

Chapter 18: Precipitation and Complexation Equilibria

Figure Ideas:

Chapter 18

- 18.1 Solubility Equilibria and K_{sp}
- 18.2 Using K_{sp} In Calculations
- 18.3 Lewis Acid–Base Complexes and Complex Ion Equilibria
- 18.4 Simultaneous Equilibria

Chapter In Context

This is the final chapter in our study of chemical equilibria. After studying acid–base equilibria in some depth, we now turn to equilibria involving sparingly soluble compounds and the equilibria of Lewis acid–base complexes. You were first introduced to sparingly soluble compounds in Chapter 5 when we covered precipitation reactions and soluble and insoluble ionic compounds. We will discover in this chapter that even insoluble ionic compounds dissolve in water to a small extent, and that this solubility can be affected by a variety of chemical species. Lewis acids and bases were briefly introduced in Chapter 16. Here we will look at equilibria involving Lewis acid–base complexes and how they can be used to influence the solubility of ionic compounds.

Need a little intro text here

- **Biology:** Biological systems are rife with examples of precipitation and complexation chemistry. The formation of seashells and coral involve precipitation of calcium carbonate, CaCO_3 . The transport of oxygen in our bodies depends on the complexation of heme Fe atoms with O_2 molecules. The transport of iron itself in the body involves complexation of Fe^{2+} ions by special iron–transport proteins. *(need to check to see if that's true, or if that's what they are called–by) (also, look into radiation treatment where iodine is used to treat radiation poisoning, and also heavy metal contamination treatment, where chelating agents are used to bind up those nasty ions).*
- **Environmental Studies/Industry:** The formation of caves and the interesting structures within them is the result of a combination of precipitation reactions coupled with Lewis acid–base reactions and Brønsted–Lowry acid–base reactions. Caves form when acidic water encounters limestone (CaCO_3) rock formations underground. The source of acid in the water is most often CO_2 formed by decomposing organic matter in the overlying soil. The CO_2 undergoes a Lewis acid–base reaction to form carbonic acid, which undergoes a Brønsted–Lowry acid–base reaction with carbonate ions in the limestone. This leads to dissolution and formation of the cave.
- **In Your World:** A common “additive” to canned food is the sodium salt of ethylenediaminetetraacetic acid, abbreviated as EDTA. EDTA is a powerful complexing agent and binds metal ions that might form from reaction of the food contents with the metal can. The uncomplexed metal ion leads to a metallic taste, whereas the metal ion complexed with EDTA does not. A clever use of complexation chemistry is the activity of household “floor wax.” The goal of floor wax is to provide a coating on the floor that is tough and attractive but that can also be removed when desired. Floor wax uses a combination of polymers that act as complexing agents and metal ions that serve to crosslink multiple polymer strands.

Chapter Goals

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18.1 Solubility Equilibria and K_{sp}



OWL Opening Exploration 18.1

As you saw in Opening Exploration, ionic compounds we labeled as “insoluble in water” in Chapter 5 actually dissolve in water to a small extent. The solubility of an ionic compound is determined by measuring the amount of a solid that dissolves in a quantity of water. Solubility values are reported in g/100 mL, g/L, or mol/L (also called molar solubility).

$$\text{Solubility of AgCl} = 1.9 \times 10^{-4} \text{ g/100 mL} = 1.9 \times 10^{-3} \text{ g/L} = 1.3 \times 10^{-5} \text{ mol/L}$$

In Chapter 5, you learned how to predict the solubility of an ionic compound based on a set of solubility rules (Table 5.X). These solubility rules are based on the measured solubility of ionic compounds, where an insoluble compound is defined as having a solubility less than about 0.01 mol/L. In this chapter we will work with experimental solubility values to more accurately describe the solubility of ionic compounds.

EXAMPLE PROBLEM: Solubility units

The molar solubility of silver sulfate is 0.0144 mol/L. Express the solubility in units of g/L and calculate the concentration of Ag^+ in a saturated silver sulfate solution.

SOLUTION:

Use the molar mass of silver sulfate (Ag_2SO_4) to convert between solubility units.

$$\frac{0.0144 \text{ mol Ag}_2\text{SO}_4}{1\text{L}} \cdot \frac{311.8 \text{ g}}{1 \text{ mol Ag}_2\text{SO}_4} = 4.49 \text{ g/L}$$

Use the molar solubility to calculate the Ag^+ concentration in a saturated Ag_2SO_4 solution.

$$\frac{0.0144 \text{ mol Ag}_2\text{SO}_4}{1\text{L}} \cdot \frac{2 \text{ mol Ag}^+}{1 \text{ mol Ag}_2\text{SO}_4} = 0.0288 \text{ M Ag}^+$$



OWL Example Problems 18.2 Solubility Units

Table 18.1 K_{sp} Values for Some Ionic Compounds

Table to come

The Solubility Product Constant

In Chapter 13, we described a solution as saturated when no additional solid could be dissolved in a solvent. In such a solution, a dynamic equilibrium occurs between the hydrated ions and the undissolved solid. For PbCl_2 , for example, the equilibrium process is represented



Notice that the equilibrium is written as a dissolution process (solid as a reactant and aqueous ions as products) and that the pure solid does not appear in the equilibrium constant expression. Because the equilibrium constant expression for dissolution reactions are always expressed as the product of the ion concentrations, the equilibrium constant is given the special name **solubility product constant**, and the symbol K_{sp} .

$$K_{sp}(\text{PbCl}_2) = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = 1.7 \times 10^{-5}$$

The K_{sp} values for some ionic compounds are shown in Table 18.1. Lead chloride is a relatively soluble ionic compound when compared to the other compounds in this table. Notice that the values range from around 10^{-4} to very small values around 10^{-50} .

