

Chapter 15

Equilibria of Other Reaction Classes

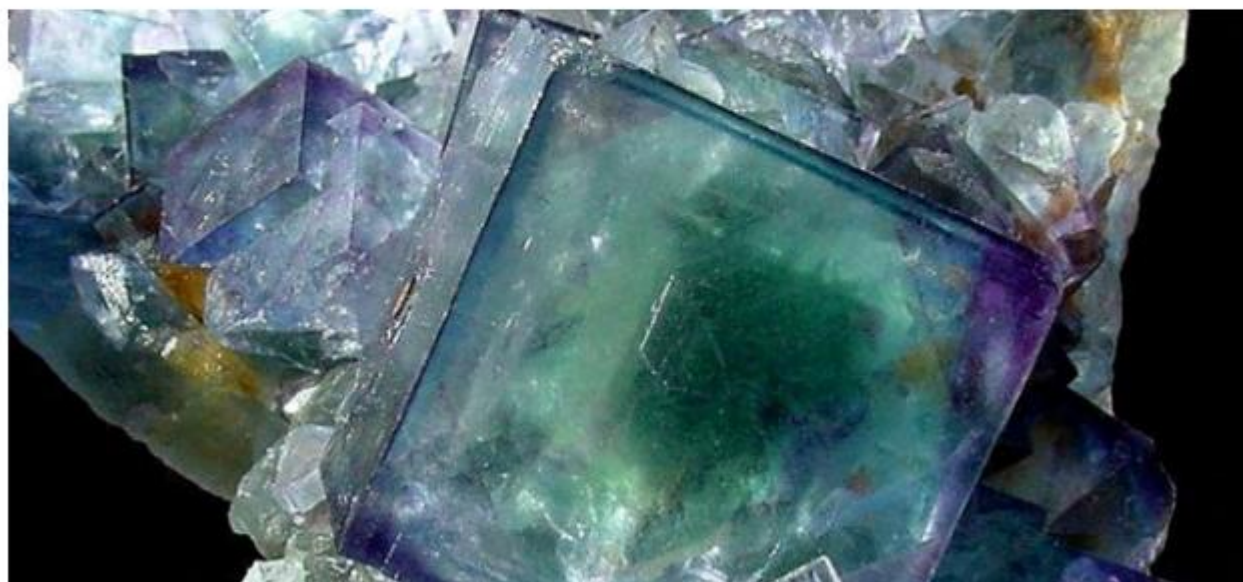


Figure 15.1 The mineral fluorite (CaF_2) is deposited through a precipitation process. Note that pure fluorite is colorless, and that the color in this sample is due to the presence of other metals in the crystal.

Chapter Outline

- 15.1 Precipitation and Dissolution
- 15.2 Lewis Acids and Bases
- 15.3 Multiple Equilibria

Introduction

In **Figure 15.1**, we see a close-up image of the mineral fluorite, which is commonly used as a semiprecious stone in many types of jewelry because of its striking appearance. These solid deposits of fluorite are formed through a process called hydrothermal precipitation. In this process, the fluorite remains dissolved in solution, usually in hot water heated by volcanic activity deep below the earth, until conditions arise that allow the mineral to come out of solution and form a deposit. These deposit-forming conditions can include a change in temperature of the solution, availability of new locations to form a deposit such as a rock crevice, contact between the solution and a reactive substance such as certain types of rock, or a combination of any of these factors.

We previously learned about aqueous solutions and their importance, as well as about solubility rules. While this gives us a picture of solubility, that picture is not complete if we look at the rules alone. Solubility equilibrium, which we will explore in this chapter, is a more complex topic that allows us to determine the extent to which a slightly soluble ionic solid will dissolve, and the conditions under which precipitation (such as the fluorite deposit in **Figure 15.1**) will occur.

15.1 Precipitation and Dissolution

By the end of this section, you will be able to:

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

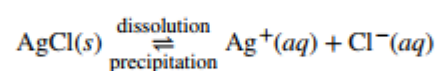
The preservation of medical laboratory blood samples, mining of sea water for magnesium, formulation of over-the-counter medicines such as Milk of Magnesia and antacids, and treating the presence of hard water in your home's water supply are just a few of the many tasks that involve controlling the equilibrium between a slightly soluble ionic solid and an aqueous solution of its ions.

In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the CO_3^{2-} ions produced in this process help soothe an upset stomach.

In this section, we will find out how we can control the dissolution of a slightly soluble ionic solid by the application of Le Châtelier's principle. We will also learn how to use the equilibrium constant of the reaction to determine the concentration of ions present in a solution.

The Solubility Product Constant

Silver chloride is what's known as a sparingly soluble ionic solid (**Figure 15.2**). Recall from the solubility rules in an earlier chapter that halides of Ag^+ are not normally soluble. However, when we add an excess of solid AgCl to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride:



This equilibrium, like other equilibria, is dynamic; some of the solid AgCl continues to dissolve, but at the same time, Ag^+ and Cl^- ions in the solution combine to produce an equal amount of the solid. At equilibrium, the opposing processes have equal rates.

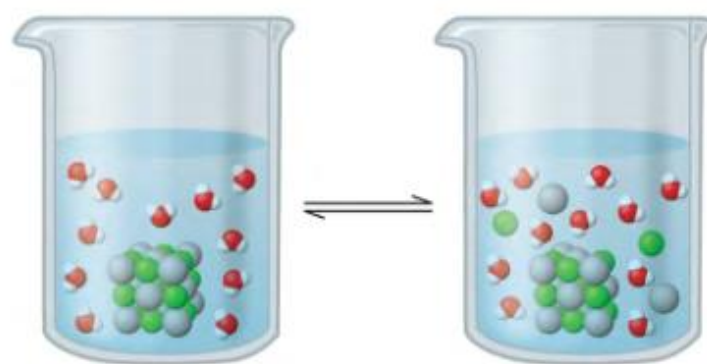
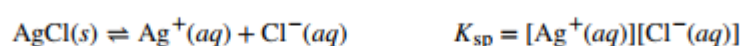


Figure 15.2 Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is called the **solubility product (K_{sp})** of the solid. Recall from the chapter on solutions and colloids that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:



When looking at dissolution reactions such as this, the solid is listed as a reactant, whereas the ions are listed as products. The solubility product constant, as with every equilibrium constant expression, is written as the product of the concentrations of each of the ions, raised to the power of their stoichiometric coefficients. Here, the solubility product constant is equal to Ag^+ and Cl^- when a solution of silver chloride is in equilibrium with undissolved AgCl . There is no denominator representing the reactants in this equilibrium expression since the reactant is a pure solid; therefore $[\text{AgCl}]$ does not appear in the expression for K_{sp} .

Some common solubility products are listed in **Table 15.1** according to their K_{sp} values, whereas a more extensive compilation of products appears in **Appendix J**. Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small K_{sp} represents a system in which the equilibrium lies to the left, so that relatively few hydrated ions would be present in a saturated solution.

Common Solubility Products by Decreasing Equilibrium Constants

Substance	K_{sp} at 25 °C
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
AgI	1.5×10^{-16}
PbS	7×10^{-29}
$\text{Al}(\text{OH})_3$	2×10^{-32}

Table 15.1

Common Solubility Products by Decreasing Equilibrium Constants

Substance	K_{sp} at 25 °C
$\text{Fe}(\text{OH})_3$	4×10^{-38}

Table 15.1

Example 15.1

Writing Equations and Solubility Products

Write the ionic equation for the dissolution and the solubility product expression for each of the following slightly soluble ionic compounds:

- (a) AgI , silver iodide, a solid with antiseptic properties
- (b) CaCO_3 , calcium carbonate, the active ingredient in many over-the-counter chewable antacids
- (c) $\text{Mg}(\text{OH})_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia
- (d) $\text{Mg}(\text{NH}_4)\text{PO}_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium
- (e) $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the mineral apatite, a source of phosphate for fertilizers

(Hint: When determining how to break (d) and (e) up into ions, refer to the list of polyatomic ions in the section on chemical nomenclature.)

Solution

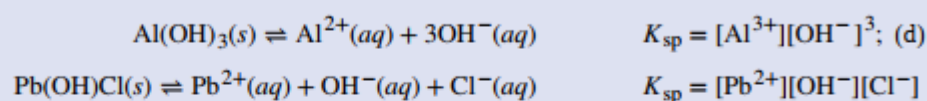
- (a) $\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$ $K_{sp} = [\text{Ag}^+][\text{I}^-]$
- (b) $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$ $K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$
- (c) $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$ $K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$
- (d) $\text{Mg}(\text{NH}_4)\text{PO}_4(s) \rightleftharpoons \text{Mg}^{2+}(aq) + \text{NH}_4^+(aq) + \text{PO}_4^{3-}(aq)$ $K_{sp} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}]$
- (e) $\text{Ca}_5(\text{PO}_4)_3\text{OH}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3\text{PO}_4^{3-}(aq) + \text{OH}^-(aq)$ $K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-]$

Check Your Learning

Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:

- (a) BaSO_4
- (b) Ag_2SO_4
- (c) $\text{Al}(\text{OH})_3$
- (d) $\text{Pb}(\text{OH})\text{Cl}$

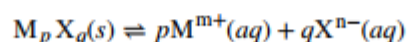
Answer: (a) $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$ $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$; (b) $\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)$ $K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$; (c)



Now we will extend the discussion of K_{sp} and show how the solubility product constant is determined from the solubility of its ions, as well as how K_{sp} can be used to determine the molar solubility of a substance.

