CHAPTER 8

Equilibria Containing Metal Ions

8.0 INTRODUCTION

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

1. Acid-base equilibria: The ions are positively charged, which makes them Lewis acidic (they interact readily with lone pairs of electrons). Consequently, many metal ions react with water in a manner similar to that of weak acids as described in Chapter 6.
2. Complex ion equilibria: Ions formed by the interaction of several Lewis bases and a metal are called **complex ions**, and the Lewis bases that interact with the metal are referred to as **ligands**. The equilibrium between the complex ion and its metal and ligands is another consideration to be made in the treatment of aqueous solutions containing metal ions.
3. Solubility equilibria: Many metal ions form sparingly soluble salts. In fact, water hardness results from the presence of metal ions (Mg^{2+}, Ca^{2+}, and Fe^{2+}) that form insoluble salts. The insoluble salts formed with the fatty acids in soaps leave a residue on washed material and sinks, and those formed with the carbonate ion produce scale in boilers and hot water pipes.

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

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- explain the acidity of some metal ions;
- define dissolution and the K_{sp} expression;
- explain solubility in terms of K_{sp} values;
- apply the common-ion effect to the dissolution process;
- explain the effect of pH on the solubility of acids and bases;
- define the formation reaction and the formation constant for complex ions; and
- explain how complex ion formation and precipitation compete for metal ions.

8.1 ACID-BASE EQUILIBRIA

While metal ions rarely have protons to donate as required by the Brønsted acid definition, they can accept electron pairs to form covalent bonds, so they are Lewis acidic. Consider an aqueous solution of iron(III) nitrate, which is a strong electrolyte that dissociates completely into Fe^{3+} and NO_3^{1-} ions. The solution is acidic even though it contains no protons because 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 shown 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 of the water ligands, which weakens them and makes the water ligands stronger acids. Thus, $Fe(H_2O)_6^{3+}$ is a Brønsted acid. The reaction of a hydrated Fe^{3+} ion with water is depicted below and in Figure 8.1.

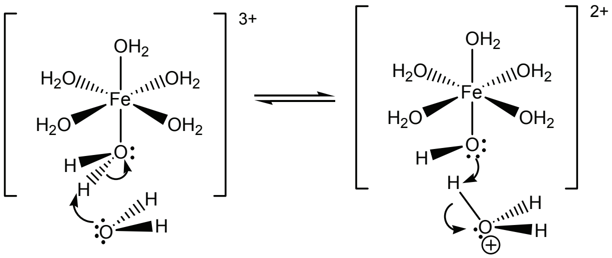

Figure 8.1 Acidity of aqueous Fe^{3+}

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^{1+}$$

The above reaction is the acid dissociation reaction of the weak acid $Fe(H_2O)_6^{3+}$, which has the following K_a:

$$K_a = \frac{[Fe(H_2O)_5(OH)^{2+}][H_3O^{1+}]}{[Fe(H_2O)_6^{3+}]} = 6\times10^{-3}$$

Note that the K_a of $Fe(H_2O)_6^{3+}$ is greater than that of acetic acid ($K_a = 1.8x10^{-5}$), so $Fe(H_2O)_6^{3+}$ is a stronger Brønsted acid than is acetic acid. To summarize, *hydrated metal ions are Brønsted acids because the positive charge on the metal ion removes electron density from the O-H bonds of the water ligands, which weakens the bonds and facilitates the loss of a proton*. The K_a values of several hydrated metal ions are listed in Table 8.1.

Table 8.1 K_a values of selected hydrated metal ions

Ion	K_a
$Fe(H_2O)_6^{3+}$	$6x10^{-3}$
$Al(H_2O)_6^{3+}$	$1x10^{-5}$
$Cu(H_2O)_6^{2+}$	$3x10^{-8}$
$Zn(H_2O)_6^{2+}$	$1x10^{-9}$
$Ni(H_2O)_6^{2+}$	$1x10^{-10}$

8.2 DISSOLUTION AND THE SOLUBILITY-PRODUCT CONSTANT

The process in which a solid dissolves is called **dissolution**, while the process in which it is formed from solution is called **precipitation**. When the rate of dissolution of an ionic solid equals its rate of precipitation, equilibrium between the solid and its ions in solution is established. This type of equilibrium is so common that its equilibrium constant is given a special name and symbol: the **solubility-product constant**, $\mathbf{K_{sp}}$. For example, consider calcium carbonate (limestone), a slightly soluble salt that is responsible for scale in containers of hard water. Its dissolution and subsequent precipitation is also responsible for formation of caves and the stalactites and stalagmites in them.

$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$ $\qquad$ $K_{sp} = [Ca^{2+}][CO_3^{2-}]$[*]

Note that K_{sp} is simply the equilibrium constant for a particular reaction type. Recall that *the activity of a solid is unity, so the solid does not appear in the K_{sp} expression.*

Most slightly soluble salts contain basic anions, which are involved in both acid-base equilibria with water and dissolution equilibria with metal ions, which can lead to a complicated set of equilibria in the case of fairly strong bases such as CO_3^{2-}. Thus, in an aqueous solution of $CaCO_3$, not only must its K_{sp} be obeyed, but so too must the K_b of the CO_3^{2-} ion. Consequently, our discussions of solubility in water will center on the solubility of neutral or only weakly basic salts such as those of the halides and sulfates. Consider the reaction table for the dissolution of Ag_2SO_4 in water.

	$Ag_2SO_4(s)$	$\rightleftharpoons$	$2Ag^{1+}$	+	SO_4^{2-}
initial	enough		0		0
Δ	-x		+2x		+x
eq	some		2x		x

x is the **molar solubility** of Ag_2SO_4 in water. The solid does not enter into the equilibrium expression, so the amount of solid remaining at equilibrium is not important, but there must be *enough* initially to assure that *some* solid is present at equilibrium. In a saturated solution of Ag_2SO_4,

$$[Ag^{1+}] = 2x \text{ and } [SO_4^{2-}] = x$$

Substituting the ion concentrations in terms of the molar solubility of Ag_2SO_4 into the K_{sp} expression, we obtain the following:

$$K_{sp} = [Ag^{1+}]^2[SO_4^{2-}] = (2x)^2(x) = 4x^3$$

$K_{sp} = 4x^3$ is the form of the solubility-product constant in terms of the molar solubility for any salt in which the cation:anion ratio is 2:1 or 1:2 (*i.e.*, any salt with the general formula M_2X or MX_2). Thus, the solubility-product constant of a compound can be determined from the molar solubility. Conversely, the molar solubility of a salt can be determined from its K_{sp} *if the acid-base reactions between the anion and water can be neglected.*[†] The molar solubility is obtained by solving the K_{sp} expression for x.

$$x = \sqrt[3]{\frac{K_{sp}}{4}}$$

Example 8.1 and Practice Example 8.1 are examples of using solubility to find K_{sp}, and Example 8.2 demonstrates using of K_{sp} to determine solubility.

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[*] Note that there is no denominator in the K_{sp} expression, so it is simply the product of the ion concentrations, which is the reason it is called the solubility product.

[†] The solubility of a basic salt, one that reacts strongly with water, is discussed in Example 8.2.

Example 8.1

What is the K_{sp} of MgF_2 if its solubility is 7.6 mg in 100. mL of H_2O?

First, construct the reaction table for the dissolution:

	$MgF_2(s)$	$\rightleftharpoons$	Mg^{2+}	+	$2F^{1-}$
Initial	**enough**		**0**		**0**
Δ	**-x**		**+x**		**+2x**
Eq	**some**		**x**		**2x**

$K_{sp} = [Mg^{2+}][F^{1-}]^2$

At equilibrium, $[Mg^{2+}] = x$ and $[F^{1-}] = 2x$. Substitution of these ion concentrations into the K_{sp} expression yields

$$K_{sp} = [Mg^{2+}][F^{1-}]^2 = (x)(2x)^2 = 4x^3$$

The above expression relates the solubility-product constant of any salt with a cation:anion ratio of 1:2 or 2:1 (MX_2 or M_2X) to its molar solubility. Next, we must determine the molar solubility from the given solubility. We begin by determining the number of moles of MgF_2 that dissolve in 100 mL. $M_m = 62.3$ mg·mmol^{-1} for MgF_2.

$$7.6\text{ mg}\times\frac{1\text{ mmol}}{62.3\text{ mg}} = 0.12\text{ mmol MgF}_2$$

The molar solubility is then determined to be

$$x = [Mg^{2+}] = \frac{0.12\text{ mmol MgF}_2}{100\text{ mL}} = 1.2\times10^{-3}\text{ M}$$

The molar solubility can then be used directly in the K_{sp} expression in terms of x,

$$K_{sp} = 4x^3 = 4(1.2\times10^{-3})^3 = 7.3\times10^{-9}$$

or it can be used to determine the concentrations of the ions,

$$[Mg^{2+}] = x = 1.2\text{x}10^{-3};\quad [F^{1-}] = 2x = 2.4\text{x}10^{-3},$$

which can then be substituted into the original K_{sp} expression

$$K_{sp} = [Mg^{2+}][F^{1-}]^2 = (1.2\text{x}10^{-3})(2.4\text{x}10^{-3})^2 = 7.3\text{x}10^{-9}$$

The two methods are identical. The steps of the second method are simply merged into one step in the first procedure. Also note that the full calculator result for x ($1.2199\text{x}10^{-3}$), not the rounded result, was used in the calculation to reduce rounding errors in the answer (Appendix A.4). If the rounded result is used, the answer is $6.9\text{x}10^{-9}$.