EXAMPLE PROBLEM: Solubility Product Constant Expressions

Write the K_{sp} expression for each of the following sparingly soluble compounds.

- (a) $PbSO_4$
 (b) $Zn_3(PO_4)_2$.

SOLUTION:

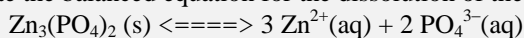
- (a) **Step 1.** Write the balanced equation for the dissolution of the ionic compound.



Step 2. Write the equilibrium constant expression. Remember that the solid, $PbSO_4$, does not appear in the equilibrium constant expression.

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

- (b) **Step 1.** Write the balanced equation for the dissolution of the ionic compound.



Step 2. Write the equilibrium constant expression. Remember that the solid, $Zn_3(PO_4)_2$, does not appear in the equilibrium expression and that each ion concentration is raised to the power of the stoichiometric coefficient in the balanced equation.

$$K_{sp} = [Zn^{2+}]^3[PO_4^{3-}]^2$$



OWL Example Problems

18.3 *Solubility Product Constant Expressions: Tutor*

18.4 *Solubility Product Constant Expressions*

Determining K_{sp} Values

Solubility product equilibrium constants are determined from measured equilibrium ion concentrations or directly from the solubility of an ionic compound, as shown in the following examples.

EXAMPLE PROBLEM: K_{sp} calculation (1)

The Pb^{2+} concentration in a saturated solution of lead chloride is measured and found to be 0.016 M. Use this information to calculate the K_{sp} for lead chloride.

SOLUTION:

- Step 1.** Write the balanced equation for the equilibrium and the K_{sp} expression.



Step 2. Use the lead concentration to determine the chloride ion concentration at equilibrium. Notice that for this salt, the anion concentration is twice the cation concentration ($[Cl^{-}] = 2 \times [Pb^{2+}]$)

$$[Cl^{-}] = \frac{0.016 \text{ mol } Pb^{2+}}{1 \text{ L}} \cdot \frac{2 \text{ mol } Cl^{-}}{1 \text{ mol } Pb^{2+}} = 0.032 \text{ M}$$

- Step 3.** Use the equilibrium concentrations to calculate K_{sp} .

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2 = (0.016 \text{ M})(0.032 \text{ M})^2 = 1.6 \times 10^{-5}$$

Alternately, you can use the relationship between the anion and cation concentrations for this salt ($[Cl^{-}] = 2 \times [Pb^{2+}]$) to calculate K_{sp} :

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2 = [Pb^{2+}](2 \times [Pb^{2+}])^2 = 4 \times [Pb^{2+}]^3 = 4(0.016 \text{ M})^3 = 1.6 \times 10^{-5}$$



OWL Example Problems

18.5 *K_{sp} Calculation (1): Tutor*

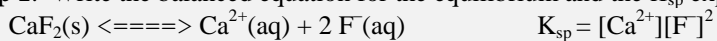
18.56 *K_{sp} Calculation (1)*

EXAMPLE PROBLEM: K_{sp} calculation (2)

The solubility of calcium fluoride, CaF_2 , is 0.0167 g/L. Use this information to calculate K_{sp} for calcium fluoride.

SOLUTION:

- Step 1.** Write the balanced equation for the equilibrium and the K_{sp} expression.



Example problem, continued

Step 2. Use solubility to calculate the ion concentrations at equilibrium.

Calcium fluoride dissolves to an extent of 0.0167 g per L of solution. In terms of calcium ion concentration,

$$[\text{Ca}^{2+}] = \frac{0.0167 \text{ g CaF}_2}{1 \text{ L}} \cdot \frac{1 \text{ mol CaF}_2}{78.08 \text{ g CaF}_2} \cdot \frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol CaF}_2} = 2.14 \times 10^{-4} \text{ M}$$

The fluoride ion concentration is equal to twice the calcium ion concentration.

$$[\text{F}^-] = \frac{2.14 \times 10^{-4} \text{ mol Ca}^{2+}}{1 \text{ L}} \cdot \frac{2 \text{ mol F}^-}{1 \text{ mol Ca}^{2+}} = 4.28 \times 10^{-4} \text{ M}$$

Step 3. Use the equilibrium concentrations to calculate K_{sp} .

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = (2.14 \times 10^{-4})(4.28 \times 10^{-4})^2 = 3.92 \times 10^{-11}$$

Alternately, you can use the relationship between the anion and cation concentrations for this salt ($[\text{F}^-] = 2 \times [\text{Ca}^{2+}]$) to calculate K_{sp} .