K_{sp} and Solubility

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

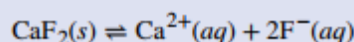


In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its **molar solubility**.

Example 15.2

Calculation of K_{sp} from Equilibrium Concentrations

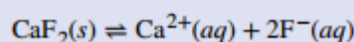
We began the chapter with an informal discussion of how the mineral fluorite (**Figure 15.1**) is formed. Fluorite, CaF_2 , is a slightly soluble solid that dissolves according to the equation:



The concentration of Ca^{2+} in a saturated solution of CaF_2 is $2.1 \times 10^{-4} \text{ M}$; therefore, that of F^- is $4.2 \times 10^{-4} \text{ M}$, that is, twice the concentration of Ca^{2+} . What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp} :



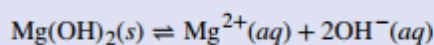
A saturated solution is a solution at equilibrium with the solid. Thus:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = 3.7 \times 10^{-11}$$

As with other equilibrium constants, we do not include units with K_{sp} .

Check Your Learning

In a saturated solution that is in contact with solid Mg(OH)_2 , the concentration of Mg^{2+} is $3.7 \times 10^{-5} \text{ M}$. What is the solubility product for Mg(OH)_2 ?



Answer: 2.0×10^{-13}

Example 15.3

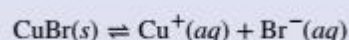
Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9} . Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3×10^{-9} .

The reaction is:



First, write out the solubility product equilibrium constant expression:

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

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the CuBr column empty as it is a solid and does not contribute to the K_{sp} :

	CuBr	\rightleftharpoons	Cu ⁺	+	Br ⁻
Initial concentration (M)			0		0
Change (M)			x		x
Equilibrium concentration (M)			0 + x = x		0 + x = x

At equilibrium:

$$\begin{aligned} K_{sp} &= [\text{Cu}^+][\text{Br}^-] \\ 6.3 \times 10^{-9} &= (x)(x) = x^2 \\ x &= \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5} \end{aligned}$$

Therefore, the molar solubility of CuBr is $7.9 \times 10^{-5} M$.

Check Your Learning

The K_{sp} of AgI is 1.5×10^{-16} . Calculate the molar solubility of silver iodide.

Answer: $1.2 \times 10^{-8} M$

Example 15.4

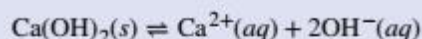
Determination of Molar Solubility from K_{sp} , Part II

The K_{sp} of calcium hydroxide, $\text{Ca}(\text{OH})_2$, is 8.0×10^{-6} . Calculate the molar solubility of calcium hydroxide.

Solution

The solubility product constant of calcium hydroxide is 8.0×10^{-6} .

The reaction is:



First, write out the solubility product equilibrium constant expression:

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

Create an ICE table, leaving the $\text{Ca}(\text{OH})_2$ column empty as it is a solid and does not contribute to the K_{sp} :

	$\text{Ca}(\text{OH})_2 \rightleftharpoons$	Ca^{2+}	+	2OH^-
Initial concentration (M)		0		0
Change (M)		x		2x
Equilibrium concentration (M)		$0 + x = x$		$0 + 2x = 2x$

At equilibrium:

$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}][\text{OH}^-]^2 \\ 8.0 \times 10^{-6} &= (x)(2x)^2 = (x)(4x^2) = 4x^3 \\ x &= \sqrt[3]{\frac{8.0 \times 10^{-6}}{4}} = 1.3 \times 10^{-2} \end{aligned}$$

Therefore, the molar solubility of $\text{Ca}(\text{OH})_2$ is $1.3 \times 10^{-2} \text{ M}$.

Check Your Learning

The K_{sp} of PbI_2 is 1.4×10^{-8} . Calculate the molar solubility of lead(II) iodide.

Answer: $1.5 \times 10^{-3} \text{ M}$

Note that solubility is not always given as a molar value. When the solubility of a compound is given in some unit other than moles per liter, we must convert the solubility into moles per liter (i.e., molarity) in order to use it in the solubility product constant expression. **Example 15.5** shows how to perform those unit conversions before determining the solubility product equilibrium.

Example 15.5

Determination of K_{sp} from Gram Solubility

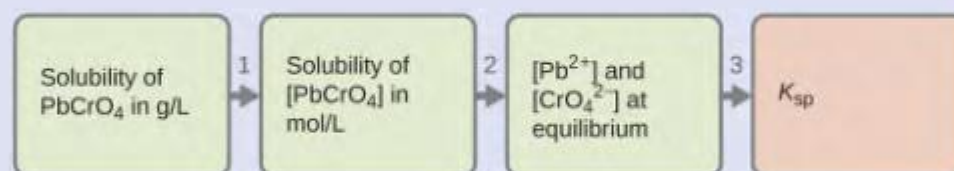
Many of the pigments used by artists in oil-based paints (**Figure 15.3**) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, PbCrO_4 , is $4.3 \times 10^{-5} \text{ g/L}$. Determine the solubility product equilibrium constant for PbCrO_4 .



Figure 15.3 Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow (PbCrO_4), examples include Prussian blue ($\text{Fe}_7(\text{CN})_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

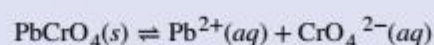
We are given the solubility of PbCrO_4 in grams per liter. If we convert this solubility into moles per liter, we can find the equilibrium concentrations of Pb^{2+} and CrO_4^{2-} , then K_{sp} :



Step 1. Use the molar mass of PbCrO_4 $\left(\frac{323.2 \text{ g}}{1 \text{ mol}}\right)$ to convert the solubility of PbCrO_4 in grams per liter into moles per liter:

$$\begin{aligned}
 [\text{PbCrO}_4] &= \frac{4.3 \times 10^{-5} \text{ g PbCrO}_4}{1 \text{ L}} \times \frac{1 \text{ mol PbCrO}_4}{323.2 \text{ g PbCrO}_4} \\
 &= \frac{1.3 \times 10^{-7} \text{ mol PbCrO}_4}{1 \text{ L}} \\
 &= 1.3 \times 10^{-7} M
 \end{aligned}$$

Step 2. The chemical equation for the dissolution indicates that 1 mol of PbCrO_4 gives 1 mol of $\text{Pb}^{2+}(\text{aq})$ and 1 mol of $\text{CrO}_4^{2-}(\text{aq})$:



Thus, both $[\text{Pb}^{2+}]$ and $[\text{CrO}_4^{2-}]$ are equal to the molar solubility of PbCrO_4 :

$$[\text{Pb}^{2+}] = [\text{CrO}_4^{2-}] = 1.3 \times 10^{-7} M$$

Step 3. Solve. $K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = (1.3 \times 10^{-7})(1.3 \times 10^{-7}) = 1.7 \times 10^{-14}$

Check Your Learning

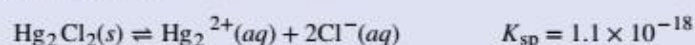
The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.2 grams per liter at 20 °C. What is its solubility product?

Answer: 1.4×10^{-4} (1.5×10^{-4} if we round the solubility to two digits before calculating K_{sp})

Example 15.6

Calculating the Solubility of Hg_2Cl_2

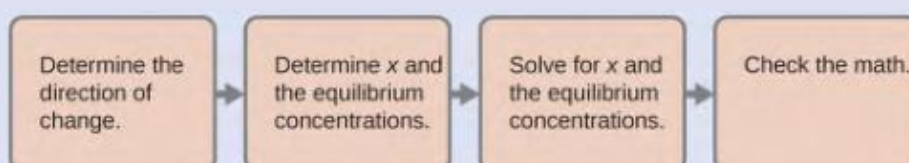
Calomel, Hg_2Cl_2 , is a compound composed of the diatomic ion of mercury(I), Hg_2^{2+} , and chloride ions, Cl^- . Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel is quite insoluble:



Calculate the molar solubility of Hg_2Cl_2 .

Solution

The molar solubility of Hg_2Cl_2 is equal to the concentration of Hg_2^{2+} ions because for each 1 mol of Hg_2Cl_2 that dissolves, 1 mol of Hg_2^{2+} forms:



Step 1. *Determine the direction of change.* Before any Hg_2Cl_2 dissolves, Q is zero, and the reaction will shift to the right to reach equilibrium.