The solubility-product constants of some slightly soluble salts can be found in Appendix D. Note that the K_{sp} values tabulated in Appendix D are all quite small, so only the solubilities of slightly soluble substances are considered. However, K_{sp} is also defined for materials that are more soluble, but it is seldom applied to them. For example, the K_{sp} of NaCl at 25 °C is 38, which corresponds to a solubility of 360 g·L^{-1}.

PRACTICE EXAMPLE 8.1

What is the K_{sp} of $Fe(OH)_2$ if the pH of a saturated solution is 9.07?

Reaction:

The equilibrium concentrations

pOH =

$[OH^{1-}]$ =

$[Fe^{2+}]$ =

Reaction Table

Reaction:

In

Δ

Eq

The solubility-product constant expression

K_{sp} =

The value of the solubility-product constant

Example 8.2

a) The K_{sp} of Ag_3PO_4 is $2.6x10^{-18}$. What is its predicted molar solubility?

The reaction table for the dissolution is

	Ag_3PO_4 (s)	$\rightleftharpoons$	$3Ag^{1+}$	+	PO_4^{3-}
Initial	**enough**		**0**		**0**
Δ	**-x**		**+3x**		**+x**
Eq	**some**		**3x**		**x**

Determine the expression for the solubility-product constant: $K_{sp} = [Ag^{1+}]^3[PO_4^{3-}]$

Substitute the equilibrium concentrations into the expression: $K_{sp} = (3x)^3(x) = 27x^4$

Solve the expression for the solubility: $x = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{2.6\times10^{-18}}{27}} = 1.8\times10^{-5}\ M$

b) The experimentally determined molar solubility is $1.5x10^{-4}$ M. Explain.

The difference between the experimental value and that determined from the K_{sp} is due to the fact that PO_4^{3-} is a fairly strong base ($K_b = 0.021$), so much of the phosphate ion produced in the dissolution is converted to HPO_4^{1-} by the reaction with water. The loss of phosphate ion causes more Ag_3PO_4 to dissolve (Le Châtelier's principle). This is why solubilities of basic salts cannot be determined from their solubility products alone.*

The values of the K_{sp} constants are one consideration when determining relative solubilities, but the form of the K_{sp} expression (the multiplier and exponent of the solubility) can also be important if the ion ratios are different. As shown in Table 8.2, the form of the K_{sp} expression depends only upon the cation:anion ratio. If the cation:anion ratios of the salts are the same, then their relative solubilities increase in the order of their K_{sp}'s; but, care must be taken when comparing salts with different ratios.

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

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

Example 8.3

List the following salts in order of increasing solubility.

$PbCl_2$ ($K_{sp} = 1.7x10^{-5}$)   AgCl ($K_{sp} = 1.2x10^{-10}$)   TlCl ($K_{sp} = 1.9x10^{-4}$)

AgCl and TlCl are both 1:1 salts, and a simple comparison of their K_{sp} values shows that TlCl is much more soluble than AgCl. However, the relative solubilities of TlCl and $PbCl_2$ cannot be determined by a comparison of their K_{sp}'s because one is a 1:1 salt ($K_{sp} = x^2$) and the other is a 1:2 salt ($K_{sp} = 4x^3$). The two molar solubilities are

$$\text{TlCl solubility} = \sqrt{1.9\times10^{-4}} = 0.014\ M \text{ and } PbCl_2 \text{ solubility} = \sqrt[3]{\frac{1.7\times10^{-5}}{4}} = 0.016\ M$$

Thus, $PbCl_2$ is slightly more soluble than TlCl even though its K_{sp} is smaller. The solubilities of the three substances are in the order AgCl << TlCl < $PbCl_2$.

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* The discrepancy does not mean that the K_{sp} is incorrect; it is still obeyed. Rather it is due to the fact that, because PO_4^{3-} also reacts with water, the $[Ag^{1+}] = 3[PO_4^{3-}]$ equality predicted from the dissolution chemical equation is no longer valid. Therefore, the assumption that $K_{sp} = 27x^4$ is not valid. We re-examine this problem in Practice Example 8.6.

The dissolution of a slightly soluble salt is suppressed by the addition of ions that appear in the dissolution equilibrium (common-ion effect). Consider the dissolution of MgF_2 in a solution that already contains Mg^{2+} from another source (a common ion). The reaction table has the following form:

	$MgF_2(s)$	$\rightleftharpoons$	Mg^{2+}	$+$	$2F^{1-}(aq)$
initial	**enough**		c_o		0
Δ	$-x$		$+x$		$+2x$
eq	**some**		$c_o + x$		$2x$

c_o is the initial molar concentration of Mg^{2+}. The K_{sp} of MgF_2 is $1.7x10^{-5}$, so we write

$$K_{sp} = [Mg^{2+}][F^{1-}]^2 = (c_o + x)(2x)^2 = 1.7x10^{-5}$$

Solution of the above for x involves a cubic equation. However, if $c_o >> x$, then $c_o + x$ can be approximated as c_o, and the equation becomes much easier to solve. In Example 8.1, the solubility of MgF_2 in water was found to be 0.0012 M, but the dissolution of MgF_2 is suppressed by the presence of additional Mg^{2+} ions in the solution. Thus, x is less than 0.0012 M, so the approximation that x is negligible with respect to c_o is valid as long as c_o is not very small. We conclude that *the concentration of the common ion is usually unaffected by the dissolution process*, so its equilibrium concentration is equal to its initial concentration. The fact that one of the concentrations is known ($[Mg^{2+}] = c_o$) simplifies the problem considerably. Solving for $[F^{1-}]$ in the K_{sp} expression, we obtain the following:

$$[F^{1-}] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = 2x$$

$K_{sp} = 7.3x10^{-9}$ for MgF_2. If the concentration of Mg^{2+} ion from the other source is 0.10 M, then the concentration of fluoride ion is

$$[F^{1-}] = \sqrt{\frac{7.3\times10^{-9}}{0.10}} = 2.7\times10^{-4}\ M = 2x$$

$[F^{1-}] = 2x$, so $x = ½[F^{1-}]$. Thus, the solubility of magnesium fluoride in a solution that is 0.10 M in Mg^{2+} ion is $1.4x10^{-4}$ M, which is negligible compared to 0.10 M and our approximation that $c_o + x = c_o$ was valid. Note that, due to the common-ion effect, the solubility of magnesium fluoride is almost ten times less in the presence of 0.10 M Mg^{2+} than it is in pure water.

PRACTICE EXAMPLE 8.2

Indicate the more soluble compound in each pair.

a) $PbSO_4$ ($K_{sp} = 2x10^{-8}$) or $CaSO_4$ ($K_{sp} = 2x10^{-5}$)

b) BaF_2 ($K_{sp} = 2x10^{-6}$) or PbF_2 ($K_{sp} = 4x10^{-8}$)

c) $BaCrO_4$ ($K_{sp} = 2x10^{-10}$) or Ag_2CrO_4 ($K_{sp} = 3x10^{-12}$)

d) Ag_3PO_4 ($K_{sp} = 2x10^{-18}$) or $Mg_3(PO_4)_2$ ($K_{sp}= 5x10^{-24}$)

Example 8.4

a) What is the solubility of AgCl in water?