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = [\text{Ca}^{2+}](2 \times [\text{Ca}^{2+}])^2 = 4 \times [\text{Ca}^{2+}]^3 = 4(2.14 \times 10^{-4} \text{ M})^3 = 3.92 \times 10^{-11}$$



OWL Example Problems
18.7 K_{sp} Calculation (2)

18.2 Using K_{sp} In Calculations



OWL Opening Exploration
18.8 Exploring the Solubility Product Constant

Solubility product constants allow us to estimate the solubility of a salt, to determine the relative solubility of salts, to identify solutions as saturated or unsaturated, and to predict if a precipitate will form when two or more salt solutions are combined.

Estimating Solubility

The solubility of a salt in pure water is defined as the amount of solid that will dissolve per liter of solution (g/L or mol/L). As we will see later, many secondary reactions can influence the solubility of an ionic compound. Because of this, when we use K_{sp} values to estimate the solubility of an ionic compound, we assume that none of these secondary reactions are taking place.

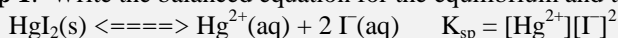
Solubility can be calculated from K_{sp} using the same techniques we have applied to other equilibrium systems (see Section 16.4), as shown in the following example.

EXAMPLE PROBLEM: Solubility

Calculate the solubility of mercury(II) iodide, HgI_2 , in units of grams per liter. $K_{\text{sp}}(\text{HgI}_2) = 4.0 \times 10^{-29}$

SOLUTION:

Step 1. Write the balanced equation for the equilibrium and the K_{sp} expression.



Step 2. Set up an ICE table where x = amount of HgI_2 that dissolves in solution (x = molar solubility of HgI_2). We will assume that the HgI_2 dissociates completely when it dissolves in water and that no solid has dissolved initially.

	$\text{HgI}_2(\text{s})$	\rightleftharpoons	$\text{Hg}^{2+}(\text{aq})$	$+$	$2 \text{I}^{-}(\text{aq})$
Initial (M)	0		0		0
Change (M)	+x		+2x		+2x
Equilibrium (M)	x		2x		2x

Example problem, continued

Step 3. Substitute the equilibrium concentrations into the K_{sp} expression and solve for x .

$$K_{sp} = [\text{Hg}^{2+}][\text{I}^-]^2 = (x)(2x)^2 = 4x^3$$

$$x = \text{solubility} = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4.0 \times 10^{-29}}{4}} = 2.2 \times 10^{-10} \text{ M}$$

Step 4.

Use x , the molar solubility of HgI_2 , to calculate solubility in units of g/L.

$$\frac{2.2 \times 10^{-10} \text{ mol HgI}_2}{1 \text{ L}} \cdot \frac{454 \text{ g HgI}_2}{\text{mol HgI}_2} = 1.0 \times 10^{-8} \text{ g/L}$$

*OWL Example Problems*

18.9 Solubility: Tutor

18.10 Solubility

The solubility of any ionic compound can be calculated using this method. It is useful to recognize the relationship between molar solubility (x in the preceding example) and K_{sp} as a function of the salt stoichiometry. These relationships are summarized in Table 18.2.

Table 18.2 Relationship between Molar Solubility and K_{sp}

General formula	Example	K_{sp} expression	K_{sp} as a function of molar solubility (x)	Solubility (x) as a function of K_{sp}
MY	AgCl	$K_{sp} = [\text{M}^+][\text{Y}^-]$	$K_{sp} = (x)(x) = x^2$	$x = \sqrt{K_{sp}}$
MY ₂	HgI ₂	$K_{sp} = [\text{M}^{2+}][\text{Y}^-]^2$	$K_{sp} = (x)(2x)^2 = 4x^3$	$x = \sqrt[3]{\frac{K_{sp}}{4}}$
MY ₃	BiI ₃	$K_{sp} = [\text{M}^{3+}][\text{Y}^-]^3$	$K_{sp} = (x)(3x)^3 = 27x^4$	$x = \sqrt[4]{\frac{K_{sp}}{27}}$
M ₂ Y ₃	Fe ₂ (SO ₄) ₃	$K_{sp} = [\text{M}^{3+}]^2[\text{Y}^{2-}]^3$	$K_{sp} = (2x)^2(3x)^3 = 108x^5$	$x = \sqrt[5]{\frac{K_{sp}}{108}}$
M ₃ Y ₂	Ca ₃ (PO ₄) ₂	$K_{sp} = [\text{M}^{2+}]^3[\text{Y}^{3-}]^2$	$K_{sp} = (3x)^3(2x)^2 = 108x^5$	$x = \sqrt[5]{\frac{K_{sp}}{108}}$

As shown in Table 18.2, the solubility of an ionic compound is related to both its K_{sp} and its stoichiometry. When comparing the solubility of two or more ionic compounds, both factors must be considered.

For example, both silver chloride (AgCl , $K_{sp} = 1.8 \times 10^{-10}$) and calcium chloride (CaCO_3 , $K_{sp} = 4.8 \times 10^{-9}$) have a 1:1 cation to anion ratio. Because they have same stoichiometry, K_{sp} alone can be used to determine the relative solubility of these compounds in water. Calcium chloride is therefore more soluble in water than silver chloride because $K_{sp}(\text{CaCO}_3)$ is greater than $K_{sp}(\text{AgCl})$.