Step 2. *Determine x and equilibrium concentrations.* Concentrations and changes are given in the following ICE table:

	$\text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg}_2^{2+} + 2\text{Cl}^-$		
Initial concentration (M)		0	0
Change (M)		x	$2x$
Equilibrium concentration (M)		$0 + x = x$	$0 + 2x = 2x$

Note that the change in the concentration of Cl^- ($2x$) is twice as large as the change in the concentration of Hg_2^{2+} (x) because 2 mol of Cl^- forms for each 1 mol of Hg_2^{2+} that forms. Hg_2Cl_2 is a pure solid, so it does not appear in the calculation.

Step 3. *Solve for x and the equilibrium concentrations.* We substitute the equilibrium concentrations into the expression for K_{sp} and calculate the value of x :

$$\begin{aligned}
 K_{\text{sp}} &= [\text{Hg}_2^{2+}][\text{Cl}^-]^2 \\
 1.1 \times 10^{-18} &= (x)(2x)^2 \\
 4x^3 &= 1.1 \times 10^{-18}
 \end{aligned}$$

$$x = \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} = 6.5 \times 10^{-7} M$$

$$[\text{Hg}_2^{2+}] = 6.5 \times 10^{-7} M = 6.5 \times 10^{-7} M$$

$$[\text{Cl}^-] = 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6} M$$

The molar solubility of Hg_2Cl_2 is equal to $[\text{Hg}_2^{2+}]$, or $6.5 \times 10^{-7} M$.

Step 4. Check the work. At equilibrium, $Q = K_{\text{sp}}$:

$$Q = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (6.5 \times 10^{-7})(1.3 \times 10^{-6})^2 = 1.1 \times 10^{-18}$$

The calculations check.

Check Your Learning

Determine the molar solubility of MgF_2 from its solubility product: $K_{\text{sp}} = 6.4 \times 10^{-9}$.

Answer: $1.2 \times 10^{-3} M$

Tabulated K_{sp} values can also be compared to reaction quotients calculated from experimental data to tell whether a solid will precipitate in a reaction under specific conditions: Q equals K_{sp} at equilibrium; if Q is less than K_{sp} , the solid will dissolve until Q equals K_{sp} ; if Q is greater than K_{sp} , precipitation will occur at a given temperature until Q equals K_{sp} .

How Sciences Interconnect

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 1.1×10^{-10} , very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 15.4).



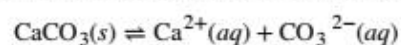
Figure 15.4 The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Visit this [website \(http://openstaxcollege.org/l/16barium\)](http://openstaxcollege.org/l/16barium) for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:



We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ($Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$) is equal to the solubility product ($K_{sp} = 4.8 \times 10^{-9}$). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with

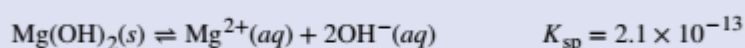
a solution of sodium carbonate, which contains CO_3^{2-} ions, the slightly soluble ionic solid CaCO_3 will precipitate, provided that the concentrations of Ca^{2+} and CO_3^{2-} ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp} . A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp} , then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as **Example 15.7** shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

Example 15.7

Precipitation of $\text{Mg}(\text{OH})_2$

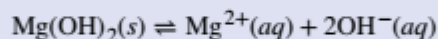
The first step in the preparation of magnesium metal is the precipitation of $\text{Mg}(\text{OH})_2$ from sea water by the addition of lime, $\text{Ca}(\text{OH})_2$, a readily available inexpensive source of OH^- ion:



The concentration of $\text{Mg}^{2+}(aq)$ in sea water is 0.0537 M. Will $\text{Mg}(\text{OH})_2$ precipitate when enough $\text{Ca}(\text{OH})_2$ is added to give a $[\text{OH}^-]$ of 0.0010 M?

Solution

This problem asks whether the reaction:



shifts to the left and forms solid $\text{Mg}(\text{OH})_2$ when $[\text{Mg}^{2+}] = 0.0537 \text{ M}$ and $[\text{OH}^-] = 0.0010 \text{ M}$. The reaction shifts to the left if Q is greater than K_{sp} . Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{\text{sp}} = 2.1 \times 10^{-13}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $\text{Mg}(\text{OH})_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp} .

Check Your Learning

Use the solubility product in **Appendix J** to determine whether CaHPO_4 will precipitate from a solution with $[\text{Ca}^{2+}] = 0.0001 \text{ M}$ and $[\text{HPO}_4^{2-}] = 0.001 \text{ M}$.

Answer: No precipitation of CaHPO_4 ; $Q = 1 \times 10^{-7}$, which is less than K_{sp}

Example 15.8

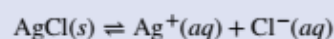
Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a $2.0 \times 10^{-4} \text{ M}$ solution of AgNO_3 and a $2.0 \times 10^{-4} \text{ M}$ solution of NaCl are mixed?

(Note: The solution also contains Na^+ and NO_3^- ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:



The solubility product is 1.8×10^{-10} (see **Appendix J**).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of AgNO_3 and NaCl is greater than K_{sp} . The volume doubles when we mix equal volumes of AgNO_3 and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[\text{Ag}^+]$ and $[\text{Cl}^-]$ are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4}) M = 1.0 \times 10^{-4} M$$

The reaction quotient, Q , is momentarily greater than K_{sp} for AgCl , so a supersaturated solution is formed:

$$Q = [\text{Ag}^+][\text{Cl}^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{\text{sp}}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp} .

Check Your Learning

Will KClO_4 precipitate when 20 mL of a 0.050-M solution of K^+ is added to 80 mL of a 0.50-M solution of ClO_4^- ? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Answer: No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{\text{sp}} = 1.07 \times 10^{-2}$

In the previous two examples, we have seen that $\text{Mg}(\text{OH})_2$ or AgCl precipitate when Q is greater than K_{sp} . In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q . Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Example 15.9

Precipitation of Calcium Oxalate

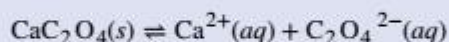
Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, for this purpose (**Figure 15.5**). At sufficiently high concentrations, the calcium and oxalate ions form solid, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is $2.2 \times 10^{-3} M$. What concentration of $\text{C}_2\text{O}_4^{2-}$ ion must be established before $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ begins to precipitate?



Figure 15.5 Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:



For this reaction:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.27 \times 10^{-9}$$

(see [Appendix J](#))

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until Q equals K_{sp} . Because we know K_{sp} and $[\text{Ca}^{2+}]$, we can solve for the concentration of $\text{C}_2\text{O}_4^{2-}$ that is necessary to produce the first trace of solid:

$$\begin{aligned} Q = K_{\text{sp}} &= [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.27 \times 10^{-9} \\ (2.2 \times 10^{-3})[\text{C}_2\text{O}_4^{2-}] &= 2.27 \times 10^{-9} \\ [\text{C}_2\text{O}_4^{2-}] &= \frac{2.27 \times 10^{-9}}{2.2 \times 10^{-3}} = 1.0 \times 10^{-6} \end{aligned}$$

A concentration of $[\text{C}_2\text{O}_4^{2-}] = 1.0 \times 10^{-6} \text{ M}$ is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Check Your Learning

If a solution contains 0.0020 mol of CrO_4^{2-} per liter, what concentration of Ag^+ ion must be reached by adding solid AgNO_3 before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer: $7.0 \times 10^{-5} M$

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in **Example 15.9**—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

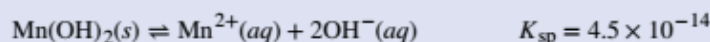
Example 15.10

Concentrations Following Precipitation

Clothing washed in water that has a manganese $[Mn^{2+}(aq)]$ concentration exceeding 0.1 mg/L ($1.8 \times 10^{-6} M$) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep $[Mn^{2+}]$ equal to $1.8 \times 10^{-6} M$?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:



We need to calculate the concentration of OH^{-} when the concentration of Mn^{2+} is $1.8 \times 10^{-6} M$. From that, we calculate the pH. At equilibrium:

$$K_{sp} = [Mn^{2+}][OH^{-}]^2$$

or

$$(1.8 \times 10^{-6})[OH^{-}]^2 = 4.5 \times 10^{-14}$$

so

$$[OH^{-}] = 1.6 \times 10^{-4} M$$

Now we calculate the pH from the pOH:

$$pOH = -\log[OH^{-}] = -\log(1.6 \times 10^{-4}) = 3.80$$

$$pH = 14.00 - pOH = 14.00 - 3.80 = 10.20$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.20, the manganese ion will be reduced to a concentration of $1.8 \times 10^{-6} M$; at that concentration or less, the ion will not stain clothing.

Check Your Learning

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is $5.37 \times 10^{-2} M$. Calculate the pH at which $[Mg^{2+}]$ is diminished to $1.0 \times 10^{-5} M$ by the addition of $Ca(OH)_2$.

Answer: 11.09

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{\text{sp}} = 1.6 \times 10^{-10}$), AgBr ($K_{\text{sp}} = 7.7 \times 10^{-13}$), and AgI ($K_{\text{sp}} = 8.3 \times 10^{-17}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^- , Br^- , and I^- ; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp} . However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^- , Br^- , and I^- to a solution of Ag^+ .