The K_{sp} for AgCl is $1.8\text{x}10^{-10}$ (Appendix D). The dissolution process is

$$\mathbf{AgCl(s) \rightleftharpoons Ag^{1+} + Cl^{1-} \qquad K_{sp} = [Ag^{1+}][Cl^{1-}] = x^2}$$

The solubility of AgCl in water is then determined to be

$$\mathbf{x = \sqrt{K_{sp}} = \sqrt{1.8\times10^{-10}} = 1.3\times10^{-5}\ M}$$

b) What is the solubility of AgCl in 0.10 M NaCl?

This is a problem of solubility in the presence of a common-ion. The reaction table is

	AgCl(s)	$\rightleftharpoons$	Ag^{1+}	+	Cl^{1-}
initial	**enough**		**0**		**0.10**
Δ	**-x**		**+x**		**+x**
eq	**some**		**x**		**0.10 + x**

x must be less than $1.3\text{x}10^{-5}$ M due to the common-ion effect exerted by the chloride ion. Consequently, $[Cl^{1-}] = 0.10 + x = 0.10$.

The silver ion concentration, which is equal to the solubility in this example, is

$$\mathbf{[Ag^{1+}] = x = \frac{K_{sp}}{[Cl^{1-}]} = \frac{1.8\times10^{-10}}{0.10} = 1.8\times10^{-9}\ M}$$

The solubility of silver chloride is ten thousand times less in 0.10 M NaCl than in water because the common ion (Cl^{1-}) suppresses the dissolution process.

8.3 PRECIPITATION AND SEPARATION OF IONS

Our discussion thus far has focused on the amount of a slightly soluble salt that dissolves, but now we consider the ion concentrations required to bring about precipitation. We start by examining the dissolution reaction of magnesium fluoride, but this time we consider the reaction from right to left; that is, we focus on the precipitation of MgF_2.

$$\mathbf{MgF_2(s) \rightleftharpoons Mg^{2+} + 2F^{1-} \qquad K_{sp} = [Mg^{2+}][F^{1-}]^2}$$

Reactions proceed right to left (MgF_2 precipitates) only when the reaction quotient exceeds the equilibrium constant; *i.e.,* when $Q > K$. The reaction quotients for the dissolution of ionic compounds are so common that they are given a special name and symbol: the **ion product**, Q_{ip}. Thus, ***precipitation occurs only if*** $Q_{ip} > K_{sp}$.

PRACTICE EXAMPLE 8.3

What is the solubility of $Sn(OH)_2$ in a solution buffered at pH = 9.00?

Dissolution reaction:

K_{sp} =

OH^{1-} produced by the dissolution can be ignored in buffered solutions because the buffer maintains a constant pH.

$[OH^{1-}]$ =

$[Sn^{2+}]$ =

solubility =

What is the solubility of $Sn(OH)_2$ in a solution buffered at pH = 2.00?

$[OH^{1-}]$ =

$[Sn^{2+}]$ =

solubility =

Note that the solubility is far greater at the lower pH because the hydroxide ion is a strong base that reacts with both Sn^{2+} and H_3O^{1+} (Section 8.5).

Example 8.5

The pH of an acidified solution that is 0.01 M in Cu^{2+}, Fe^{2+}, Mg^{2+} and Sn^{2+} is increased by adding NaOH. Which hydroxide precipitates at each pH?

Refer to Appendix D to obtain the solubility-product constants in the margin. All of the metal ions are +2, so all of the hydroxides have 1:2 cation:anion ratios. All of the metal ion concentrations are 0.01 M, so a generic ion product can be written as

$$\mathcal{Q}_{ip} = [M^{2+}][OH^{1-}]^2 = (0.01)[OH^{1-}]^2$$

a) pH = 4

The hydroxide ion concentration in the solution is obtained from the pH.

$$pOH = 14 - pH = 14 - 4 = 10,\ \text{so}\ [OH^{1-}] = 10^{-pOH} = 10^{-10}\ M$$

$$\mathcal{Q}_{ip} = [M^{2+}][OH^{1-}]^2 = (0.01)(10^{-10})^2 = 10^{-22}$$

$\mathcal{Q}_{ip}$ exceeds the K_{sp} of only $Sn(OH)_2$. Thus, at pH = 4, only $Sn(OH)_2$ precipitates, while the other ions remain in solution. The reaction mixture could then be filtered to remove the solid $Sn(OH)_2$, which could then be re-dissolved in an acidic solution. Thus, two solutions would result: one with Fe^{2+}, Cu^{2+} and Mg^{2+} ions and one with only Sn^{2+} ions. In other words, the Sn^{2+} ions have been separated from the original mixture. To be completely accurate, *most* of the Sn^{2+} ions have been separated. The K_{sp} of $Sn(OH)_2$ must still be satisfied, so some Sn^{2+} remains in the solution with the other ions. We address this problem in Example 8.8.

b) pH = 6

$$pOH = 14 - pH = 14 - 6 = 8,\ \text{so}\ [OH^{1-}] = 10^{-pOH} = 10^{-8}\ M$$

$$\mathcal{Q}_{ip} = [M^{2+}][OH^{1-}]^2 = (0.01)(10^{-8})^2 = 10^{-18}$$

Sn^{2+} has been removed, so $\mathcal{Q}_{ip}$ exceeds the K_{sp} of only $Cu(OH)_2$. Thus, $Cu(OH)_2$ precipitates leaving a solution of Fe^{2+} and Mg^{2+} ions. Again, the $Cu(OH)_2$ could be filtered and re-dissolved to produce three solutions: one with Mg^{2+} and Fe^{2+} ions, one with Cu^{2+} ions, and one with Sn^{2+} ions.

c) pH = 8

Proceeding as above, the ion product for those ions still in solution is

$$\mathcal{Q}_{ip} = [M^{2+}][OH^{1-}]^2 = (0.01)(10^{-6})^2 = 10^{-14}$$

which exceeds the K_{sp} of $Fe(OH)_2$, so $Fe(OH)_2$ precipitates leaving a solution of Mg^{2+} ions and trace amounts of the other ions as noted in Parts a and b. After a final filtration of $Fe(OH)_2$ followed by re-dissolving the solid in acid, we end up with four solutions each containing only one of the four ions. This is an example of separations chemistry because the four ions that were together in one solution are now separated into four different solutions.

K_{sp} values for Example 8.5

Hydroxide	K_{sp}
$Sn(OH)_2$	1.4×10^{-28}
$Cu(OH)_2$	2.2×10^{-20}
$Fe(OH)_2$	8.0×10^{-16}
$Mg(OH)_2$	1.8×10^{-11}

Example 8.6

At what pH does $Mg(OH)_2$ begin to precipitate from a solution that is 0.01 M in Mg^{2+}?

We know $[Mg^{2+}]$ and K_{sp}, so we need only solve the K_{sp} expression for $[OH^{1-}]$.

$$\mathbf{Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^{1-} \qquad K_{sp} = 1.8x10^{-11} = [Mg^{2+}][OH^{1-}]^2}$$

Solving for the hydroxide ion concentration and substituting the known K_{sp} and $[Mg^{2+}]$, we obtain the following:

$$[OH^{1-}] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1.8\times10^{-11}}{0.01}} = 4\times10^{-5}\ M$$

Converting $[OH^{1-}]$ to pH, we obtain the answer:

$$\mathbf{pOH = -\log(4x10^{-5}) = 4.4;\quad pH = 14.0 - 4.4 = 9.6}$$

$Mg(OH)_2$ begins to precipitate when the pH reaches 9.6.

The four ions in Example 8.5 were separated from solution, but some of each metal ion remains in solution after each precipitation because the equilibrium between the metal and hydroxide ions is maintained even after precipitation. Increasing the hydroxide ion concentration shifts the equilibrium to the left, but it does not eliminate all of the metal ions. Thus, after $Sn(OH)_2$ is precipitated, the following equilibrium is still maintained:

$$\mathbf{Sn(OH)_2(s) \rightleftharpoons Sn^{2+} + 2OH^{1-} \qquad K_{sp} = [Sn^{2+}][OH^{1-}]^2}$$

Solving the K_{sp} expression for the equilibrium concentration of Sn^{2+}, we obtain

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

If we want to separate the tin(II) ions from the other ions, then we want to minimize this concentration and maximize the amount that precipitates; *i.e.,* a good separation is one in which the Sn^{2+} ion concentration is very low after the precipitation. To reduce the tin(II) concentration, we simply need to add more hydroxide, but care must be taken not to increase the pH so high that the hydroxides of other metal ions begin to precipitate as well. Example 8.7 demonstrates how to determine the concentration of a remaining ion, and Example 8.8 shows how to optimize a separation by precipitating the maximum amount of one substance without precipitating another.

