following.

\[
\underbrace{+} \text{HF} \rightleftharpoons \underbrace{-}\text{H}_2\text{O} + \underbrace{+}\text{F}^{1-}
\]

5. By what number should the above be multiplied? Use a negative sign to indicate that the direction of the reaction must be reversed from the defined direction.

multiply HF dissociation by ____________

6. The equilibrium constant for the reaction produced in Step 5:

\(K = \) ____________

7. The equilibrium constant for dissolving CaF\(_2\) in acid:

\(K = \) ____________
8.5-5. Solubility of Ag$_3$PO$_4$

**EXERCISE 8.18:**

In Section 8.2-5., we saw that the solubility of Ag$_3$PO$_4$ in water was over eight times greater than that determined with $K_{sp}$ due to a competition between Ag$^{1+}$ and H$_2$O for PO$_4^{3-}$. We now revisit that solubility as a competing equilibria problem. We assume that the equilibrium can be determined with the following:

$$\text{Ag}_3\text{PO}_4(s) \rightleftharpoons 3 \text{Ag}^{1+} + \text{PO}_4^{3-} \quad K_{sp} = 2.6 \times 10^{-18}$$

$$\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^{1-} \quad K_b = 0.021$$

Assume that the reaction is Ag$_3$PO$_4(s)$ + H$_2$O $\rightleftharpoons$ 3 Ag$^{1+}$ + HPO$_4^{2-}$ + OH$^{1-}$ and determine the equilibrium constant for the solubility:

\[ K = \ldots \]

If the pH of a saturated solution is 9.00, what is the solubility of Ag$_3$PO$_4$? As shown in Figure 7.3, all phosphate is in the form of HPO$_4^{2-}$ at pH = 9.00.

\[ \text{solubility} = \ldots \]

The observed solubility is $1.5 \times 10^{-4}$ M, but that determined with $K_{sp}$ alone is $1.8 \times 10^{-5}$ M. Thus, it is competing equilibria like this that lead to such poor agreement between predicted and experimental solubilities for salts of relatively strong bases when only $K_{sp}$ is used in the calculations.

**8.6 Exercises and Solutions**

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.