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of **selective precipitation**, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

Chemistry in Everyday Life

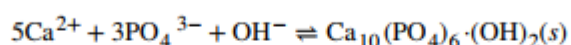
The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 15.6). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{2-}) are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.



Figure 15.6 Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, known as lime, $\text{Ca}(\text{OH})_2$. The lime is converted into calcium carbonate, a strong base, in the water. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, which then precipitates out of the solution:



The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this [site \(http://openstaxcollege.org//16Wastewater\)](http://openstaxcollege.org//16Wastewater) for more information on how phosphorus is removed from wastewater.

Selective precipitation can also be used in qualitative analysis. In this method, reagents are added to an unknown chemical mixture in order to induce precipitation. Certain reagents cause specific ions to precipitate out; therefore, the addition of the reagent can be used to determine whether the ion is present in the solution.

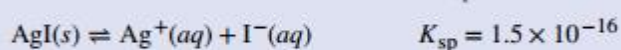
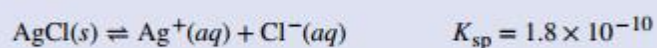
Example 15.11

Precipitation of Silver Halides

A solution contains 0.0010 mol of KI and 0.10 mol of KCl per liter. AgNO_3 is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

Solution

The two equilibria involved are:



If the solution contained about *equal* concentrations of Cl^- and I^- , then the silver salt with the smallest K_{sp} (AgI) would precipitate first. The concentrations are not equal, however, so we should find the $[\text{Ag}^+]$ at which AgCl begins to precipitate and the $[\text{Ag}^+]$ at which AgI begins to precipitate. The salt that forms at the lower $[\text{Ag}^+]$ precipitates first.

For AgI: AgI precipitates when Q equals K_{sp} for AgI (1.5×10^{-16}). When $[\text{I}^-] = 0.0010 \text{ M}$:

$$Q = [\text{Ag}^+][\text{I}^-] = [\text{Ag}^+](0.0010) = 1.5 \times 10^{-16}$$

$$[\text{Ag}^+] = \frac{1.5 \times 10^{-16}}{0.0010} = 1.5 \times 10^{-13}$$

AgI begins to precipitate when $[\text{Ag}^+]$ is $1.5 \times 10^{-13} \text{ M}$.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.8×10^{-10}). When $[Cl^-] = 0.10\text{ M}$:

$$Q_{sp} = [Ag^+][Cl^-] = [Ag^+](0.10) = 1.8 \times 10^{-10}$$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.10} = 1.8 \times 10^{-9}\text{ M}$$

AgCl begins to precipitate when $[Ag^+]$ is $1.8 \times 10^{-9}\text{ M}$.

AgI begins to precipitate at a lower $[Ag^+]$ than AgCl, so AgI begins to precipitate first.

Check Your Learning

If silver nitrate solution is added to a solution which is 0.050 M in both Cl^- and Br^- ions, at what $[Ag^+]$ would precipitation begin, and what would be the formula of the precipitate?

Answer: $[Ag^+] = 1.5 \times 10^{-11}\text{ M}$; AgBr precipitates first

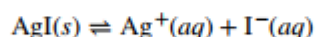
Common Ion Effect

As we saw when we discussed buffer solutions, the hydronium ion concentration of an aqueous solution of acetic acid decreases when the strong electrolyte sodium acetate, $NaCH_3CO_2$, is added. We can explain this effect using Le Châtelier's principle. The addition of acetate ions causes the equilibrium to shift to the left, decreasing the concentration of H_3O^+ to compensate for the increased acetate ion concentration. This increases the concentration of CH_3CO_2H :



Because sodium acetate and acetic acid have the acetate ion in common, the influence on the equilibrium is called the **common ion effect**.

The common ion effect can also have a direct effect on solubility equilibria. Suppose we are looking at the reaction where silver iodide is dissolved:



If we were to add potassium iodide (KI) to this solution, we would be adding a substance that shares a common ion with silver iodide. Le Châtelier's principle tells us that when a change is made to a system at equilibrium, the reaction will shift to counteract that change. In this example, there would be an excess of iodide ions, so the reaction would shift toward the left, causing more silver iodide to precipitate out of solution.

Example 15.12

Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide (CdBr₂). The K_{sp} of CdS is 1.0×10^{-28} .

Solution

The first thing you should notice is that the cadmium sulfide is dissolved in a solution that contains cadmium ions. We need to use an ICE table to set up this problem and include the CdBr₂ concentration as a contributor of cadmium ions:

$$\text{CdS}(s) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{S}^{2-}(aq)$$

	CdS	\rightleftharpoons	Cd ²⁺	+	S ²⁻
Initial concentration (<i>M</i>)			0.010		0
Change (<i>M</i>)			<i>x</i>		<i>x</i>
Equilibrium concentration (<i>M</i>)			0.010 + <i>x</i>		0 + <i>x</i> = <i>x</i>

$$K_{sp} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$

$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

$$x^2 + 0.010x - 1.0 \times 10^{-28} = 0$$

We can solve this equation using the quadratic formula, but we can also make an assumption to make this calculation much simpler. Since the K_{sp} value is so small compared with the cadmium concentration, we can assume that the change between the initial concentration and the equilibrium concentration is negligible, so that $0.010 + x \sim 0.010$. Going back to our K_{sp} expression, we would now get:

$$K_{sp} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$

$$(0.010)(x) = 1.0 \times 10^{-28}$$

$$x = 1.0 \times 10^{-26}$$

Therefore, the molar solubility of CdS in this solution is 1.0×10^{-26} *M*.

Check Your Learning

Calculate the molar solubility of aluminum hydroxide, Al(OH)₃, in a 0.015-*M* solution of aluminum nitrate, Al(NO₃)₃. The K_{sp} of Al(OH)₃ is 2×10^{-32} .

Answer: 1×10^{-10} *M*

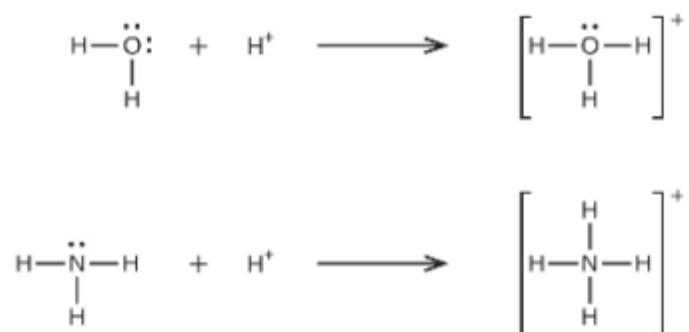
15.2 Lewis Acids and Bases

By the end of this section, you will be able to:

- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions
- Perform equilibrium calculations involving formation constants

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

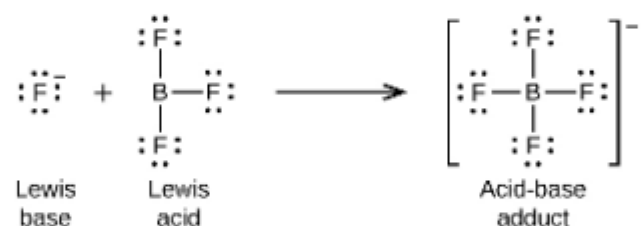
A **coordinate covalent bond** (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.



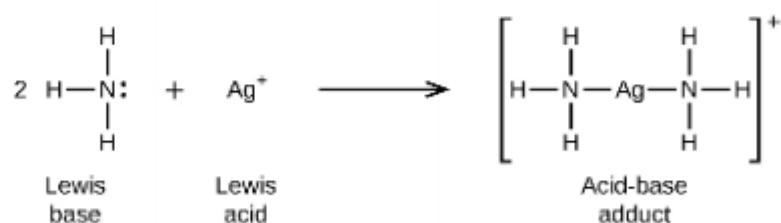
A **Lewis acid** is any species (molecule or ion) that can accept a pair of electrons, and a **Lewis base** is any species (molecule or ion) that can donate a pair of electrons.

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid. A **Lewis acid-base adduct**, a compound that contains a coordinate covalent bond between the Lewis acid and the Lewis base, is formed. The following equations illustrate the general application of the Lewis concept.