When comparing the relative solubility of silver chloride (AgCl , $K_{sp} = 1.8 \times 10^{-10}$) and silver dichromate (Ag_2CrO_4 , $K_{sp} = 9.0 \times 10^{-12}$), it is not possible to only use K_{sp} values. The two salts do not have same stoichiometry (Table 18.2) and thus the molar solubility must be calculated for each salt. Although silver chloride has the greater K_{sp} value, the calculated solubility shows that silver dichromate is more soluble in water. The solubility of Ag_2CrO_4 in water (1.3×10^{-4} mol/L) is about 10 times greater than the solubility of AgCl (1.3×10^{-5} mol/L).

EXAMPLE PROBLEM: Relative Solubility

Determine the relative solubility of the following lead compounds: CaSO_4 ($K_{\text{sp}} = 2.4 \times 10^{-5}$), Ca(OH)_2 ($K_{\text{sp}} = 7.9 \times 10^{-6}$), and CaF_2 ($K_{\text{sp}} = 3.9 \times 10^{-11}$).

SOLUTION:

Because the three compounds do not have the same stoichiometry, the solubility must be calculated for each one. Using the relationships shown in Table 18.2,

$$\text{CaSO}_4: \quad \text{solubility} = x = \sqrt{K_{\text{sp}}} = \sqrt{2.4 \times 10^{-5}} = 4.8 \times 10^{-3} \text{ mol/L}$$

$$\text{Ca(OH)}_2: \quad \text{solubility} = x = \sqrt[3]{\frac{K_{\text{sp}}}{4}} = \sqrt[3]{\frac{7.9 \times 10^{-6}}{4}} = 0.013 \text{ mol/L}$$

$$\text{CaF}_2: \quad \text{solubility} = x = \sqrt[3]{\frac{K_{\text{sp}}}{4}} = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} = 2.1 \times 10^{-4} \text{ mol/L}$$

Ca(OH)_2 is the most soluble and CaF_2 is the least soluble of the three compounds.

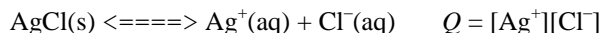


OWL Example Problems
18.11 Relative Solubility

Predicting if a Solid Will Precipitate or Dissolve

In Chapter 15, we used Q , the reaction quotient, to determine whether or not a system is at equilibrium. The reaction quotient can also be used with precipitation equilibria to determine if a solution is at equilibrium and to answer questions such as, for example, if 3 g of solid silver sulfate is added to 250 mL of water, will the solid dissolve completely?

Recall that the reaction quotient has the same form as the equilibrium expression, but differs in that the concentrations may or may not be equilibrium concentrations. For example, the reaction quotient for the silver chloride equilibrium is written



Comparing Q to K_{sp} for a specific solubility equilibrium allows us to determine if a system is at equilibrium. There are three possible relationships between the two values:

- $Q = K_{\text{sp}}$ The system is at equilibrium and the solution is saturated. No further change in ion concentration will occur and no additional solid will dissolve or precipitate.
- $Q < K_{\text{sp}}$ The system is not at equilibrium and the solution is unsaturated. The ion concentration is too small, so additional solid will dissolve until $Q = K_{\text{sp}}$. If no additional solid is present, the solution will remain unsaturated.
- $Q > K_{\text{sp}}$ The system is not at equilibrium and the solution is supersaturated. The ion concentration is too large, so additional solid will precipitate until $Q = K_{\text{sp}}$.



OWL Concept Exploration
18.12 Q and K_{sp} : Simulation

Flashback

15.3 Using Equilibrium Constants in Calculations



15.X
Calculating the Reaction Quotient

Flashback

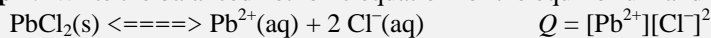
14.X Solutions: Definitions

EXAMPLE PROBLEM: Q and K_{sp}

If 5.0 mL of 1.0×10^{-3} M NaCl is added to 1.0 mL of 1.0×10^{-3} M $\text{Pb}(\text{NO}_3)_2$, will solid PbCl_2 ($K_{sp} = 1.7 \times 10^{-5}$) precipitate? If a precipitate will not form, what chloride ion concentration will cause a precipitate of lead chloride to form?

SOLUTION:

Step 1. Write the balanced net ionic equation for the equilibrium and the Q expression.



Step 2. Calculate the concentration of Pb^{2+} and Cl^{-} . The total volume of the solution is 6.0 mL.

$$[\text{Pb}^{2+}] = \frac{(0.0010 \text{ L})(1.0 \times 10^{-3} \text{ mol Pb}^{2+}/\text{L})}{0.0060 \text{ L}} = 1.7 \times 10^{-4} \text{ M}$$

$$[\text{Cl}^{-}] = \frac{(0.0050 \text{ L})(1.0 \times 10^{-3} \text{ mol Cl}^{-}/\text{L})}{0.0060 \text{ L}} = 8.3 \times 10^{-4} \text{ M}$$

Step 3. Substitute the ion concentrations into the equilibrium expression and calculate Q .

$$Q = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = (1.7 \times 10^{-4})(8.3 \times 10^{-4})^2 = 1.2 \times 10^{-10}$$

Step 4. Compare Q and K_{sp} .

