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.

$Fe(NO_3)_3$ is a strong electrolyte that dissociates completely into Fe^{3+} and NO_3^{1-} ions. The small, highly charged iron(III) ion interacts with the surrounding water molecules in a Lewis acid-base reaction to produce $Fe(H_2O)_6^{3+}$, the octahedral ion in Figure 8.1. Ions, such as $Fe(H_2O)_6^{3+}$, 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.
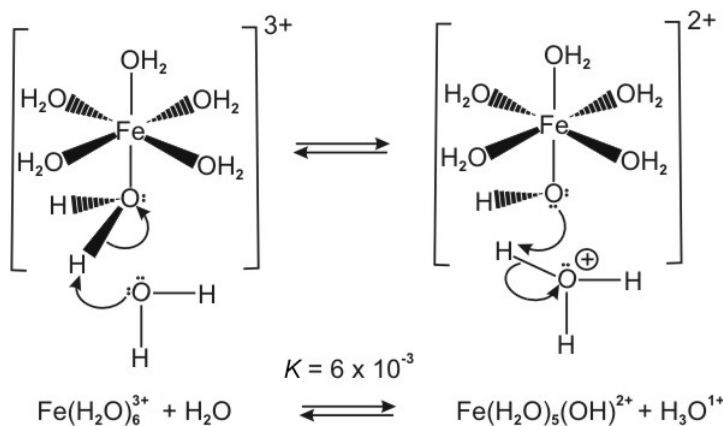

Figure 8.1: Acidity of Metal Ions

Thus, the acidity of Fe^{3+} ions arises from the following reaction:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^{1+} \qquad K = 6e{-}03$$

which is the reaction of a weak acid with water, so the equilibrium constant is the K_a of the weak acid $Fe(H_2O)_6^{3+}$. Note that $Fe(H_2O)_6^{3+}$ is a stronger acid than acetic acid ($K_a = 1.8e{-}05$). The K_a values of several hydrated metal ions are listed in the table.

| Hydrated Metal Ion	K_a
$Fe(H_2O)_6^{3+}$	6e−03
$Al(H_2O)_6^{3+}$	1e−05
$Cu(H_2O)_6^{2+}$	3e−08
$Zn(H_2O)_6^{2+}$	1e−09
$Ni(H_2O)_6^{2+}$	1e−10

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:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K = [Ca^{2+}][CO_3^{2-}]$$
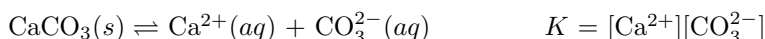
This type of process, the equilibrium between a solid and its ions in solution, is an important one and forms the topic of this section.

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: $AgCl \rightleftharpoons Ag^{1+} + Cl^{1-}$. The activity of the solid is unity, so the form of the equilibrium constant, K_{sp}, for the reaction is $K_{sp} = [Ag^{1+}][Cl^{1-}]$. 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 CO_3^{2-} and PO_4^{3-}. Consequently, our discussions of solubility in water centers on the solubility of neutral or only weakly basic anions, such as Cl^{1-} and SO_4^{2-}. The reaction table for the dissociation of Ag_2SO_4 in water has the following form:

	$Ag_2SO_4(s)$	$\rightleftharpoons$	$2\ Ag^{1+}$	$+$	SO_4^{2-}	$K_{sp} = 1.4 \times 10^{-5}$
initial	enough		0		0	M
Δ			$+2x$		$+x$	M
equilibrium	some		$2x$		x	M

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

$$K_{\text{sp}} = 1.4 \times 10^{-5} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}] = (2x)^2(x) = 4x^3$$

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.

$$x = \sqrt[3]{\frac{K_{\text{sp}}}{4}} = [\text{SO}_4^{2-}] = \frac{1}{2}[\text{Ag}^{1+}]$$

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

- molar solubility of silver sulfate; $x = 0.015\ M$
- $[\text{SO}_4{}^{2-}] = x = 0.015\ M$
- $[\text{Ag}^{1+}] = 2x = 0.030\ M$

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

$$K_{\text{sp}} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}] = (0.030)^2(0.015) = 1.4e{-}05$$

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

$[\text{Mg}^{2+}]$ = —————————— M $\qquad$ $[\text{F}^{1-}]$ = —————————— M $\qquad$ 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!

$[\text{OH}^{1-}]$ = —————————— M $\qquad$ $[\text{Fe}^{2+}]$ = —————————— M $\qquad$ 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; $K_{\text{sp}} = 2.6 \times 10^{-18}$.