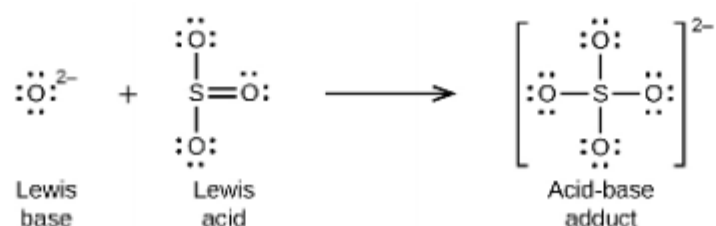
The boron atom in boron trifluoride, BF_3 , has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



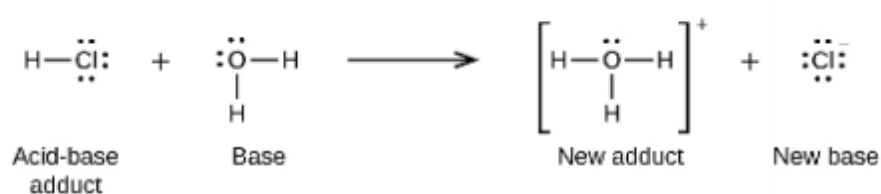
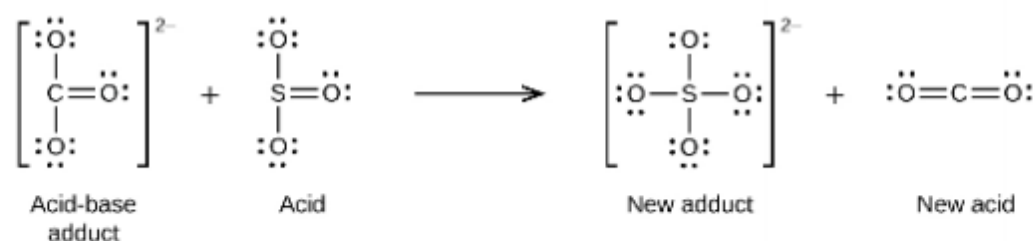
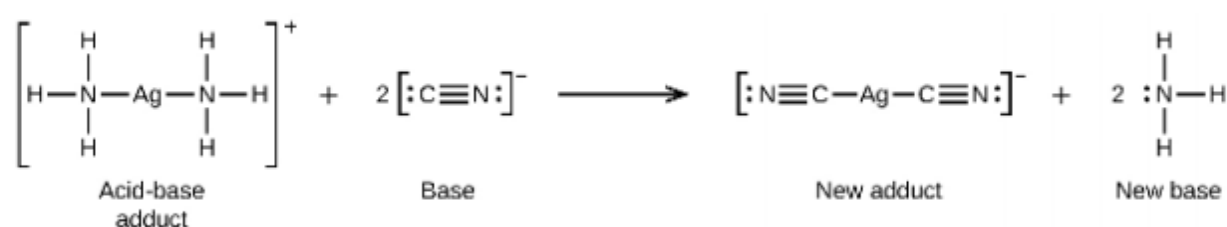
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:



Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:

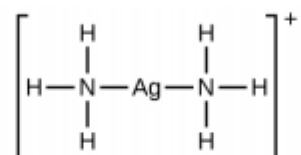


Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:

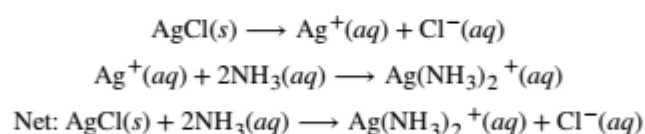


The last displacement reaction shows how the reaction of a Brønsted-Lowry acid with a base fits into the Lewis concept. A Brønsted-Lowry acid such as HCl is an acid-base adduct according to the Lewis concept, and proton transfer occurs because a more stable acid-base adduct is formed. Thus, although the definitions of acids and bases in the two theories are quite different, the theories overlap considerably.

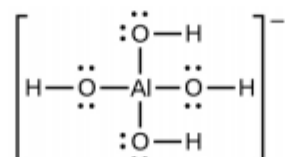
Many slightly soluble ionic solids dissolve when the concentration of the metal ion in solution is decreased through the formation of complex (polyatomic) ions in a Lewis acid-base reaction. For example, silver chloride dissolves in a solution of ammonia because the silver ion reacts with ammonia to form the **complex ion** $\text{Ag}(\text{NH}_3)_2^+$. The Lewis structure of the $\text{Ag}(\text{NH}_3)_2^+$ ion is:



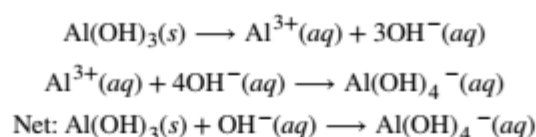
The equations for the dissolution of AgCl in a solution of NH_3 are:



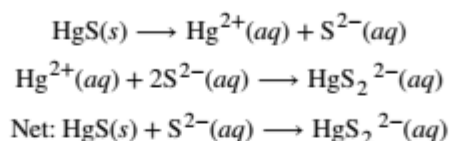
Aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion $\text{Al}(\text{OH})_4^-$. The Lewis structure of the $\text{Al}(\text{OH})_4^-$ ion is:



The equations for the dissolution are:

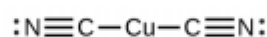


Mercury(II) sulfide dissolves in a solution of sodium sulfide because HgS reacts with the S^{2-} ion:

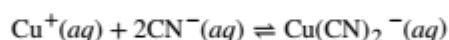


A complex ion consists of a central atom, typically a transition metal cation, surrounded by ions, or molecules called **ligands**. These ligands can be neutral molecules like H_2O or NH_3 , or ions such as CN^- or OH^- . Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. The ligands aggregate themselves around the central atom, creating a new ion with a charge equal to the sum of the charges and, most often, a transitional metal ion. This more complex arrangement is why the resulting ion is called a *complex ion*. The complex ion formed in these reactions cannot be predicted; it must be determined experimentally. The types of bonds formed in complex ions are called coordinate covalent bonds, as electrons from the ligands are being shared with the central atom. Because of this, complex ions are sometimes referred to as coordination complexes. This will be studied further in upcoming chapters.

The equilibrium constant for the reaction of the components of a complex ion to form the complex ion in solution is called a **formation constant (K_f)** (sometimes called a stability constant). For example, the complex ion Cu(CN)_2^- is shown here:



It forms by the reaction:



At equilibrium:

$$K_f = Q = \frac{[\text{Cu(CN)}_2^-]}{[\text{Cu}^+][\text{CN}^-]^2}$$

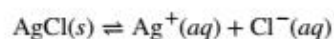
The inverse of the formation constant is the **dissociation constant (K_d)**, the equilibrium constant for the *decomposition* of a complex ion into its components in solution. We will work with dissociation constants further in the exercises for this section. **Appendix K** and **Table 15.2** are tables of formation constants. In general, the larger the formation constant, the more stable the complex; however, as in the case of K_{sp} values, the stoichiometry of the compound must be considered.

Common Complex Ions by Decreasing Formulation Constants

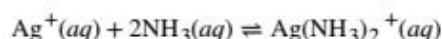
Substance	K_f at 25 °C
$[\text{Cd(CN)}_4]^{2-}$	1.3×10^7
$\text{Ag(NH}_3)_2^+$	1.7×10^7
$[\text{AlF}_6]^{3-}$	7×10^{19}

Table 15.2

As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M}$):



However, if NH_3 is present in the water, the complex ion, $\text{Ag}(\text{NH}_3)_2^+$, can form according to the equation:



with

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.6 \times 10^7$$

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of AgCl combine with NH_3 to form $\text{Ag}(\text{NH}_3)_2^+$. As a consequence, the concentration of silver ions, $[\text{Ag}^+]$, is reduced, and the reaction quotient for the dissolution of silver chloride, $[\text{Ag}^+][\text{Cl}^-]$, falls below the solubility product of AgCl :

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

More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

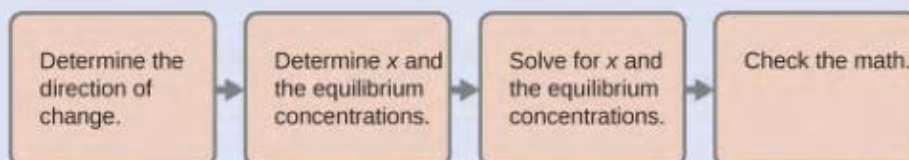
Example 15.13

Dissociation of a Complex Ion

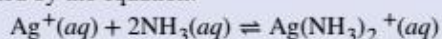
Calculate the concentration of the silver ion in a solution that initially is 0.10 M with respect to $\text{Ag}(\text{NH}_3)_2^+$.

Solution

We use the familiar path to solve this problem:



Step 1. *Determine the direction of change.* The complex ion $\text{Ag}(\text{NH}_3)_2^+$ is in equilibrium with its components, as represented by the equation:



We write the equilibrium as a formation reaction because **Appendix K** lists formation constants for complex ions. Before equilibrium, the reaction quotient is larger than the equilibrium constant [$K_f = 1.6 \times 10^7$, and $Q = \frac{0.10}{0 \times 0}$, it is infinitely large], so the reaction shifts to the left to reach equilibrium.

Step 2. *Determine x and equilibrium concentrations.* We let the change in concentration of Ag^+ be x . Dissociation of 1 mol of $\text{Ag}(\text{NH}_3)_2^+$ gives 1 mol of Ag^+ and 2 mol of NH_3 , so the change in $[\text{NH}_3]$ is $2x$ and that of $\text{Ag}(\text{NH}_3)_2^+$ is $-x$. In summary:

	$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$		
Initial concentration (M)	0	0	0.10
Change (M)	x	$2x$	$-x$
Equilibrium concentration (M)	$0 + x$	$0 + 2x$	$0.10 - x$

Step 3. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$1.6 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2}$$

Both Q and K_f are much larger than 1, so let us assume that the changes in concentrations needed to reach equilibrium are small. Thus $0.10 - x$ is approximated as 0.10:

$$1.6 \times 10^7 = \frac{0.10}{(x)(2x)^2}$$

$$x^3 = \frac{0.10}{4(1.6 \times 10^7)} = 1.6 \times 10^{-9}$$

$$x = \sqrt[3]{1.6 \times 10^{-9}} = 1.2 \times 10^{-3}$$

Because only 1.2% of the $\text{Ag}(\text{NH}_3)_2^+$ dissociates into Ag^+ and NH_3 , the assumption that x is small is justified.