PRACTICE EXAMPLE 8.4

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} of TlCl = $1.9x10^{-4}$ $\qquad$ K_{sp} of $PbCl_2$ = $1.7x10^{-5}$

Concentrations of ions after mixing but before precipitation occurs

$[Tl^{1+}]$ =

$[Pb^{2+}]$ =

$[Cl^{1-}]$ =

Ion products

TlCl

Q_{ip} =

$PbCl_2$

Q_{ip} =

Precipitates that form:

Example 8.7

What is the concentration of Sn^{2+} ions remaining after precipitation of $Sn(OH)_2$ at pH = 4.0?

We are given $K_{sp} = 1.4\text{x}10^{-28}$ and $[OH^{1-}] = 1\text{x}10^{-10}$ M and asked for $[Sn^{2+}]$.

$$[Sn^{2+}] = \frac{K_{sp}}{[OH^{1-}]^2} = \frac{1.4\times10^{-28}}{(1\times10^{-10})^2} = 1\times10^{-8}\ \text{M} = 0.01\ \mu\text{M}$$

The concentration of the Sn^{2+} remaining after the precipitation is about one hundred millionth molar! The concentration of Sn^{2+} in solution went from 0.01 M to 0.01 μM, so 99.9999% of the Sn^{2+} was separated from solution.

Example 8.8

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

The K_{sp} values are $Fe(OH)_2 = 8\text{x}10^{-16}$ and $Sn(OH)_2 = 1\text{x}10^{-28}$. The K_{sp} of $Sn(OH)_2$ is by far the smaller, so it will precipitate well before the $Fe(OH)_2$. The $[OH^{1-}]$ required to begin precipitation for each is:

$$Fe^{2+}:\ [OH^{1-}] = \sqrt{\frac{K_{sp}}{[Fe^{2+}]}} = \sqrt{\frac{8\times10^{-16}}{0.010}} = 3\times10^{-7}\ \text{M and}$$

$$Sn^{2+}:\ [OH^{1-}] = \sqrt{\frac{K_{sp}}{[Sn^{2+}]}} = \sqrt{\frac{1\times10^{-28}}{0.010}} = 1\times10^{-13}\ \text{M}$$

Optimum separation requires that $[Sn^{2+}]$ be as low as possible after precipitation, so we make $[OH^{1-}]$ as high as possible but well below $3\text{x}10^{-7}$ M to insure that $Fe(OH)_2$ does not precipitate. We choose a hydroxide ion concentration of $1\text{x}10^{-7}$ M, which is well above that required to precipitate $Sn(OH)_2$ but only $^1/_3$ that required to precipitate $Fe(OH)_2$. At pH = 7.0,

$$[Sn^{2+}] = \frac{K_{sp}}{[OH^{1-}]^2} = \frac{1\times10^{-28}}{(1\times10^{-7})^2} = 1\times10^{-14}\ \text{M}$$

Thus, only 10^{-10}% of the original Sn^{2+} remains in solution! The Q_{ip} of $Fe(OH)_2$ is $(0.010)(1.0\text{x}10^{-7})^2 = 1.0\text{x}10^{-16}$, which does not exceed its K_{sp}, so ~100% of Sn^{2+} precipitates with no precipitation of $Fe(OH)_2$. This is a good separation.

Example 8.9

What mass of Ag_2CrO_4 is formed when 50. mL of 0.10 M K_2CrO_4 and 50. mL of 0.10 M $AgNO_3$ are mixed?

The net equation for the precipitation: $2Ag^{1+} + CrO_4^{2-} \rightarrow Ag_2CrO_4(s)$

The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12}, so the equilibrium constant for the precipitation is large ($K_{sp}^{-1} \sim 10^{12}$). Thus, this reaction goes essentially to completion. We next determine the limiting reactant. Initially, there are

$$50.\text{ mL solution} \times \frac{0.10\text{ mmol Ag}^{1+}}{\text{mL solution}} = 5.0\text{ mmol Ag}^{1+}\text{ ions}$$

$$50.\text{ mL solution} \times \frac{0.10\text{ mmol CrO}_4^{2-}}{\text{mL solution}} = 5.0\text{ mmol CrO}_4^{2-}\text{ ions}$$

Two moles of silver ions are required for every one mole of chromate ion, but there are equal numbers of moles of each reactant initially. Consequently, silver ion is the limiting reactant, and the reaction table for the precipitation has the following form:

	$2Ag^{1+}$	$+ CrO_4^{2-}$	$\rightarrow$	$Ag_2CrO_4(s)$	
initial	**5.0**	**5.0**		**0**	**mmol**
Δ	**-5.0**	**-2.5**		**+2.5**	**mmol**
final	**0**	**2.5**		**2.5**	**mmol**

The silver ion concentration is not zero at equilibrium because silver chromate is slightly soluble. The reaction table for the dissolution of Ag_2CrO_4 in the presence of the excess chromate ion is discussed in Example 8.10. However, the numbers of moles of all other species present at equilibrium are given in the above table. The mass of Ag_2CrO_4 (M_m = 332 g·mol^{-1} = 332 mg·mmol^{-1}) that forms is

$$2.5\text{ mmol} \times \frac{332\text{ mg}}{\text{mmol}} = 8.3\times10^{2}\text{ mg} = 0.83\text{ g}$$

Example 8.10

What are the concentrations of the ions in the solution produced in Example 8.9?

In a reaction as extensive as the precipitation of Ag_2CrO_4, the amount of product formed can be determined from stoichiometry without using equilibrium considerations (Example 8.9). However, Ag_2CrO_4 is slightly soluble, and we now determine how much of the solid dissolves. First, determine the concentration of the chromate ion after precipitation. The resulting solution has a total volume of 100. mL (assuming additive volumes), and contains 2.5 mmol CrO_4^{2-}, so the concentration of the chromate ion is

$$[CrO_4^{2-}] = \frac{2.5\text{ mmol}}{100.\text{ mL}} = 0.025\text{ M}$$

PRACTICE EXAMPLE 8.5

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?

K_{sp} of PbF_2 = ________________ from Appendix D

mmoles of Pb^{2+} =

mmoles of F^{1-} =

<u>Limiting Reactant</u>

mmol PbF_2 from Pb^{2+}

mmol PbF_2 from F^{1-}

limiting reactant is ____________

<u>Reaction Table for the precipitation</u>

Reaction:

Initial

Δ

Final

Total volume =

<u>Fluoride ion concentration in final solution</u>

$[F^{1-}]$ = = __________ M

<u>$[Pb^{2+}]$ from K_{sp} and excess F^{1-} ion concentration:</u>

$[Pb^{2+}]$ = = __________M

Next, carry out the dissolution of the precipitated Ag_2CrO_4 in the presence of excess CrO_4^{2-}. The initial line of the reaction table for the dissolution is based on the final line of the precipitation reaction table shown in Example 8.9.

	$Ag_2CrO_4(s) \rightleftharpoons$	$2Ag^{1+}$	+	CrO_4^{2-}	$K_{sp} = 1.1x10^{-12}$
initial	**enough**	**0**		**0.025**	**M**
Δ	**-x**	**+2x**		**+x**	**M**
eq	**some**	**2x**		**0.025 +x**	**M**

Thus, $K_{sp} = 1.1x10^{-12} = [Ag^{1+}]^2[CrO_4^{2-}] = (2x)^2(0.025+x)$. However, x is expected to be negligible compared to 0.025 because K_{sp} is very small and there is a common-ion effect due to the excess reactant. Consequently, $[CrO_4^{2-}] = 0.025$ M. Using this assumption, we can solve for $[Ag^{1+}]$ directly.

$$[Ag^{1+}] = \sqrt{\frac{K_{sp}}{[CrO_4^{1-}]}} = \sqrt{\frac{1.1\times10^{-12}}{0.025}} = 6.6\times10^{-6}\ M = 6.6\ \mu M$$

The assumption is valid because the amount that dissolves is negligible compared to the initial chromate ion concentration.