In this case, Q (1.2×10^{-10}) is less than K_{sp} (1.7×10^{-5}) and the solution is unsaturated. Lead chloride will not precipitate.

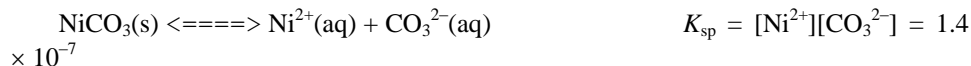
Step 5. Determine the chloride ion concentration required for lead chloride precipitation. Substitute the lead ion concentration into the K_{sp} expression to calculate the chloride ion concentration in a saturated solution of lead chloride.

$$\begin{aligned} K_{sp} &= [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \\ 1.7 \times 10^{-5} &= (1.7 \times 10^{-4})[\text{Cl}^{-}]^2 \\ [\text{Cl}^{-}] &= 0.32 \text{ M} \end{aligned}$$

The chloride ion concentration in a saturated solution of lead chloride (where $[\text{Pb}^{2+}] = 1.7 \times 10^{-4}$) is equal to 0.32 M. If $[\text{Cl}^{-}] > 0.32 \text{ M}$, the solution will be supersaturated ($Q > K_{sp}$), and a precipitate of lead chloride will form.

*OWL Example Problems*18.13 Q and K_{sp} : Tutor18.14 Q and K_{sp} **The Common-Ion Effect**

As we saw in Chapter 17, adding a chemical species that is common to an existing equilibrium (a common ion) will cause the equilibrium position to shift, forming additional reactant or product. Because solubility equilibria are always written so that the aqueous ions are reaction products, adding a common ion causes the equilibrium to shift to the left (towards the formation of additional reactant), decreasing the solubility of the ionic compound. For example, consider the sparingly soluble salt nickel(II) carbonate, NiCO_3 .



When an ion common to the equilibrium is added, as NiCl_2 or Na_2CO_3 , for example, the equilibrium shifts to the left and additional solid nickel(II) carbonate precipitates from solution. The common ion effect plays a role in the solubility of ionic compounds in natural systems and even in most laboratory setting. For example, when examining how much PbCl_2 will dissolve in a natural water system, additional Cl^{-} could be present from dissolved NaCl. The effect of a common ion on the solubility of an ionic compound is demonstrated in the following example problem.

*OWL Concept Exploration*18.15 *The Common Ion Effect: Simulation*

EXAMPLE PROBLEM: K_{sp} and the Common Ion Effect

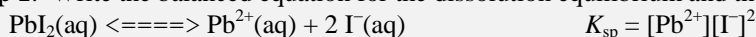
Calculate the solubility of PbI_2 (a) in pure water and (b) in a solution in which $[\text{I}^-] = 0.15 \text{ M}$.

SOLUTION:

(a) Use the relationship between solubility and K_{sp} from Table 18.2 to calculate the solubility of PbI_2 in pure water.

$$x = \text{solubility of PbI}_2 \text{ in pure water} = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{8.7 \times 10^{-9}}{4}} = 1.3 \times 10^{-3} \text{ mol/L}$$

(b) **Step 1.** Write the balanced equation for the dissolution equilibrium and the K_{sp} expression for PbI_2 .



Step 2. Set up an *ICE* table, where the variable y represents the amount of PbI_2 that dissociates in 0.15 M I^- . The variable y also represents the molar solubility of PbI_2 in the presence of the common ion.

	$\text{PbI}_2(\text{aq}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$	
Initial (M)	0	0.15
Change (M)	+y	+2y
Equilibrium (M)	y	0.15 + 2y

Step 3. Substitute the equilibrium concentrations into the K_{sp} expression and solve for y . Because the addition of a common ion will shift the equilibrium to the left and decrease the solubility of PbI_2 , it is reasonable to assume that $2y \ll 0.15$.

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = (y)(0.15 + 2y)^2 \approx (y)(0.15)^2$$

$$y = \text{solubility of PbI}_2 \text{ in } 0.15 \text{ M I}^{-} = \frac{K_{sp}}{(0.15)^2} = \frac{8.7 \times 10^{-9}}{(0.15)^2} = 3.9 \times 10^{-7} \text{ mol/L}$$

Note that our assumption ($2y \ll 0.15$) was valid. The solubility of PbI_2 has decreased from $1.3 \times 10^{-3} \text{ M}$ in pure water to $3.9 \times 10^{-7} \text{ M}$ in the presence of a common ion, the iodide ion. The presence of a common ion will always decrease the solubility of a sparingly soluble salt.

*OWL Example Problems*18.16 K_{sp} and the Common Ion Effect: Tutor18.17 K_{sp} and the Common Ion Effect**18.3 Lewis Acid–Base Chemistry and Complex Ion Equilibria***OWL Opening Exploration*

18.19 Acid-Base Models

In Chapter 16 we defined three types of acids and bases, Arrhenius, Brønsted-Lowry, and Lewis. The two most important and most commonly used acid-base models are Brønsted-Lowry and Lewis. The chemistry of Brønsted-Lowry acids and bases was covered in Chapters 16 and 17.