Now we determine the equilibrium concentrations:

$$[\text{Ag}^+] = 0 + x = 1.2 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3] = 0 + 2x = 2.4 \times 10^{-3} \text{ M}$$

$$[\text{Ag}(\text{NH}_3)_2^+] = 0.10 - x = 0.10 - 0.0012 = 0.099$$

The concentration of free silver ion in the solution is 0.0012 M.

Step 4. Check the work. The value of Q calculated using the equilibrium concentrations is equal to K_f within the error associated with the significant figures in the calculation.

Check Your Learning

Calculate the silver ion concentration, $[\text{Ag}^+]$, of a solution prepared by dissolving 1.00 g of AgNO_3 and 10.0 g of KCN in sufficient water to make 1.00 L of solution. (Hint: Because $Q < K_f$, assume the reaction goes to completion then calculate the $[\text{Ag}^+]$ produced by dissociation of the complex.)

Answer: $3 \times 10^{-21} \text{ M}$

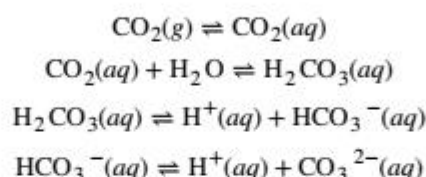
15.3 Multiple Equilibria

By the end of this section, you will be able to:

- Describe examples of systems involving two (or more) simultaneous chemical equilibria
- Calculate reactant and product concentrations for multiple equilibrium systems
- Compare dissolution and weak electrolyte formation

There are times when one equilibrium reaction does not adequately describe the system being studied. Sometimes we have more than one type of equilibrium occurring at once (for example, an acid-base reaction and a precipitation reaction).

The ocean is a unique example of a system with **multiple equilibria**, or multiple states of solubility equilibria working simultaneously. Carbon dioxide in the air dissolves in sea water, forming carbonic acid (H_2CO_3). The carbonic acid then ionizes to form hydrogen ions and bicarbonate ions (HCO_3^-), which can further ionize into more hydrogen ions and carbonate ions (CO_3^{2-}):



The excess H^+ ions make seawater more acidic. Increased ocean acidification can then have negative impacts on reef-building coral, as they cannot absorb the calcium carbonate they need to grow and maintain their skeletons (**Figure 15.7**). This in turn disrupts the local biosystem that depends upon the health of the reefs for its survival. If enough local reefs are similarly affected, the disruptions to sea life can be felt globally. The world's oceans are presently in the midst of a period of intense acidification, believed to have begun in the mid-nineteenth century, and which is now accelerating at a rate faster than any change to oceanic pH in the last 20 million years.

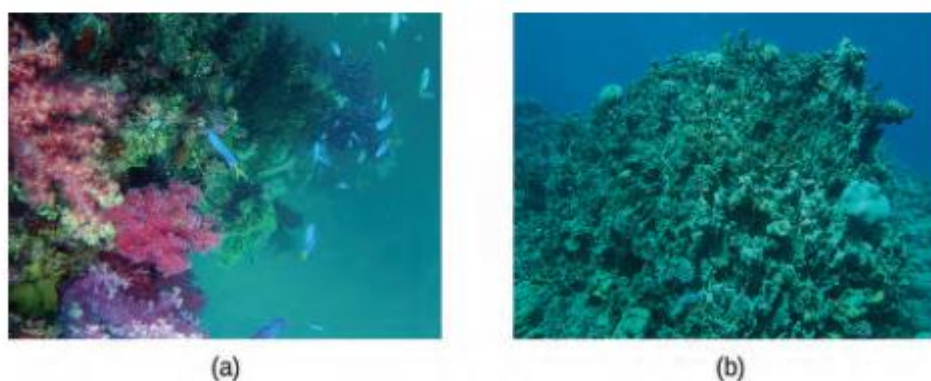


Figure 15.7 Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonate skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library; credit b: modification of work by "prilfish"/Flickr)

Slightly soluble solids derived from weak acids generally dissolve in strong acids, unless their solubility products are extremely small. For example, we can dissolve CuCO_3 , FeS , and $\text{Ca}_3(\text{PO}_4)_2$ in HCl because their basic anions react

to form weak acids (H_2CO_3 , H_2S , and H_2PO_4^-). The resulting decrease in the concentration of the anion results in a shift of the equilibrium concentrations to the right in accordance with Le Châtelier's principle.

Of particular relevance to us is the dissolution of hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, in acid. Apatites are a class of calcium phosphate minerals (Figure 15.8); a biological form of hydroxylapatite is found as the principal mineral in the enamel of our teeth. A mixture of hydroxylapatite and water (or saliva) contains an equilibrium mixture of solid $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and dissolved Ca^{2+} , PO_4^{3-} , and OH^- ions:

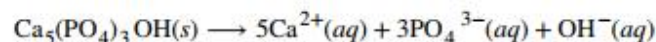
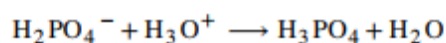
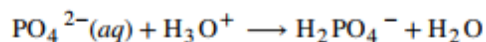
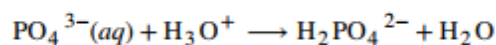
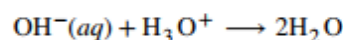


Figure 15.8 Crystal of the mineral hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is shown here. Pure apatite is white, but like many other minerals, this sample is colored because of the presence of impurities.

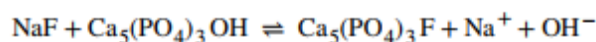
When exposed to acid, phosphate ions react with hydronium ions to form hydrogen phosphate ions and ultimately, phosphoric acid:



Hydroxide ion reacts to form water:



These reactions decrease the phosphate and hydroxide ion concentrations, and additional hydroxylapatite dissolves in an acidic solution in accord with Le Châtelier's principle. Our teeth develop cavities when acid waste produced by bacteria growing on them causes the hydroxylapatite of the enamel to dissolve. Fluoride toothpastes contain sodium fluoride, NaF , or stannous fluoride [more properly named tin(II) fluoride], SnF_2 . They function by replacing the OH^- ion in hydroxylapatite with F^- ion, producing fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$:



The resulting $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is slightly less soluble than $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, and F^- is a weaker base than OH^- . Both of these factors make the fluorapatite more resistant to attack by acids than hydroxylapatite. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Chemistry in Everyday Life

Role of Fluoride in Preventing Tooth Decay

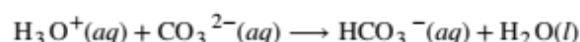
As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (Figure 15.9).



Figure 15.9 Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

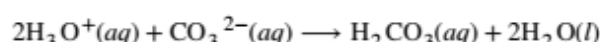
Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

When acid rain attacks limestone or marble, which are calcium carbonates, a reaction occurs that is similar to the acid attack on hydroxylapatite. The hydronium ion from the acid rain combines with the carbonate ion from calcium carbonates and forms the hydrogen carbonate ion, a weak acid:

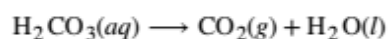


Calcium hydrogen carbonate, $\text{Ca}(\text{HCO}_3)_2$, is soluble, so limestone and marble objects slowly dissolve in acid rain.

If we add calcium carbonate to a concentrated acid, hydronium ion reacts with the carbonate ion according to the equation:



(Acid rain is usually not sufficiently acidic to cause this reaction; however, laboratory acids are.) The solution may become saturated with the weak electrolyte carbonic acid, which is unstable, and carbon dioxide gas can be evolved:



These reactions decrease the carbonate ion concentration, and additional calcium carbonate dissolves. If enough acid is present, the concentration of carbonate ion is reduced to such a low level that the reaction quotient for the dissolution of calcium carbonate remains less than the solubility product of calcium carbonate, even after all of the calcium carbonate has dissolved.

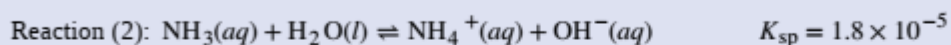
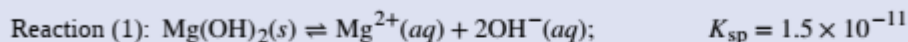
Example 15.14

Prevention of Precipitation of $\text{Mg}(\text{OH})_2$

Calculate the concentration of ammonium ion that is required to prevent the precipitation of $\text{Mg}(\text{OH})_2$ in a solution with $[\text{Mg}^{2+}] = 0.10 \text{ M}$ and $[\text{NH}_3] = 0.10 \text{ M}$.

