Chapter 15

Equilibria of Other Reaction Classes

Figure 15.1 The mineral fluorite (CaF_2) is formed when dissolved calcium and fluoride ions precipitate from groundwater within the Earth's crust. Note that pure fluorite is colorless, and that the color in this sample is due to the presence of other metal ions in the crystal.

Chapter Outline

15.1 Precipitation and Dissolution

15.2 Lewis Acids and Bases

15.3 Coupled Equilibria

Introduction

The mineral fluorite, CaF_2 **Figure 15.1**, is commonly used as a semiprecious stone in many types of jewelry because of its striking appearance. Deposits of fluorite are formed through a process called hydrothermal precipitation in which calcium and fluoride ions dissolved in groundwater combine to produce insoluble CaF_2 in response to some change in solution conditions. For example, a decrease in temperature may trigger fluorite precipitation if its solubility is exceeded at the lower temperature. Because fluoride ion is a weak base, its solubility is also affected by solution pH, and so geologic or other processes that change groundwater pH will also affect the precipitation of fluorite. This chapter extends the equilibrium discussion of other chapters by addressing some additional reaction classes (including precipitation) and systems involving coupled equilibrium reactions.
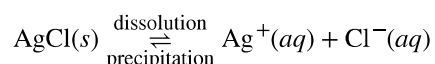
15.1 Precipitation and Dissolution

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

Solubility equilibria are established when the dissolution and precipitation of a solute species occur at equal rates. These equilibria underlie many natural and technological processes, ranging from tooth decay to water purification. An understanding of the factors affecting compound solubility is, therefore, essential to the effective management of these processes. This section applies previously introduced equilibrium concepts and tools to systems involving dissolution and precipitation.

The Solubility Product

Recall from the chapter on solutions that the solubility of a substance can vary from essentially zero (*insoluble* or *sparingly soluble*) to infinity (*miscible*). A solute with finite solubility can yield a *saturated* solution when it is added to a solvent in an amount exceeding its solubility, resulting in a heterogeneous mixture of the saturated solution and the excess, undissolved solute. For example, a saturated solution of silver chloride is one in which the equilibrium shown below has been established.

$$AgCl(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} Ag^+(aq) + Cl^-(aq)$$

In this solution, an excess of solid AgCl dissolves and dissociates to produce aqueous Ag^+ and Cl^- ions at the same rate that these aqueous ions combine and precipitate to form solid AgCl (**Figure 15.2**). Because silver chloride is a sparingly soluble salt, the equilibrium concentration of its dissolved ions in the solution is relatively low.
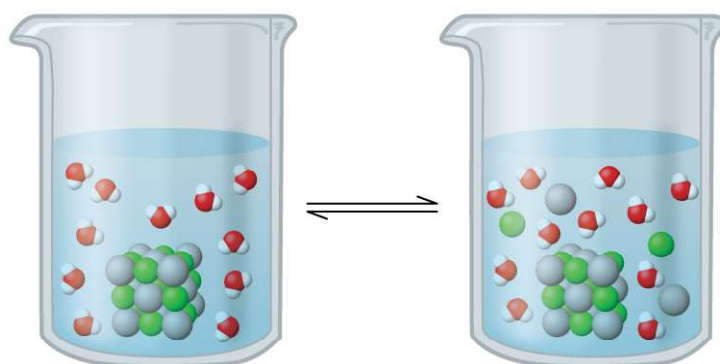

Figure 15.2   Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

The equilibrium constant for solubility equilibria such as this one is called the **solubility product constant, K_{sp}**, in this case

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+(aq)][Cl^-(aq)]$$
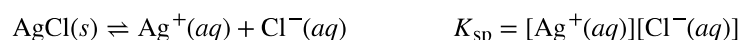
Recall that only gases and solutes are represented in equilibrium constant expressions, so the K_{sp} does not include a term for the undissolved AgCl. A listing of solubility product constants for several sparingly soluble compounds is provided in **Appendix J**.
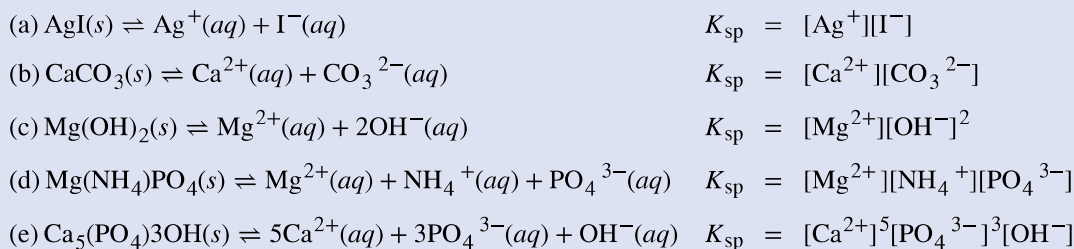
Example 15.1