In Lewis acid–base chemistry, a Lewis base is defined as a species that donates a lone pair of electrons to a Lewis acid, which is defined as an electron-pair acceptor. The product of a Lewis acid-base reaction is a **Lewis acid-base adduct** (or **acid-base complex**). The new bond formed between the Lewis acid and Lewis base is called a **coordinate-covalent bond** because both bonding electrons come from a single species, the Lewis base. The components of Brønsted-Lowry and Lewis acid-base reactions are summarized in Table 18.3

Flashback

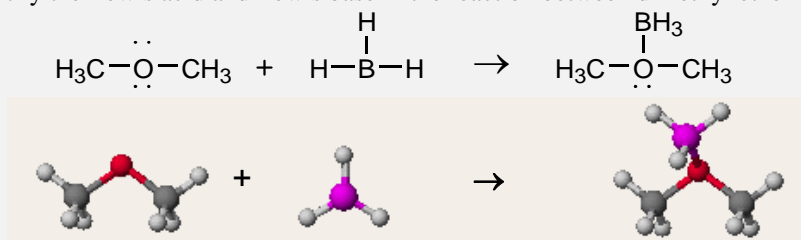
16.1 Introduction to Acids and Bases

Table 18.3 Brønsted-Lowry and Lewis Acid-Base Models

Acid-Base Model	Acid definition	Base definition	Reaction product(s)
Brønsted-Lowry	proton donor	proton acceptor	Conjugate base and conjugate acid
Lewis	electron-pair acceptor	electron-pair donor	Lewis acid-base complex

EXAMPLE PROBLEM: Lewis Acids and Bases

Identify the Lewis acid and Lewis base in the reaction between dimethyl ether (CH_3OCH_3) and borane (BH_3).

**SOLUTION:**

Dimethyl ether can act as a Lewis base because it can donate an electron pair to a Lewis acid. Borane has an empty, unhybridized $2p$ orbital that can accept an electron pair from a Lewis base, so it is a Lewis acid.



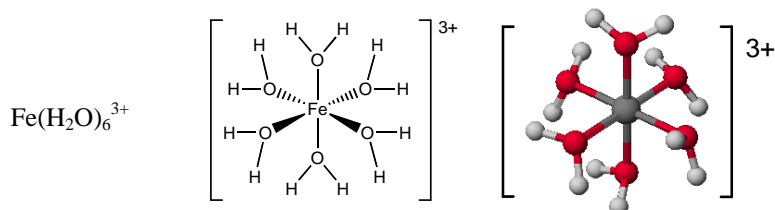
OWL Example Problems

18.20 *Lewis Acids and Bases: Exercise*

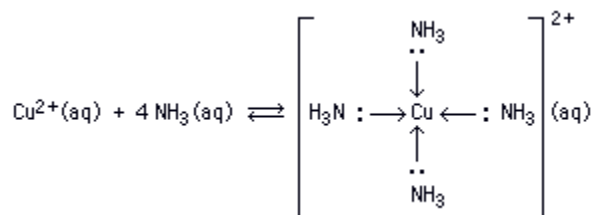
18.21 *Lewis Acids: Tutor*

18.22 *Lewis Bases: Tutor*

When a Lewis acid-base complex carries an overall charge, it is called a **complex ion**. You have encountered complex ions in many aqueous chemical reactions. For example, when an iron(III) ion is written as $\text{Fe}^{3+}(\text{aq})$, this represents the aqueous ion surrounded by up to six water molecules. The water molecules act as Lewis bases and the iron(III) ion is a Lewis acid.



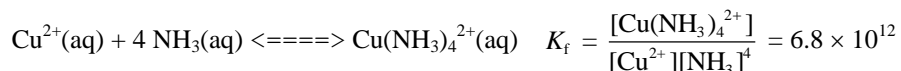
Consider the reaction Lewis acid-base reaction between aqueous Cu^{2+} ions and NH_3 .



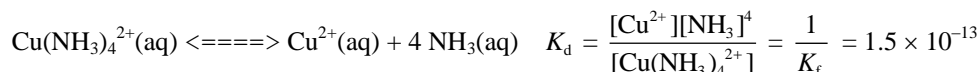
The copper-ammonia complex ion is composed of a central Cu^{2+} ion bonded to four NH_3 molecules. In this example, Cu^{2+} is the Lewis acid and the four ammonia molecules are Lewis bases. Notice that arrows (\rightarrow) are used to indicate the formation of four coordinate-covalent bonds in which the bonding electrons come from the Lewis base. It is very common to find Lewis acid-base complexes in which one Lewis acid species (such as a metal cation) is coordinated to multiple Lewis base species.

Complex Ion Equilibria

Chemical equilibria involving complex ions can be written to show the formation or dissociation of a complex ion. When written to show the formation of a complex ion from the reaction of a Lewis acid with a Lewis base, the equilibrium constant is given the special name **formation constant**, and the symbol K_f . For the complex ion, $\text{Cu}(\text{NH}_3)_4^{2+}$,



When written in the reverse reaction, the equilibrium constant is called a **dissociation constant**, K_d . The dissociation constant is equal to the inverse of K_f ($K_d = 1/K_f$)



Many formation reactions are strongly product-favored and have large K_f values. Table 18.4 summarizes the values of K_f and K_d for a number of common complex ions.