8.4 COMPLEX IONS

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, we will consider only the overall process in which all of the ligands are added or removed in one step. The equilibrium constant governing the one-step formation of the complex ion from the metal ion and the ligands is called the **formation constant** and given the symbol **K_f**. Table 8.3 contains the formation constants at 25 °C for some common complex ions. As an example, consider formation of the complex ion $Ag(NH_3)_2^{1+}$.

$$Ag^{1+} + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{1+}$$

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

$$K_f = \frac{[Ag(NH_3)_2^{1+}]}{[Ag^{1+}][NH_3]^2} = 1.7\times10^7$$

Biochemists prefer the reverse of the formation reaction, so tables of **dissociation constants, K_d**, are also available, but the K_d of an ion is merely the reciprocal of its K_f. K_d is used in Example 8.11 because the reaction deals with the dissociation of the ion.

Table 8.3 Selected formation constants at 25 °C

Complex Ion	K_f	Formation Reaction
$Ag(NH_3)_2^{1+}$	$1.7x10^7$	$Ag^{1+} + 2NH_3 \rightleftharpoons Ag(NH_3)_2^{1+}$
$Ag(CN)_2^{1-}$	$3.0x10^{20}$	$Ag^{1+} + 2CN^{1-} \rightleftharpoons Ag(CN)_2$
$Cu(NH_3)_4^{2+}$	$4.8x10^{12}$	$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$
$Fe(CN)_6^{4-}$	$1.0x10^{35}$	$Fe^{2+} + 6CN^{1-} \rightleftharpoons Fe(CN)_6^{4-}$
$Fe(CN)_6^{3-}$	$1\ x10^{42}$	$Fe^{3+} + 6CN^{1-} \rightleftharpoons Fe(CN)_6^{3-}$
$Ni(NH_3)_6^{2+}$	$5.6x10^8$	$Ni^{2+} + 6NH_3 \rightleftharpoons Ni(NH_3)_6^{2+}$
$Zn(OH)_4^{2-}$	$2.8x10^{15}$	$Zn^{2+} + 4OH^{1-} \rightleftharpoons Zn(OH)_4^{2-}$

Example 8.11

What is the concentration of free Cu^{2+} in a 0.26-M solution of $Cu(NH_3)_4^{2+}$?

Construct the reaction table for the dissociation of the complex ion. The dissociation constant (K_d) is the reciprocal of the formation constant ($K_f = 4.8\text{x}10^{12}$).

$$Cu(NH_3)_4^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq) \qquad K_d = 2.1\text{x}10^{-13}$$

	$Cu(NH_3)_4^{2+}(aq)$	$Cu^{2+}(aq)$	$4NH_3(aq)$
initial	**0.26**	**0**	**0**
Δ	**-x**	**x**	**4x**
eq	**0.26 - x**	**x**	**4x**

K << 1, so a assume that x can be ignored in the subtraction to obtain

$$K_d = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} = \frac{(x)(4x)^4}{0.26 - x} = \frac{256x^5}{0.26} = 2.1\times10^{-13}$$

Solve the above for x and verify that x is negligible compared to 0.26 M.

$$x = [Cu^{2+}] = \sqrt[5]{\frac{(0.26)(2.1\times10^{-13})}{256}} = 7.3\times10^{-4}\text{ M}$$

8.5 COMPETING OR SIMULTANEOUS EQUILIBRIA

The reaction between silver and chloride ions to form AgCl is a Lewis acid-base reaction between a Lewis acid (Ag^{1+}) and a Lewis base (Cl^{1-}). The formation of $Ag(NH_3)_2^{1+}$ ions is also a Lewis acid-base reaction in which NH_3 is the base. Thus, when AgCl is added to an NH_3 solution, there is competition between Cl^{1-} and NH_3 for silver ions. Consequently, some Ag^{1+} ions are pulled into solution as the complex ion, which has the effect of making the AgCl more soluble in ammonia than in water. The effect can be quantified by considering the dissolution of AgCl and the formation of $Ag(NH_3)_2^{1+}$ simultaneously.

$$AgCl(s) \rightleftharpoons \cancel{Ag^{1+}} + Cl^{1-} \qquad K_{sp} = 1.8\times10^{-10}$$

$$\cancel{Ag^{1+}} + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{1+} \qquad K_f = 1.7\times10^{7}$$

$$2NH_3(aq) + AgCl(s) \rightleftharpoons Ag(NH_3)_2^{1+} + Cl^{1-} \qquad K = K_{sp}\times K_f = \frac{[Ag(NH_3)_2^{1+}][Cl^{1-}]}{[NH_3]^2}$$

Summing the chemical equations for the dissolution and formation reactions produces the chemical equation for the dissolution of AgCl in ammonia. Consequently, its equilibrium constant is the product of the equilibrium constants of the two reactions that add to produce it. The solubility of AgCl in ammonia is explored in Example 8.12.

Example 8.12

What is the solubility of AgCl in 1.0 M NH_3?

The reaction table for the dissolution of AgCl in 1.0 M ammonia is

	$2NH_3(aq)$ +	$AgCl(s)$ ⇌	$Ag(NH_3)_2^{1+}(aq)$ +	$Cl^{1-}(aq)$
initial	1.0	enough	0	0
Δ	-2x	-x	+x	+x
eq	1.0 - 2x	some	x	x

The value of the equilibrium constant is $K = K_{sp}K_f = (1.8\times10^{-10})(1.7\times10^{7}) = 3.1\times10^{-3}$

$$K = 3.1\times10^{-3} = \frac{[Ag(NH_3)_2^{1+}][Cl^{1-}]}{[NH_3]^2} = \frac{x^2}{(1.0 - 2x)^2}$$

which is most easily solved by taking the square root of both sides.

$$\sqrt{3.1\times10^{-3}} = 0.056 = \frac{x}{1.0 - 2x}$$

Multiplication of both sides by 1.0 - 2x yields 0.056 - 0.11x = x. Solving for x:

$$x = \frac{0.056}{1.11} = 0.050\text{ M} = [Ag(NH_3)_2^{1+}] = [Cl^{1-}]$$

The solubility of AgCl in 1.0 M NH_3 is 0.050 M, which is nearly 4,000 times more soluble than in pure water. (1.3×10^{-5} M Example 8.4)

Ligands are Lewis bases, so when a ligand is in solution with two Lewis acids, the acids compete for the ligand, and the competition results in an equilibrium that is related to the equilibria between the ligand and each of the two acids. For example, fluoride ion is a Lewis base that reacts with Ca^{2+} to produce CaF_2, a slightly soluble salt, and with H_3O^{1+} to produce HF. Thus, when CaF_2 is added to a solution of a strong acid, both the Ca^{2+} and the H_3O^{1+} ions compete for the fluoride ions. Consequently, some F^{1-} ions are pulled into solution as HF molecules. One Ca^{2+} ion goes into solution for each two F^{1-} ions as some of the CaF_2 dissolves, making CaF_2 more soluble in acid than in water. The process, which is characterized by the K_{sp} reaction of CaF_2 and the reverse of the K_a reaction of 2HF, is described below.

$$CaF_2(s) \rightleftharpoons Ca^{2+} + \cancel{2F}^{1-} \qquad K_1 = K_{sp}(CaF_2)$$

$$\cancel{2F}^{1-} + 2H_3O^{1+} \rightleftharpoons 2HF(aq) + 2H_2O \qquad K_2 = \left(\frac{1}{K_a(HF)}\right)^2$$

$$CaF_2(s) + 2H_3O^{1+} \rightleftharpoons Ca^{2+} + 2HF(aq) + 2H_2O \qquad K = K_1K_2 = \frac{K_{sp}(CaF_2)}{K_a(HF)^2}$$

PRACTICE EXAMPLE 8.6

In Example 8.2, we showed that the solubility of Ag_3PO_4 is over eight times greater than predicted from its K_{sp}. We attributed this to the fact that PO_4^{3-} reacts with both Ag^{1+} and H_2O; *i.e.*, there are competing equilibria. Let us revisit that solubility as a competing equilibrium problem. Assume the following competing equations:

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^{1+} + PO_4^{3-} \qquad K_{sp} = 2.6\times10^{-8}$$

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

What is the chemical equation for dissolving Ag_3PO_4 in water that accounts for the competing equilibria, and what is its equilibrium constant?

K = = ____________

What is the solubility of Ag_3PO_4 in a solution buffered at pH = 9.00, where all phosphate is in the form of HPO_4^{2-} (Figure 7.8)?

Reaction Table:

In

Δ

Eq

K =

$[HPO_4^{2-}]$ = x = ______________ M

How does this compare to the experimental solubility of Ag_3PO_4 (1.5×10^{-4} M)? Compare that to the solubility predicted using K_{sp} alone (1.8×10^{-5} M).

Example 8.13

What is the solubility of CaF_2 in a solution buffered at pH = 2.00?