The reaction table for the dissolution has the following form:

$$\mathbf{Ag_3PO_4}(s) \quad \rightleftharpoons \quad \mathbf{3\ Ag^{1+}} \quad + \quad \mathbf{PO_4^{3-}}$$

	$\mathbf{Ag_3PO_4}(s)$	$\mathbf{3\ Ag^{1+}}$	$\mathbf{PO_4^{3-}}$
initial	enough	0	0
Δ		$+3x$	$+x$
equilibrium	some	$3x$	x

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

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

However, the measured solubility is 1.5×10^{-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 OH^{1-}. Therefore, $K_{\text{sp}} = [\text{Ag}^{1+}]^3[\text{PO}_4^{3-}]$ 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 Ag_3PO_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.

Cation:Anion Ratio	K_{sp}
1:1	x^2
1:2 or 2:1	$4x^3$
1:3 or 3:1	$27x^4$
2:3 or 3:2	$108x^5$

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.

PbCl$_2$	$K_{\text{sp}} = 1.7\text{e}{-}5$
AgCl	$K_{\text{sp}} = 1.2\text{e}{-}10$
TlCl	$K_{\text{sp}} = 1.9\text{e}{-}4$

Least soluble salt:
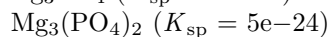   PbCl$_2$
   AgCl
   TlCl
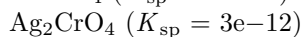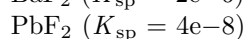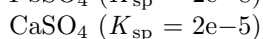
Intermediate salt:
   PbCl$_2$
   AgCl
   TlCl

Most soluble salt:
   PbCl$_2$
   AgCl
   TlCl

8.2-8. Predicting the More Soluble Salt Exercise
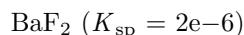
8.2-9. Common-Ion Effect

Consider the dissolution of $Ag_2SO_4(s)$ in 1.0 M Na_2SO_4.

	$\mathbf{Ag_2SO_4(s)}$	$\rightleftharpoons$	$\mathbf{2\ Ag^{1+}}$	$+$	$\mathbf{SO_4^{2-}}$	$\mathbf{K_{sp} = 1.4 \times 10^{-5}}$
initial	enough		0		1.0	M
Δ			$+2x$		$+x$	M
equilibrium	some		$2x$		$0.10 + x$	M

$$K_{sp} = [Ag^{1+}]^2[SO_4^{2-}] = (2x)^2(1.0 + x)$$

which would involve solving a cubic equation. However, in the beginning of this section, we determined that the solubility of Ag_2SO_4 in water was 0.015 M, and the presence of the common ion (sulfate) will decrease the dissociation, so $x < 0.015$ M. 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_2SO_4 due to the presence of the common ion.

8.2-10. Common-Ion Solubility from pH Exercise

8.2-11. Solubility of AgCl Exercise

EXERCISE 8.7:

$K_{sp} = 1.8e{-}10$ for AgCl. Determine the solubility of AgCl in the following:

water   0.10 M NaCl

     solubility = _____ M solubility = _____ M

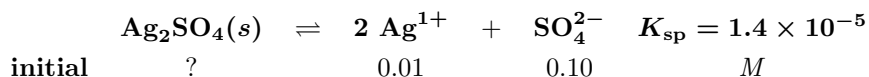# 8.3 Precipitation and Separation of Ions

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 $Ag_2SO_4(s)$ suspended in a solution that is 0.01 M in Ag^{1+} and 0.10 M in $[SO_4{}^{2-}]$. 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.

$$\mathbf{Ag_2SO_4(s)} \quad \rightleftharpoons \quad \mathbf{2\ Ag^{1+}} \quad + \quad \mathbf{SO_4^{2-}} \quad \mathbf{K_{sp} = 1.4 \times 10^{-5}}$$

$$\text{initial} \qquad ? \qquad\qquad 0.01 \qquad\quad 0.10 \qquad\qquad M$$

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 **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, $Q_{ip} = [Ag^{1+}]^2[SO_4^{1-}] = (0.01)^2(0.10) = 1 \times 10^{-5}$ 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.

$$K_{sp} \text{ of TlCl} = 1.9e{-}4$$

$$K_{sp} \text{ of } PbCl_2 = 1.7e{-}5$$

Concentrations after mixing:

$[Cl^{1-}] = $ _____ M

$[Tl^{1+}] = $ _____ M

$[Pb^{2+}] = $ _____ M

Ion-products:

TlCl: _____

$PbCl_2$:   _____

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 $Q_{ip} = K_{sp}$.

$[OH^{1-}] =$ _____ M

Convert the hydroxide ion concentration into a pOH.

$pOH =$ _____

Convert the pOH into a pH.

$pH =$ _____

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 that 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:

$$[Sn^{2+}] = \frac{K_{sp}}{[OH^{1-}]^2}$$

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?
    Sn^{2+}
    Fe^{2+}

Which of the following would be the best pH to use for the separation?
    6
    7
    8
    9
    10
    11

What are the concentrations of the metal ions in solution after precipitation?