Table 18.4 Formation Constants for Some Complex Ions

Formation Equilibrium	K_f
$\text{Ag}^+ + 2 \text{Br}^- \rightleftharpoons [\text{AgBr}_2]^-$	1.3×10^7
$\text{Ag}^+ + 2 \text{Cl}^- \rightleftharpoons [\text{AgCl}_2]^-$	2.5×10^5
$\text{Ag}^+ + 2 \text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$	5.6×10^{18}
$\text{Ag}^+ + 2 \text{S}_2\text{O}_3^{2-} \rightleftharpoons [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	2.0×10^{13}
$\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$	1.6×10^7
$\text{Al}^{3+} + 6 \text{F}^- \rightleftharpoons [\text{AlF}_6]^{3-}$	5.0×10^{-3}
$\text{Al}^{3+} + 4 \text{OH}^- \rightleftharpoons [\text{Al}(\text{OH})_4]^-$	7.7×10^{35}
$\text{Au}^+ + 2 \text{CN}^- \rightleftharpoons [\text{Au}(\text{CN})_2]^-$	2.0×10^{38}
$\text{Cd}^{2+} + 4 \text{CN}^- \rightleftharpoons [\text{Cd}(\text{CN})_4]^{2-}$	1.3×10^{17}
$\text{Cd}^{2+} + 4 \text{Cl}^- \rightleftharpoons [\text{CdCl}_4]^{2-}$	1.0×10^4
$\text{Cd}^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{Cd}(\text{NH}_3)_4]^{2+}$	1.0×10^7
$\text{Co}^{2+} + 6 \text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+}$	7.7×10^4
$\text{Cu}^+ + 2 \text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_2]^-$	1.0×10^{16}
$\text{Cu}^+ + 2 \text{Cl}^- \rightleftharpoons [\text{CuCl}_2]^-$	1.0×10^5
$\text{Cu}^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$	6.8×10^{12}
$\text{Fe}^{2+} + 6 \text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	7.7×10^{36}
$\text{Hg}^{2+} + 4 \text{Cl}^- \rightleftharpoons [\text{HgCl}_4]^{2-}$	1.2×10^{15}
$\text{Ni}^{2+} + 4 \text{CN}^- \rightleftharpoons [\text{Ni}(\text{CN})_4]^{2-}$	1.0×10^{31}
$\text{Ni}^{2+} + 6 \text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}$	5.6×10^8
$\text{Zn}^{2+} + 4 \text{OH}^- \rightleftharpoons [\text{Zn}(\text{OH})_4]^{2-}$	2.9×10^{15}
$\text{Zn}^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{2+}$	2.9×10^9

Using Formation Constants

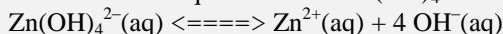
The principles and techniques we have used for treating other equilibrium systems are also applied to predicting the concentrations of species in complex ion equilibria. In general, the mathematical treatment of these systems is more complex due to the large stoichiometric coefficients and the resulting need to solve equations of high order, as shown in the following example.

EXAMPLE PROBLEM: Using formation constants

Calculate the concentration of free Zn^{2+} ion when 0.010 mol $\text{Zn}(\text{NO}_3)_2$ is added to 1.00 L of solution that is buffered at pH 12.00. $K_f[\text{Zn}(\text{OH})_4^{2-}] = 2.9 \times 10^{15}$

SOLUTION:

Step 1. First, assume that the $\text{Zn}(\text{NO}_3)_2$ dissociates completely (it is a strong electrolyte) to form Zn^{2+} and NO_3^- . Because K_f is large, we will approach this problem by first assuming that all of the Zn^{2+} and OH^- react to form the complex ion. We will use the dissociation equilibrium for $\text{Zn}(\text{OH})_4^{2-}$ and K_d to calculate the free Zn^{2+} concentration.



$$K_d = \frac{[\text{Zn}^{2+}][\text{OH}^-]^4}{[\text{Zn}(\text{OH})_4^{2-}]} = 1/K_f = 3.4 \times 10^{-16}$$

Example problem, continued

Step 2. Calculate the solution $[\text{OH}^-]$ from the solution pH.

$$\begin{aligned} \text{pOH} &= 14.00 - \text{pH} = 14.00 - 12.00 = 2.00 \\ [\text{OH}^-] &= 10^{-\text{pOH}} = 10^{-2.00} = 1.0 \times 10^{-2} \text{ M} \end{aligned}$$

Step 3. Set up an *ICE* table, where the unknown variable x represents the amount of complex ion that dissociates in solution and is also equal to the concentration of free Zn^{2+} in solution. The initial concentration of $\text{Zn}(\text{OH})_4^{2-}$ is equal to the concentration of the limiting reactant, Zn^{2+} . (Recall that we assumed that all of the Zn^{2+} and OH^- react to form the complex ion when combined in solution.)