The solution is buffered, so the hydronium concentration is constant.

$$[H_3O^{1+}] = 10^{-pH} = 10^{-2.00} = 0.010\ M$$

The solution is buffered, so we assume that the hydronium ion concentration change is negligible. The reaction table for the dissolution is then constructed as follows:

	$CaF_2(s)$	+	$2H_3O^{1+}$	⇌	Ca^{2+}	+	$2HF(aq)$	+	$2H_2O$
in	**enough**		**0.010**		**0**		**0**		
Δ	**-x**		**0**		**+x**		**+2x**		
eq.	**some**		**0.010**		**x**		**2x**		

Look up the K_{sp} of CaF_2 and the K_a of HF to determine the value of the equilibrium constant as discussed in the text.

$$K = \frac{K_{sp}}{K_a^2} = \frac{3.9\times10^{-11}}{(7.2\times10^{-4})^2} = 7.5\times10^{-5}$$

Setup the equilibrium constant expression and solve for x.

$$7.5\times10^{-5} = \frac{[Ca^{2+}][HF]^2}{[H_3O^{1+}]^2} = \frac{(x)(2x)^2}{(0.010)^2}$$

$$4x^3 = 7.5\times10^{-9};\quad x = \sqrt[3]{\frac{7.5\times10^{-9}}{4}} = 1.2\times10^{-3}\ M$$

CaF_2 is about 20 times more soluble at pH = 2 than at pH = 7.

The equilibrium constant for the dissolution of a basic salt in acid involves the K_a of the weak acid in the denominator, so it gets larger as the base gets stronger (the K_a of its conjugate acid gets smaller). Thus, the degree to which the solubility of a basic salt is enhanced in acid increases as the base strength of the anion increases. We conclude that *slightly soluble salts are more soluble in basic solution (OH^{1-}, CN^{1-}, NH_3) if the Lewis acidic metal ion forms a complex ion with the base (Example 8.12), and they are more soluble in acidic solution if the ligand is a base that can react with the acid (Example 8.13)*.

Some anions form a slightly soluble salt and a complex ion with the same cation. In these cases, a precipitate forms with the addition of the anion to a solution of the cation only to dissolve as the complex ion with further addition of the anion. Example 8.14 treats an example of this behavior.

Example 8.14

A precipitate of $Cr(OH)_3$ ($K_{sp} = 6x10^{-31}$) is produced as hydroxide ion is added slowly to an acidified solution that is 0.04 M in Cr^{3+}. However, the precipitate dissolves as the $Cr(OH)_4^{1-}$ ion ($K_f = 8x10^{29}$) with the addition of more base. Assume that the volume of added base is negligible and determine the pH at which precipitate first forms and the pH at which it completely disappears.

Use the K_{sp} to treat the precipitation.

$$Cr(OH)_3(s) \rightleftharpoons Cr^{3+} + 3OH^{1-} \qquad K_{sp} = 6x10^{-31} = [Cr^{3+}][OH^{1-}]^3$$

Solve the K_{sp} for the hydroxide ion concentration and substitute the known values:

$$[OH^{1-}] = \sqrt[3]{\frac{K_{sp}}{[Cr^{3+}]}} = \sqrt[3]{\frac{6\times10^{-31}}{0.04}} = 2\times10^{-10}\ M$$

$$pOH = -log(2x10^{-10}) = 9.6 \quad \& \quad pH = 14.0 - 9.6 = 4.4$$

$Cr(OH)_3$ forms at pH = 4.4. It is dissolved in excess base by the following reaction.

$$Cr(OH)_3(s) + OH^{1-} \rightleftharpoons Cr(OH)_4^{1-}$$

The above chemical equation is the sum of the dissolution reaction for $Cr(OH)_3$ and the formation reaction for $Cr(OH)_4^{1-}$

$$Cr(OH)_3(s) \rightleftharpoons Cr^{3+} + 3OH^{1-} \qquad K_{sp} = 6x10^{-31}$$

$$Cr^{3+} + 4OH^{1-} \rightleftharpoons Cr(OH)_4^{1-} \qquad K_f = 8x0^{29}$$

so its equilibrium constant is $K = K_{sp}K_f = (6\times10^{-31})(8\times10^{29}) = 0.5 = \frac{[Cr(OH)_4^{1-}]}{[OH^{1-}]}$

When all of the solid dissolves, $[Cr(OH)_4^{1-}]$ = 0.04 M, so we can solve the above expression for $[OH^{1-}]$.

$$[OH^{1-}] = \frac{[Cr(OH)_4^{1-}]}{K} = \frac{0.04}{0.5} = 0.08\ M$$

$$pOH = -log(0.08) = 1.1 \quad \& \quad pH = 14.0 - 1.1 = 12.9$$

Thus, solid begins to form at a pH = 4.4, but it is completely gone again at a pH = 12.9.

Polyprotic acids also have simultaneous equilibria to consider and their chemical equations can also be added to produce a third chemical equation that does not include the concentration of the intermediate ion. In Chapter 7, we examined the case of H_2S where the HS^{1-} ion is eliminated by the addition of the two dissociations.

$$H_2S + H_2O \rightleftharpoons \boxed{HS^{1-}} + H_3O^{1+} \qquad K_1 = 1.0\text{x}10^{-7}$$

$$\boxed{HS^{1-}} + H_2O \rightleftharpoons S^{2-} + H_3O^{1+} \qquad K_2 = 1.3\text{x}10^{-13}$$

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

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.

Example 8.15

a) To what pH should the solution that is 0.010 M in each Fe^{2+} and Mn^{2+} be saturated with H_2S to achieve an optimum separation of the ions?

The ions will precipitate as their sulfides, so we first get their K_{sp}'s from Appendix D.

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

FeS is less soluble, so it is the sulfide that precipitates first. To achieve optimum separation, we want to minimize the $[Fe^{2+}]$ remaining in solution after the addition of S^{2-} ion. To do this, we must maximize $[S^{2-}]$, but it cannot exceed the concentration where MnS precipitates. The minimum sulfide ion concentration required to precipitate 0.010 M Mn^{2+} is determined as follows:

$$[S^{2-}] = \frac{K_{sp}}{[Mn^{2+}]} = \frac{5.6\times10^{-16}}{0.010} = 5.6\times10^{-14}\ \text{M}$$

The above sulfide ion concentration minimizes the $[Fe^{2+}]$ remaining in solution without precipitation of any MnS. We use this concentration and the fact that a saturated solution of H_2S is 0.10 M in the K_{12} expression for H_2S to determine the required $[H_3O^{1+}]$ and pH.

$$[H_3O^{1+}] = \sqrt{\frac{K_{12}[H_2S]}{[S^{2-}]}} = \sqrt{\frac{(1.3\times10^{-20})(0.10)}{5.6\times10^{-14}}} = 1.5\times10^{-4}\ \text{M} \Rightarrow \text{pH} = 3.82$$

If pH > 3.82 when the solution is saturated with H_2S, MnS will precipitate. Thus. a pH < 3.82 is required. An optimum separation would occur at pH ~ 3.80. The solution would be buffered at pH = 3.80 and then H_2S gas would be bubbled into the solution until saturation. The FeS that is produced would be filtered from solution leaving a solution that was still 0.01 M in Mn^{2+}, but the concentration of Fe^{2+} would be greatly reduced.

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

Use the K_{12} expression to determine $[S^{2-}]$ at pH = 3.80

$$[S^{2-}] = \frac{K_{12}[H_2S]}{[H_3O^{1+}]^2} = \frac{(1.3\times10^{-20})(0.10)}{(10^{-3.80})^2} = 5.2\times10^{-14}\ M$$

Determine Q_{ip} for the above $[S^{2-}]$ and the given metal ion concentrations.

$$Q_{ip} = [M^{2+}][S^{2-}] = (0.010)(5.2x10^{-14}) = 5.2x10^{-16}$$

$Q_{ip} < K_{sp}$ for MnS ($5.2x10^{-16} < 5.6x10^{-16}$), so MnS does not precipitate: $[Mn^{2+}] = 0.010$ M. FeS does precipitate and the metal ion concentration is determined from its K_{sp} and the sulfide ion concentration.

$$[Fe^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{6.3\times10^{-18}}{5.2\times10^{-14}} = 1.2\times10^{-4}\ M$$

$(1.2x10^{-4}/0.010)x100\%$ = 1.2% of the iron is still in solution, so this is not a very good separation.