Solution

Two equilibria are involved in this system:



To prevent the formation of solid $\text{Mg}(\text{OH})_2$, we must adjust the concentration of OH^- so that the reaction quotient for Equation (1), $Q = [\text{Mg}^{2+}][\text{OH}^-]^2$, is less than K_{sp} for $\text{Mg}(\text{OH})_2$. (To simplify the calculation, we determine the concentration of OH^- when $Q = K_{\text{sp}}$.) $[\text{OH}^-]$ can be reduced by the addition of NH_4^+ , which shifts Reaction (2) to the left and reduces $[\text{OH}^-]$.

Step 1. We determine the $[\text{OH}^-]$ at which $Q = K_{\text{sp}}$ when $[\text{Mg}^{2+}] = 0.10 \text{ M}$:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.10)[\text{OH}^-]^2 = 1.5 \times 10^{-11}$$

$$[\text{OH}^-] = 1.2 \times 10^{-5} \text{ M}$$

Solid $\text{Mg}(\text{OH})_2$ will not form in this solution when $[\text{OH}^-]$ is less than $1.2 \times 10^{-5} \text{ M}$.

Step 2. We calculate the $[\text{NH}_4^+]$ needed to decrease $[\text{OH}^-]$ to $1.2 \times 10^{-5} \text{ M}$ when $[\text{NH}_3] = 0.10$.

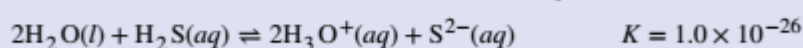
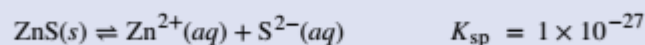
$$K_{\text{b}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[\text{NH}_4^+](1.2 \times 10^{-5})}{0.10} = 1.8 \times 10^{-5}$$

$$[\text{NH}_4^+] = 0.15 \text{ M}$$

When $[\text{NH}_4^+]$ equals 0.15 M , $[\text{OH}^-]$ will be $1.2 \times 10^{-5} \text{ M}$. Any $[\text{NH}_4^+]$ greater than 0.15 M will reduce $[\text{OH}^-]$ below $1.2 \times 10^{-5} \text{ M}$ and prevent the formation of $\text{Mg}(\text{OH})_2$.

Check Your Learning

Consider the two equilibria:



and calculate the concentration of hydronium ion required to prevent the precipitation of ZnS in a solution that is 0.050 M in Zn^{2+} and saturated with H_2S ($0.10 \text{ M H}_2\text{S}$).

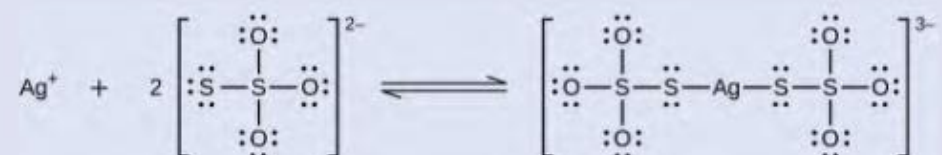
Answer: $[\text{H}_3\text{O}^+] > 0.2 \text{ M}$ ($[\text{S}^{2-}]$ is less than $2 \times 10^{-26} \text{ M}$ and precipitation of ZnS does not occur.)

Therefore, precise calculations of the solubility of solids from the solubility product are limited to cases in which the only significant reaction occurring when the solid dissolves is the formation of its ions.

Example 15.15

Multiple Equilibria

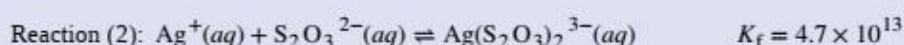
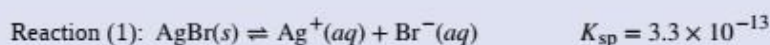
Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, called hypo) to form the complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ($K_f = 4.7 \times 10^{13}$). The reaction with silver bromide is:



What mass of $\text{Na}_2\text{S}_2\text{O}_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $\text{S}_2\text{O}_3^{2-}$ ion:



In order for 1.00 g of AgBr to dissolve, the $[\text{Ag}^+]$ in the solution that results must be low enough for Q for Reaction (1) to be smaller than K_{sp} for this reaction. We reduce $[\text{Ag}^+]$ by adding $\text{S}_2\text{O}_3^{2-}$ and thus cause Reaction (2) to shift to the right. We need the following steps to determine what mass of $\text{Na}_2\text{S}_2\text{O}_3$ is needed to provide the necessary $\text{S}_2\text{O}_3^{2-}$.

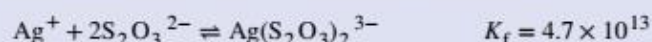
Step 1. We calculate the $[\text{Br}^-]$ produced by the complete dissolution of 1.00 g of AgBr (5.33×10^{-3} mol AgBr) in 1.00 L of solution:

$$[\text{Br}^-] = 5.33 \times 10^{-3} \text{ M}$$

Step 2. We use $[\text{Br}^-]$ and K_{sp} to determine the maximum possible concentration of Ag^+ that can be present without causing reprecipitation of AgBr:

$$[\text{Ag}^+] = 6.2 \times 10^{-11} \text{ M}$$

Step 3. We determine the $[\text{S}_2\text{O}_3^{2-}]$ required to make $[\text{Ag}^+] = 6.2 \times 10^{-11} \text{ M}$ after the remaining Ag^+ ion has reacted with $\text{S}_2\text{O}_3^{2-}$ according to the equation:



Because 5.33×10^{-3} mol of AgBr dissolves:

$$(5.33 \times 10^{-3}) - (6.2 \times 10^{-11}) = 5.33 \times 10^{-3} \text{ mol Ag}(\text{S}_2\text{O}_3)_2^{3-}$$

Thus, at equilibrium: $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] = 5.33 \times 10^{-3} \text{ M}$, $[\text{Ag}^+] = 6.2 \times 10^{-11} \text{ M}$, and $Q = K_f = 4.7 \times 10^{13}$:

$$K_f = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2} = 4.7 \times 10^{13}$$

$$[\text{S}_2\text{O}_3^{2-}] = 1.4 \times 10^{-3} \text{ M}$$

When $[S_2O_3^{2-}]$ is $1.4 \times 10^{-3} M$, $[Ag^+]$ is $6.2 \times 10^{-11} M$ and all AgBr remains dissolved.

Step 4. We determine the total number of moles of $S_2O_3^{2-}$ that must be added to the solution.

This equals the amount that reacts with Ag^+ to form $Ag(S_2O_3)_2^{3-}$ plus the amount of free $S_2O_3^{2-}$ in solution at equilibrium. To form $5.33 \times 10^{-3} \text{ mol}$ of $Ag(S_2O_3)_2^{3-}$ requires $2 \times (5.33 \times 10^{-3}) \text{ mol}$ of $S_2O_3^{2-}$. In addition, $1.4 \times 10^{-3} \text{ mol}$ of unreacted $S_2O_3^{2-}$ is present (Step 3). Thus, the total amount of $S_2O_3^{2-}$ that must be added is:

$$2 \times (5.33 \times 10^{-3} \text{ mol } S_2O_3^{2-}) + 1.4 \times 10^{-3} \text{ mol } S_2O_3^{2-} = 1.21 \times 10^{-2} \text{ mol } S_2O_3^{2-}$$

Step 5. We determine the mass of $Na_2S_2O_3$ required to give $1.21 \times 10^{-2} \text{ mol } S_2O_3^{2-}$ using the molar mass of $Na_2S_2O_3$:

$$1.21 \times 10^{-2} \text{ mol } S_2O_3^{2-} \times \frac{158.1 \text{ g } Na_2S_2O_3}{1 \text{ mol } Na_2S_2O_3} = 1.9 \text{ g } Na_2S_2O_3$$

Thus, 1.00 L of a solution prepared from 1.9 g $Na_2S_2O_3$ dissolves 1.0 g of AgBr.

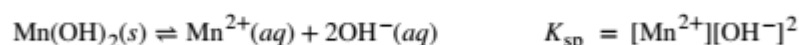
Check Your Learning

$AgCl(s)$, silver chloride, is well known to have a very low solubility: $Ag(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, $K_{sp} = 1.77 \times 10^{-10}$. Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed: $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$, $K_f = 1.7 \times 10^7$. What mass of NH_3 is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $Ag(NH_3)_2^+$?

Answer: 1.00 L of a solution prepared with 4.84 g NH_3 dissolves 2.0 g of AgCl.

Dissolution versus Weak Electrolyte Formation

We can determine how to shift the concentration of ions in the equilibrium between a slightly soluble solid and a solution of its ions by applying Le Châtelier's principle. For example, one way to control the concentration of manganese(II) ion, Mn^{2+} , in a solution is to adjust the pH of the solution and, consequently, to manipulate the equilibrium between the slightly soluble solid manganese(II) hydroxide, manganese(II) ion, and hydroxide ion:



This could be important to a laundry because clothing washed in water that has a manganese concentration exceeding 0.1 mg per liter may be stained by the manganese. We can reduce the concentration of manganese by increasing the concentration of hydroxide ion. We could add, for example, a small amount of NaOH or some other base such as the silicates found in many laundry detergents. As the concentration of OH^- ion increases, the equilibrium responds by shifting to the left and reducing the concentration of Mn^{2+} ion while increasing the amount of solid $Mn(OH)_2$ in the equilibrium mixture, as predicted by Le Châtelier's principle.