$[Fe^{2+}] = $ _____ M $\qquad\qquad\qquad$ $[Sn^{2+}] = $ _____ 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 Ag_2CrO_4 ($K_{sp} = 1.1e{-}12$, $M_m = 331.7$ g/mol) that is formed and the concentrations of Ag^{1+} and $CrO_4{}^{2-}$ in the resulting solution when 50. mL of 0.10 M K_2CrO_4 and 50. mL of 0.10 M $AgNO_3$ are mixed.

The equilibrium constant for the precipitation is $\sim$1e+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.

	2 Ag^{1+}	+	$CrO_4{}^{2-}$	⇌	$Ag_2CrO_4(s)$	
initial						mmol
Δ						mmol
equilibrium						mmol

mass (in grams) of Ag_2CrO_4 that precipitates = _____ g

$[CrO_4{}^{2-}] = $ _____ 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 $[CrO_4{}^{2-}]$ determined above to find the limiting reactant concentration, which will be small but not zero.

$[Ag^{1+}] = $ _____ M

8.3-9. Reaction Table Exercise

EXERCISE 8.13:

What is the concentration of lead ions in a solution formed by mixing 24 mL of 0.10 M $Pb(NO_3)_2$ and 50. mL of 0.12 M KF?

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

	Cation		Anion		Product	
		+		→		
initial						mmol
Δ						mmol
equilibrium						mmol

$[F^{1-}] =$ _____ M $\qquad\qquad$ $[Pb^{2+}] =$ _____ 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 $[Fe(H_2O)_6]^{3+}$ 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.
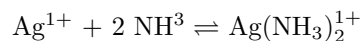
8.4-1. The Formation and Dissociation Constants

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.

Complex Ion	K_f	K_d
$Ag(NH_3)_2^{1+}$	1.7e07	5.9e−08
$Ag(CN)_2^{1-}$	3.0e20	3.3e−21
$Cu(NH_3)_4^{2+}$	4.8e12	2.1e−13
$Fe(CN)_6^{4-}$	1.0e35	1.0e−35
$Fe(CN)_6^{3-}$	1.0e42	1.0e−42
$Ni(NH_3)_6^{2+}$	5.6e08	1.8e−09
$Zn(OH)_4^{2-}$	2.8e15	3.6e−16

Table 8.3: Formation and Dissociation Constants at 25 °C

As an example, consider formation of the complex ion $Ag(NH_3)_2^{1+}$.

$$Ag^{1+} + 2\,NH^3 \rightleftharpoons Ag(NH_3)_2^{1+}$$

The equilibrium constant for the reaction is the formation constant of the $Ag(NH_3)_2^{1+}$ ion.

$$K_f = \frac{[Ag(NH_3)_2^{1+}]}{[Ag^{1+}][NH_3]^2} = 1.7 \times 10^7$$

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

<u>**EXERCISE 8.14:**</u>

What is the concentration of free Cu^{2+} in a 0.26 M solution of $Cu(NH_3)_4^{2+}$ ($K_d = 2.1 \times 10^{-13}$)?

Use x for the amount of $Cu(NH_3)_4^{2+}$ that reacts and determine the equilibrium line for the reaction table.

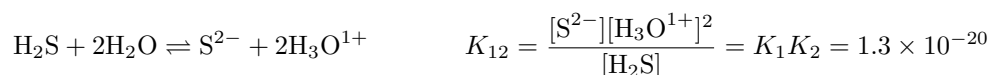|	$Cu(NH_3)_4^{2+}$	$\rightleftharpoons$	Cu^{2+}	+	$4NH_3$	
equilibrium						M

Assume that x is negligible compared to the initial concentration of $Cu(NH_3)_4^{2+}$ to set up the equilibrium constant expression and solve for x ($[Cu^{2+}]$).

$[Cu^{2+}] = $ ——————— 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 H_2S can be combined to eliminate HS^{1-} ion as follows:

$$H_2S + 2H_2O \rightleftharpoons S^{2-} + 2H_3O^{1+} \qquad K_{12} = \frac{[S^{2-}][H_3O^{1+}]^2}{[H_2S]} = K_1K_2 = 1.3 \times 10^{-20}$$

If $[H_2S]$ is known, K_{12} allows us to determine the pH required for a given $[S^{2-}]$ or to determine $[S^{2-}]$ from a given pH. H_2S 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 H_2S. Both $[H_2S]$ 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 H_2S concentration can no longer be assumed to be 0.10 M because the HS^{1-} 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_2S to achieve an optimum separation of ions?