8.6 CHAPTER SUMMARY AND OBJECTIVES

Metal ions are Lewis acids, and the Brønsted acidity of metal ions results from the protons of the water molecules that are bound to the metal. The positive charge of the metal ion withdraws electron density from the O–H bonds and weakens them. The weaker O–H bonds make the water ligands stronger acids.

The equilibrium constant for the dissolution of a slightly soluble salt is called the solubility-product constant, K_{sp}. The molar solubility of the soluble salt can be determined from the value of the salt's K_{sp} when the anion is neutral or only slightly basic. The form of the K_{sp} in terms of the molar solubility depends only on the cation:anion ratio. The solubility of a salt decreases in the presence of a common ion due to the common-ion effect.

Precipitation of a slightly soluble salt occurs when the ion product exceeds the solubility-product constant of the salt. By careful variation of the anion concentration in a solution of several different metal ions, the ion product of one salt at a time can be made to exceed its solubility-product constant and selective precipitation can be achieved. The ions in a mixture can be separated from one another by this procedure.

The equilibrium constant for the reaction in which a complex ion is formed from the metal and the ligands is called the formation constant, K_f. Formation constants are typically quite large and the ligands of a complex ion can compete with the anions of insoluble salts for the metal ion. As a result, the solubility of a slightly soluble salt can be enhanced substantially in the presence of a ligand with which the metal forms a complex ion. The equilibrium constant of the dissolution of the salt in the presence of the ligand is obtained by combining the formation and solubility-product constants.

After studying the material presented in this chapter, you should be able to:

1. explain the acidity of metal ions and write the acid-dissociation reaction associated with the acidity (Section 8.1);
2. write the dissolution reaction of a slightly soluble salt (Section 8.2);
3. write the expression for the solubility-product constant, K_{sp}, of a given salt (Section 8.2);
4. calculate the solubility of an ionic compound given its K_{sp} value, and *vice versa* (Section 8.2);
5. calculate the solubility of an ionic compound in the presence of one of its ions (Section 8.2);
6. predict whether a precipitation will occur given the concentrations of the ions and the K_{sp} of the salt (Section 8.3);
7. determine the appropriate anion concentration to achieve maximum separation of two ions by the selective precipitation of one (Section 8.3);
8. write the formation reaction for a given complex ion (Section 8.4);
9. write the formation constant expression for a given complex ion (Section 8.4);
10. calculate the solubility of a slightly soluble salt in the presence of a substance that forms a complex ion with the metal (Section 8.5);
11. write the reaction for the dissolution of a basic salt in acid (Section 8.5);
12. determine the pH at which a solution should be saturated with H_2S to separate two cations in solution as their sulfides (Section 8.5); and
13. determine the equilibrium constant for the dissolution of a basic salt in acid (Section 8.5).

Answers to Practice Examples

8.1 $K_{sp} = 8.1\text{x}10^{-16}$

8.2 $CaSO_4$; BaF_2; Ag_2CrO_4; Ag_3PO_4

8.3 $1.4\text{x}10^{-18}$ M at pH = 9.00; $1.4\text{x}10^{-4}$ M at pH = 2.00

8.4 TlCl precipitates

8.5 $[Pb^{2+}] = 1.4\text{x}10^{-4}$ M

8.6 $Ag_3PO_4(s) + H_2O \rightleftharpoons 3Ag^{1+} + HPO_4^{2-} + OH^{1-}$

$K = (2.6\text{x}10^{-18})(0.021) = 4.5\text{x}10^{-20}$

$[Ag^{1+}] = 3x$; $[HPO4^{2-}] = x$; $[OH^{1-}] = 10^{-5.00} = 1.0\text{x}10^{-5}$

$K = (3x)^3(x)(1.0\text{x}10^{-5}) = 4.5\text{x}10^{-20}$

$x = 1.2\text{x}10^{-4}$ M, which is a much better approximation of the solubility than using K_{sp} alone. While Ag_3PO_4 is a basic salt, the pH of a saturated solution will differ somewhat from pH = 9 as assumed here.

8.7 EXERCISES

ACID-BASE EQUILIBRIA

1. Explain why $Fe(H_2O)_6^{3+}$ is a stronger acid than $Fe(H_2O)_6^{2+}$.

2. What is the conjugate base of $Al(H_2O)_6^{3+}$?

3. Write the chemical equation that explains the acidity of an aqueous $CuSO_4$ solution and calculate the pH of a 0.20 M $CuSO_4$ solution.

4. Write the chemical equation that explains the acidity of an aqueous $NiSO_4$ solution and calculate the pH of a 0.10 M $NiSO_4$ solution.

DISSOLUTION AND THE SOLUBILITY-PRODUCT CONSTANT

Refer to Appendix D for solubility product constants for the remaining exercises. Assume that all solutions are at 25 °C.

5. Write the chemical equation and the K_{sp} expression for the dissolution process of each of the following substances:

a) CoS **b)** HgI_2 **c)** $Al(OH)_3$

6. Write the chemical equation and the K_{sp} expression for the dissolution process of each of the following substances:

a) $Ba_3(PO_4)_2$ **b)** $MgNH_4PO_4$ **c)** Ag_2S

7. Express the K_{sp} expression of each of the compounds in Exercise 5 in terms of its molar solubility (x).

8. Express the K_{sp} expression of each of the compounds in Exercise 6 in terms of its molar solubility (x).

9. Write the chemical equations for the dissolution of each of the following substances and determine their molar solubilities:

a) AgI **b)** CaF_2

10. Write the chemical equations for the dissolution of each of the following substances and determine their molar solubilities:

a) $PbBr_2$ **b)** $BaSO_4$

11. The solubility of mercury(I) chloride is 0.0020 $g\cdot L^{-1}$. What is the K_{sp} of Hg_2Cl_2? Note: mercury(I) exists as Hg_2^{2+} ions.

12. The solubility of lithium phosphate is 0.39 $g\cdot L^{-1}$. What is the K_{sp} of lithium phosphate? Neglect the reaction of PO_4^{3-} with water.

13. The Au^{3+} concentration in a saturated solution of gold(III) chloride is 33 μM. What is the solubility-product constant of $AuCl_3$?

14. What is the molar solubility of silver chromate? What is the concentration of silver ions in a saturated solution of silver chromate?

15. What is the pH of saturated barium hydroxide?

16. Calculate the pH of a saturated solution of zinc hydroxide.

17. A 386-mg sample of $PbCl_2$ is washed with 10.0 mL of 0.10 M HCl. What is the maximum fraction of $PbCl_2$ that can dissolve in the wash?

18. What is the molar solubility of calcium fluoride in each of the following?

a) water **b)** 0.15 M KF **c)** 0.20 M $Ca(NO_3)_2$

19. What is the molar solubility of lead(II) sulfate in:

a) water **b)** 0.20 M $MgSO_4$ **c)** 0.11 M $Pb(NO_3)_2$

20. What is the molar solubility of $Fe(OH)_3$ in a solution buffered at pH = 5.00? What is the solubility at pH = 8.00?

PRECIPITATION AND SEPARATION OF IONS

21. Rank the following sulfides in order of decreasing solubility:

CdS CoS CuS FeS MnS

22. Rank the following sulfides in order of decreasing solubility:

CuS Cu_2S Ag_2S SnS ZnS

23. Would a precipitate form in a solution that contained the following concentrations?

a) 0.01 M NaCl and 0.02 M $Pb(NO_3)_2$

b) 1.0 mM $AgNO_3$ and 1 μM NaCl

c) 5.0 mM KI and 2.0 mM $Pb(NO_3)_2$

24. The Co^{2+} and Cu^{2+} ions in a solution that is 0.01 M each are to be separated by precipitation of CuS.

a) What sulfide ion concentration (to one significant figure) should be used to obtain optimum separation?

b) What is the $[Cu^{2+}]$ after precipitation at this sulfide ion concentration?

25. Construct the reaction table for mixing 20.0 mL of 0.124 M $Ca(NO_3)_2$ and 30.0 mL of 0.0852 M KF.

a) What mass of precipitate forms?

b) What is the concentration of the excess reactant at equilibrium?

c) What is the concentration of the limiting reactant at equilibrium?

26. Construct the reaction table for mixing 55 mL of 0.10 M $AgNO_3$ and 75 mL of 0.20 M K_2CrO_4.

- **a)** What mass of precipitate forms?
- **b)** What is the concentration of the excess reactant at equilibrium?
- **c)** What is the concentration of the limiting reactant at equilibrium?