	$\text{Zn}(\text{OH})_4^{2-}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 4 \text{OH}^-(\text{aq})$		
Initial (M)	0.010	0	
Change (M)	-x	+x	
Equilibrium (M)	$0.010 - x$	x	1.0×10^{-2}

Step 4. Substitute the equilibrium concentrations into the K_d expression and solve for x . We will assume that x is very small when compared to the initial complex ion concentration for two reasons. First, K_d is very small (3.4×10^{-16}), and second, the presence of a common ion (OH^-) will shift the equilibrium to the left, decreasing the amount of dissociated complex ion.

$$K_d = 3.4 \times 10^{-16} = \frac{[\text{Zn}^{2+}][\text{OH}^-]^4}{[\text{Zn}(\text{OH})_4^{2-}]} = \frac{(x)(1.0 \times 10^{-2})^4}{0.010 - x} \approx \frac{(x)(1.0 \times 10^{-2})^4}{0.010}$$

$$x = [\text{Zn}^{2+}] = 3.4 \times 10^{-10} \text{ M}$$



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18.4 Simultaneous Equilibria



OWL Opening Exploration
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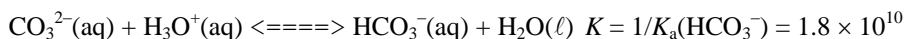
There are many factors that affect the solubility of ionic compounds. As shown previously, adding an ion common to the equilibrium decreases the solubility of a sparingly soluble salt. In this section, we address two additional factors that affect the solubility of ionic compounds, pH and the formation of complex ions, and demonstrate how these factors can be used to isolate one metal ion from a mixture. These are examples of simultaneous equilibria, where more than one equilibrium system is present in a solution.

Solubility and pH

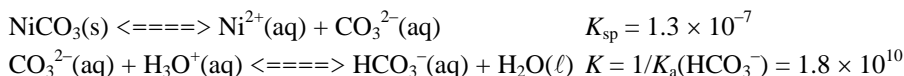
Consider the dissolution of nickel(II) carbonate.



In a saturated solution, Ni^{2+} and CO_3^{2-} are in equilibrium with solid NiCO_3 . If a strong acid is added to the solution, the carbonate ion can react to form the bicarbonate ion and water.



Adding these two equilibrium reactions shows the effect of adding a strong acid to a saturated NiCO_3 solution.



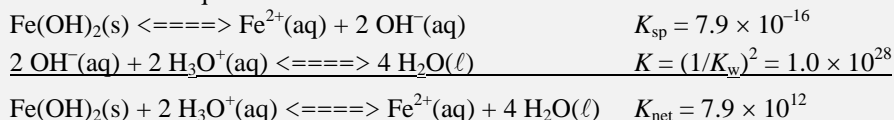
The reaction between NiCO_3 and acid is product-favored. In general, the solubility of any ionic compound containing a basic anion is increased in the presence of acid.

EXAMPLE PROBLEM: Solubility and pH (1)

Write an equation to show why the solubility of $\text{Fe}(\text{OH})_2$ increases in the presence of a strong acid and calculate the equilibrium constant for the reaction of this sparingly soluble salt with acid.

SOLUTION:

Iron(II) hydroxide contains a basic anion so its solubility increases in the presence of acid. Use $K_{\text{sp}}[\text{Fe}(\text{OH})_2]$ and K_{w} to calculate the overall equilibrium constant for this reaction.



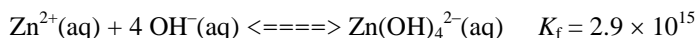
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Solubility and Complex Ions

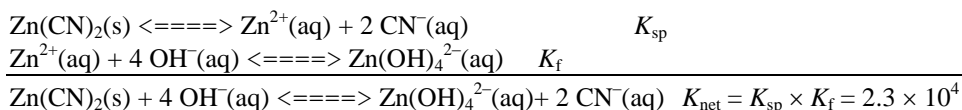
The formation of a complex ion can be used to increase the solubility of sparingly soluble ionic compounds. Consider the insoluble compound zinc cyanide, $\text{Zn}(\text{CN})_2$.



The zinc ion also forms a complex ion with hydroxide ions.



The complex ion equilibrium can be used to increase the solubility of zinc cyanide.



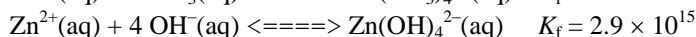
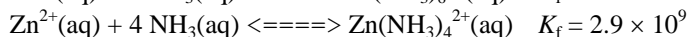
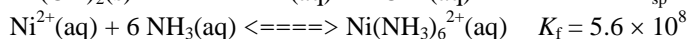
When complex ion equilibria are combined with equilibria involving insoluble salts, excess Lewis base (OH^- in this example) is added to shift the equilibrium even further to the right.



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Solubility, Ion Separation, and Qualitative Analysis

The principles of simultaneous equilibria as applied to sparingly soluble compounds and complex ions can be used to separate mixtures of ions, an experiment typically performed in the laboratory. For example, consider a solution that contains a mixture of Ni^{2+} and Zn^{2+} . Is it possible to physically separate the two ions by precipitating one of them while the other remains dissolved in solution? Examination of Tables 18.2 and 18.4 show that while both ions form insoluble hydroxide salts and complex ions with ammonia, only zinc forms a complex ion with the hydroxide ion.



Using this information, a possible separation scheme could involve reacting the ion mixture with excess hydroxide ion. The Ni^{2+} present in solution will precipitate as $\text{Ni}(\text{OH})_2$, and the Zn^{2+} will remain dissolved in solution as the $\text{Zn}(\text{OH})_4^{2-}$ complex ion. Carefully pouring the solution containing $\text{Zn}(\text{OH})_4^{2-}$ into a separate test tube separates the two ions.



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