Example 15.16

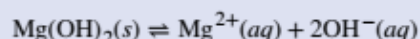
Solubility Equilibrium of a Slightly Soluble Solid

What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ in water at equilibrium?

- (a) MgCl_2
- (b) KOH
- (c) an acid
- (d) NaNO_3
- (e) Mg(OH)_2

Solution

The equilibrium among solid Mg(OH)_2 and a solution of Mg^{2+} and OH^- is:



- (a) The reaction shifts to the left to relieve the stress produced by the additional Mg^{2+} ion, in accordance with Le Châtelier's principle. In quantitative terms, the added Mg^{2+} causes the reaction quotient to be larger than the solubility product ($Q > K_{sp}$), and Mg(OH)_2 forms until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is less and $[\text{Mg}^{2+}]$ is greater than in the solution of Mg(OH)_2 in pure water. More solid Mg(OH)_2 is present.
- (b) The reaction shifts to the left to relieve the stress of the additional OH^- ion. Mg(OH)_2 forms until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is greater and $[\text{Mg}^{2+}]$ is less than in the solution of Mg(OH)_2 in pure water. More solid Mg(OH)_2 is present.
- (c) The concentration of OH^- is reduced as the OH^- reacts with the acid. The reaction shifts to the right to relieve the stress of less OH^- ion. In quantitative terms, the decrease in the OH^- concentration causes the reaction quotient to be smaller than the solubility product ($Q < K_{sp}$), and additional Mg(OH)_2 dissolves until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is less and $[\text{Mg}^{2+}]$ is greater than in the solution of Mg(OH)_2 in pure water. More Mg(OH)_2 is dissolved.
- (d) NaNO_3 contains none of the species involved in the equilibrium, so we should expect that it has no appreciable effect on the concentrations of Mg^{2+} and OH^- . (As we have seen previously, dissolved salts change the activities of the ions of an electrolyte. However, the salt effect is generally small, and we shall neglect the slight errors that may result from it.)
- (e) The addition of solid Mg(OH)_2 has no effect on the solubility of Mg(OH)_2 or on the concentration of Mg^{2+} and OH^- . The concentration of Mg(OH)_2 does not appear in the equation for the reaction quotient:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q , and no shift is required to restore Q to the value of the equilibrium constant.

Check Your Learning

What is the effect on the amount of solid NiCO_3 that dissolves and the concentrations of Ni^{2+} and CO_3^{2-} when each of the following are added to a mixture of the slightly soluble solid NiCO_3 and water at equilibrium?

- (a) $\text{Ni(NO}_3)_2$

- (b) KClO_4
- (c) NiCO_3
- (d) K_2CO_3
- (e) HNO_3 (reacts with carbonate giving HCO_3^- or H_2O and CO_2)

Answer: (a) mass of $\text{NiCO}_3(\text{s})$ increases, $[\text{Ni}^{2+}]$ increases, $[\text{CO}_3^{2-}]$ decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid NiCO_3 ; (d) mass of $\text{NiCO}_3(\text{s})$ increases, $[\text{Ni}^{2+}]$ decreases, $[\text{CO}_3^{2-}]$ increases; (e) mass of $\text{NiCO}_3(\text{s})$ decreases, $[\text{Ni}^{2+}]$ increases, $[\text{CO}_3^{2-}]$ decreases

Key Terms

common ion effect effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

complex ion ion consisting of a transition metal central atom and surrounding molecules or ions called ligands

coordinate covalent bond (also, dative bond) bond formed when one atom provides both electrons in a shared pair

dissociation constant (K_d) equilibrium constant for the decomposition of a complex ion into its components in solution

formation constant (K_f) (also, stability constant) equilibrium constant for the formation of a complex ion from its components in solution

Lewis acid any species that can accept a pair of electrons and form a coordinate covalent bond

Lewis acid-base adduct compound or ion that contains a coordinate covalent bond between a Lewis acid and a Lewis base

Lewis base any species that can donate a pair of electrons and form a coordinate covalent bond

ligand molecule or ion that surrounds a transition metal and forms a complex ion; ligands act as Lewis bases

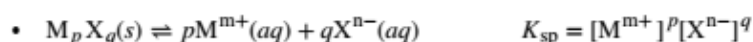
molar solubility solubility of a compound expressed in units of moles per liter (mol/L)

multiple equilibrium system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

selective precipitation process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product (K_{sp}) equilibrium constant for the dissolution of a slightly soluble electrolyte

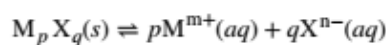
Key Equations



Summary

15.1 Precipitation and Dissolution

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp} , of the solid. When we have a heterogeneous equilibrium involving the slightly soluble solid $M_p X_q$ and its ions M^{m+} and X^{n-} :



We write the solubility product expression as:

$$K_{sp} = [M^{m+}]^p [X^{n-}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp} , provided the only significant reaction that occurs when the solid dissolves is the formation of its ions.

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product.

A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Châtelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

15.2 Lewis Acids and Bases

G.N. Lewis proposed a definition for acids and bases that relies on an atom's or molecule's ability to accept or donate electron pairs. A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts. In a complex ion, we have a central atom, often consisting of a transition metal cation, which acts as a Lewis acid, and several neutral molecules or ions surrounding them called ligands that act as Lewis bases. Complex ions form by sharing electron pairs to form coordinate covalent bonds. The equilibrium reaction that occurs when forming a complex ion has an equilibrium constant associated with it called a formation constant, K_f . This is often referred to as a stability constant, as it represents the stability of the complex ion. Formation of complex ions in solution can have a profound effect on the solubility of a transition metal compound.

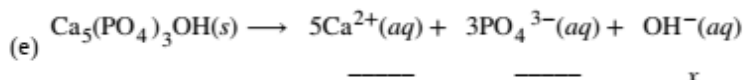
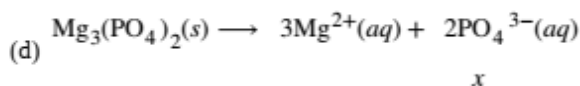
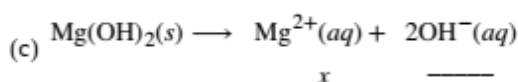
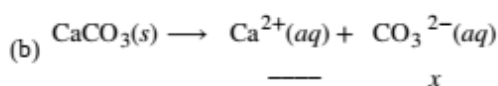
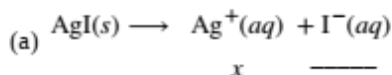
15.3 Multiple Equilibria

Several systems we encounter consist of multiple equilibria, systems where two or more equilibria processes are occurring simultaneously. Some common examples include acid rain, fluoridation, and dissolution of carbon dioxide in sea water. When looking at these systems, we need to consider each equilibrium separately and then combine the individual equilibrium constants into one solubility product or reaction quotient expression using the tools from the first equilibrium chapter. Le Châtelier's principle also must be considered, as each reaction in a multiple equilibria system will shift toward reactants or products based on what is added to the initial reaction and how it affects each subsequent equilibrium reaction.

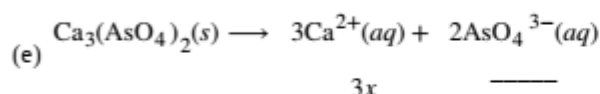
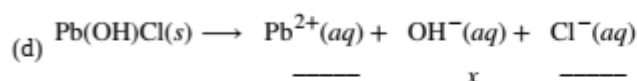
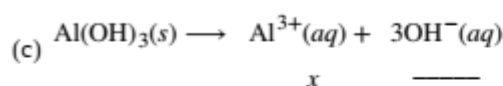
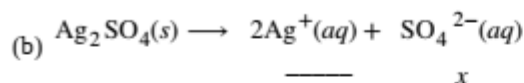
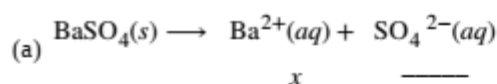
Exercises

15.1 Precipitation and Dissolution

1. Complete the changes in concentrations for each of the following reactions:



2. Complete the changes in concentrations for each of the following reactions:



3. How do the concentrations of Ag^+ and CrO_4^{2-} in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain.

4. How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS ?

5. What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised?

6. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: CoSO_3 , CuI , PbCO_3 , PbCl_2 , Ti_2S , KClO_4 ?

7. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl , BaSO_4 , CaF_2 , Hg_2I_2 , MnCO_3 , ZnS , PbS ?

8. Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:

(a) PbCl_2

(b) Ag_2S

(c) $\text{Sr}_3(\text{PO}_4)_2$

(d) SrSO_4

9. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

(a) LaF_3

(b) CaCO_3

(c) Ag_2SO_4

(d) Pb(OH)_2