27. Construct the reaction table for mixing 35.0 mL of 0.175 M $AgNO_3$ and 25.0 mL of 0.200 M KI.

- **a)** What mass of AgI forms?
- **b)** What is the concentration of the excess reactant at equilibrium?
- **c)** What is the concentration of the limiting reactant at equilibrium?

28. To what pH (to 0.1 pH unit) should a solution that is 0.020 M each in Ca^{2+} and Cd^{2+} ions be adjusted in order to best separate ions by precipitation of one of the hydroxides? What are the concentrations of the metal ions after the pH is adjusted to this value?

29. To what pH (to 0.1 pH unit) should a solution that is 0.030 M in Pb^{2+} and 0.030 M in Mg^{2+} be buffered in order to obtain maximum separation of the ions by precipitation of one of the hydroxides? What are the concentrations of the metal ions after the solution is buffered at this pH?

30. An acidic solution is 5 mM in each of the following metal ions: Co^{2+}, Ba^{2+}, Cu^{2+} and Zn^{2+}.

- **a)** Which of the metals precipitate as their hydroxides at pH = 6.00?
- **b)** Which of the metals precipitate as their hydroxides at pH = 8.00?
- **c)** At what pH does $Ba(OH)_2$ begin to precipitate?

31. Indicate whether or not a precipitate would form when the following solutions are mixed:

- **a)** 5.0 mL of 0.10 M HCl and 5.0 mL of 1.0 mM $Pb(NO_3)_2$
- **b)** 5.0 mL of 0.10 M KOH and 5.0 mL of 0.10 mM $Mn(NO_3)_2$
- **c)** 5.0 mL of 0.10 M Na_2SO_4 and 5.0 mL of 0.10 mM $Ba(NO_3)_2$

32. What $[I^{1-}]$ is needed to start precipitation of AgI from a saturated solution of AgCl?

33. Solid NaCl is added to a solution that is 0.10 M in Pb^{2+} and 0.10 M in Ag^{1+}.

- **a)** Which compound precipitates first?
- **b)** What is the concentration of the first ion precipitated when the second ion starts to precipitate?

COMPLEX IONS

Refer to Table 8.3 for formation constants

34. What is the concentration of free Cu^{2+} in a solution made by mixing 25.0 mL of 1.00 M $CuSO_4$ and 1.00 L of 0.500 M NH_3?

35. What is the concentration of free Ni^{2+} in a solution made by mixing 10.0 mL of 0.652 M $NiSO_4$ and 475 mL of 2.00 M NH_3?

36. What is the free silver ion concentration in a 0.24 M $Ag(NH_3)_2^{1+}$ solution?

37. What is the free cyanide ion concentration in a 0.10 M $Fe(CN)_6^{3-}$ solution?

COMPETING EQUILIBRIA

38. Use the data in Table 8.3 and Appendix D to determine the equilibrium constants for the following reactions.

- **a)** $AgCN(s) + CN^{1-} \rightleftharpoons Ag(CN)_2^{1-}$
- **b)** $CuS(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+} + S^{2-}$

39. Use the data in Table 8.3 and Appendix D to determine the equilibrium constants for the following reactions.

- **a)** $Fe(OH)_2(s) + 6CN^{1-} \rightleftharpoons Fe(CN)_6^{4-} + 2OH^{1-}$
- **b)** $Ag_2S(s) + 4NH_3(aq) \rightleftharpoons 2Ag(NH_3)_2^{1+} + S^{2-}$

40. Consider the dissolution of CaF_2 in hydrochloric acid.

- **a)** Write the reaction for the dissolution.
- **b)** What is the equilibrium constant for the reaction?

41. Consider the dissolution of $Al(OH)_3$ in hydrochloric acid.

- **a)** Write the reaction for the dissolution.
- **b)** What is the equilibrium constant for the reaction?

42. The pH of a solution that is 0.05 M in Zn^{2+} is slowly raised.

- **a)** At what pH does $Zn(OH)_2$ (K_{sp}= $4.5x10^{-17}$) begin to precipitate?
- **b)** Refer to Table 8.3 and determine the equilibrium constant for the reaction: $Zn(OH)_2(s) + 2OH^{1-}(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$
- **c)** At what pH does the solid $Zn(OH)_2$ dissolve again?

43. At what pH should a solution be saturated with H_2S to separate 0.020 M Pb^{2+} and Zn^{2+}? What are the concentrations of the ions after separation?

44. At what pH should a solution be saturated with H_2S to separate 0.010 M Co^{2+} and Fe^{2+}? What are the concentrations of the ions after separation?

MISCELLANEOUS PROBLEMS

45. Indicate whether each of the following salts produces an acidic, a neutral, or a basic solution in water.

$Fe(NO_3)_3$
$ZnSO_4$
KF
KCl
$AlBr_3$
NH_4Cl

46. For which of the following compounds does solubility increase as the pH of the solution is lowered?

$CaCO_3$
ZnS
PbI_2
$AgBr$
$PbSO_3$
$Mg(OH)_2$

47. Consider the following equilibrium:

$$PbI_2(s) + 3OH^{1-}(aq) \rightleftharpoons Pb(OH)_3^{1-}(aq) + 2I^{1-}(aq)$$

Use LeChâtelier's Principle to predict the effect on the solubility of PbI_2 of each of the following:

a) H^{1+} (H_3O^{1+}) ions are added.
b) The concentration of I^{1-} is decreased.
c) The amount of PbI_2 is increased.
d) The pH of the solution is increased.

48. To image the upper gastrointestinal (GI) tract for medical evaluation of intestinal disorders, a suspension of $BaSO_4$ is ingested. The heavy element Ba absorbs X-rays so that the soft tissue of the intestine becomes visible to X-ray imaging. In order to minimize the physiological absorption of Ba, which is toxic, the suspension is frequently prepared using a Na_2SO_4 solution. Calculate the difference in the Ba^{2+} solubility in a solution of pure water and a solution of 0.10 M Na_2SO_4. (This concentration has approximately the same osmotic balance as cellular fluids.) The K_{sp} of $BaSO_4$ is 1.1×10^{-10}.

49. In a foundry that produces plumbing fittings, the brass components are cleaned with nitric acid, which dissolves and oxidizes the copper and zinc of brass resulting in a solution of Cu^{2+} and Zn^{2+}. Given that K_{sp} of $Cu(OH)_2$ is 2.2×10^{-20} and K_{sp} of $Zn(OH)_2$ is 4.5×10^{-17}, determine the pH to which the effluent must be adjusted to precipitate the copper and zinc hydroxides such that the levels of Cu and Zn in the water are below the federal clean water standards of 50. ppm? Are the solubilities of these two species sufficiently different such that the copper and zinc could be separated during this neutralization process? Assume the density of the water sample is 1.00 g·cm^{-3}.

50. Kidney stones are caused by the precipitation of either calcium oxalate, $Ca(C_2O_4)$, or calcium phosphate, $Ca_3(PO_4)_2$, in the kidneys. If the normal concentration of Ca^{2+} in the kidneys is 2.5 mM, at what concentration of oxalate ion will kidney stones begin to form? K_{sp} of $Ca(C_2O_4) = 2.3 \times 10^{-9}$.

51. Explain why the solubility of PbF_2 increases with the addition of HNO_3, but the solubility of $PbCl_2$ is unaffected.

52. The compound hydroxyapatite, $Ca_5(PO_4)_3OH$, forms the hard enamel layer that coats our teeth. Drinking fluorinated water, or brushing with fluorinated tooth paste, replaces some of the OH^{1-} ions with F^{1-}. The two dissolution reactions

$$Ca_5(PO_4)_3OH \rightleftharpoons 5Ca^{2+} + 3PO_4^{3-} + OH^{1-} \quad \text{and}$$

$$Ca_5(PO_4)_3F \rightleftharpoons 5Ca^{2+} + 3PO_4^{3-} + F^{1-}$$

have comparable equilibrium constants. Which of the two materials, $Ca_5(PO_4)_3OH$ or $Ca_5(PO_4)_3F$, is predicted to be more resistant to the weak acids formed during food digestion? (Hint: What effect do the relative base strengths of the hydroxide and fluoride ions have?)

53. A sample of drinking water was found to contain 500 ppm of Fe^{3+}, which is well above clean water levels. How much phosphate ion must be added to 1000 L of the water supply in order to precipitate excess iron from the solution so that the final Fe^{3+} concentration is less than 50. ppm? Assume the density of the water sample is 1.00 g·cm^{-3}.