- $K_{sp}(MnS) = 5.6e-16$
- $K_{sp}(FeS) = 6.3e-18$

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-}] = $ _____ M

Use the K_{12} expression in the previous section to determine the $[H_3O^{1+}]$ required to deliver the above sulfide ion concentration.

$[H_3O^{1+}] = $ _____ M

The optimum separation pH to the nearest 0.1 pH units is

pH = _____

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-}] = $ _____ M $[Mn^{2+}] = $ _____ M $[Fe^{2+}] = $ _____ M

Is this a good separation?

     Yes
     No

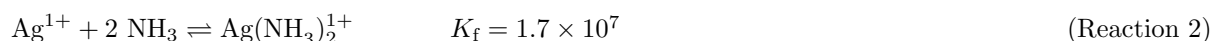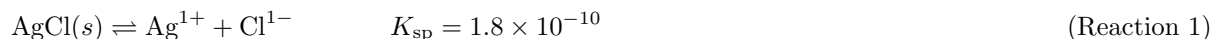# 8.5 Competing or Simultaneous Equilibria

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^{1-} compete for Ag^{1+}.

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

$$Ag^{1+} + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^{1+} \qquad K_f = 1.7 \times 10^7 \qquad \text{(Reaction 2)}$$

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.

$$2\,NH_3 + AgCl(s) \rightleftharpoons Ag(NH_3)_2^{1+} + Cl^{1-} \qquad \text{(Reaction 3)}$$

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

$$K = 3.1 \times 10^{-3} = \frac{[Ag(NH_3)_2^{1+}][Cl^{1-}]}{[NH_3]^2}$$

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. ($K = 3.1 \times 10^{-3}$ for the reaction below.)

	2 NH_3	+	AgCl(s)	$\rightleftharpoons$	$Ag(NH_3)_2^{1+}$	+	Cl^{1-}	
initial								M
Δ								M
equilibrium								M

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.

solubility of AgCl = _____ M

8.5-3. Acids and Bases Dissolve One Another

The solubility of AgCl is 4×10^3 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^{1-}, CN^{1-}, 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^{1-} 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^{1-} is a base and Ag^{1+} and H_3O^{1+} are acids that can compete for the base. An example of this type is considered in the following exercise.

8.5-4. Determining K Exercise

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_3O^{1+} and Ca^{2+} for the F^{1-} ion.

What is the equilibrium constant for the dissociation of CaF_2 in strong acid?

$$CaF_2(s) + 2\ H_3O^{1+} \rightleftharpoons Ca^{2+} + 2\ HF + 2\ H_2O$$
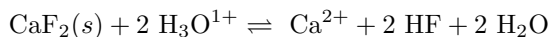
- K_{sp} for $CaF_2 = 3.9 \times 10^{-11}$
- K_a for HF $= 7.2 \times 10^{-4}$

1. The chemical equation for the K_{sp} of CaF_2 is the following.

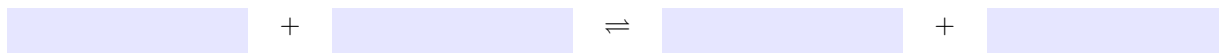   [   ] $\rightleftharpoons$ [   ] + [   ]

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.

   [   ] + [   ] $\rightleftharpoons$ [   ] + [   ]

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:

   $K =$ ———————
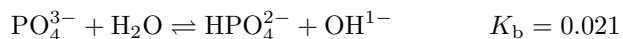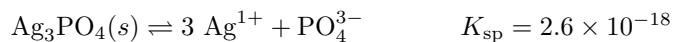
7. The equilibrium constant for dissolving CaF_2 in acid:

   $K =$ ———————

8.5-5. Solubility of Ag_3PO_4

<u>EXERCISE 8.18</u>:

In Section 8.2-5., we saw that the solubility of Ag_3PO_4 in water was over eight times greater than that determined with K_{sp} due to a competition between Ag^{1+} and H_2O 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:

$$Ag_3PO_4(s) \rightleftharpoons 3\ Ag^{1+} + PO_4^{3-} \qquad K_{sp} = 2.6 \times 10^{-18}$$

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^{1-} \qquad K_b = 0.021$$

Assume that the reaction is $Ag_3PO_4(s) + H_2O \rightleftharpoons 3\ Ag^{1+} + HPO_4^{2-} + OH^{1-}$ and determine the equilibrium constant for the solubility:

$K =$ _____

If the pH of a saturated solution is 9.00, what is the solubility of Ag_3PO_4? As shown in Figure 7.3, all phosphate is in the form of HPO_4^{2-} at pH = 9.00.

solubility = _____

The observed solubility is 1.5×10^{-4} M, but that determined with K_{sp} alone is 1.8×10^{-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.