Writing Equations and Solubility Products

Write the dissolution equation 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) $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia

(d) $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium

(e) $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

Solution

(a) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ $\qquad\qquad\qquad\qquad\qquad K_{sp} = [Ag^+][I^-]$

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

(c) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ $\qquad\qquad K_{sp} = [Mg^{2+}][OH^-]^2$

(d) $Mg(NH_4)PO_4(s) \rightleftharpoons Mg^{2+}(aq) + NH_4{}^+(aq) + PO_4{}^{3-}(aq)$ $\quad K_{sp} = [Mg^{2+}][NH_4{}^+][PO_4{}^{3-}]$

(e) $Ca_5(PO_4)3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4{}^{3-}(aq) + OH^-(aq)$ $\quad K_{sp} = [Ca^{2+}]^5[PO_4{}^{3-}]^3[OH^-]$
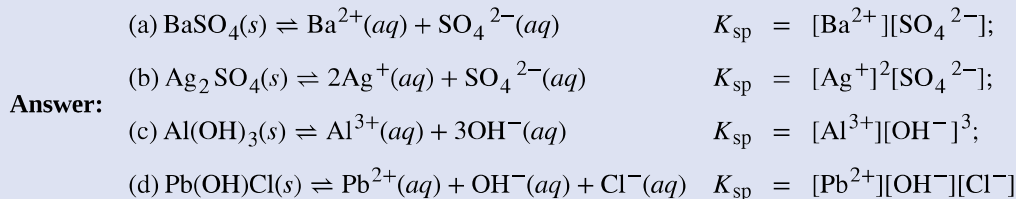
Check Your Learning

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

(a) $BaSO_4$

(b) Ag_2SO_4

(c) $Al(OH)_3$

(d) $Pb(OH)Cl$

Answer:

(a) $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq)$ $\qquad\qquad\qquad K_{sp} = [Ba^{2+}][SO_4{}^{2-}]$;

(b) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4{}^{2-}(aq)$ $\qquad\qquad K_{sp} = [Ag^+]^2[SO_4{}^{2-}]$;

(c) $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$ $\qquad\qquad\quad K_{sp} = [Al^{3+}][OH^-]^3$;

(d) $Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^-(aq) + Cl^-(aq)$ $\quad K_{sp} = [Pb^{2+}][OH^-][Cl^-]$

K_{sp} and Solubility

The K_{sp} of a slightly soluble ionic compound may be simply related to its measured solubility provided the dissolution process involves only dissociation and solvation, for example:

$$M_pX_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$$
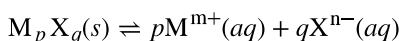
For cases such as these, one may derive K_{sp} values from provided solubilities, or vice-versa. Calculations of this sort are most conveniently performed using a compound's molar solubility, measured as moles of dissolved solute per liter of saturated solution.

Example 15.2

Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
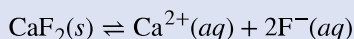
The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15×10^{-4} M. What is the solubility product

of fluorite?

Solution

According to the stoichiometry of the dissolution equation, the fluoride ion molarity of a CaF_2 solution is equal to twice its calcium ion molarity:
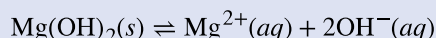
$$[F^-] = (2 \text{ mol } F^- \ / 1 \text{ mol } Ca^{2+}) = (2)(2.15 \times 10^{-4} \ M) = 4.30 \times 10^{-4} \ M$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2.15 \times 10^{-4})(4.30 \times 10^{-4})^2 = 3.98 \times 10^{-11}$$

Check Your Learning

In a saturated solution of $Mg(OH)_2$, the concentration of Mg^{2+} is $1.31 \times 10^{-4} \ M$. What is the solubility product for $Mg(OH)_2$?

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

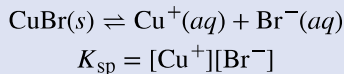**Answer:** 8.99×10^{-12}

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 dissolution equation and solubility product expression are

$$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$$
$$K_{sp} = [Cu^+][Br^-]$$

Following the ICE approach to this calculation yields the table

	CuBr (s) $\rightleftharpoons$ Cu$^+$(aq)	+	Br$^-$(aq)
Initial concentration (M)		0	0
Change (M)		+x	+x
Equilibrium concentration (M)		x	x

Substituting the equilibrium concentration terms into the solubility product expression and solving for x yields

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

Since the dissolution stoichiometry shows one mole of copper(I) ion and one mole of bromide ion are produced for each moles of Br dissolved, 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.
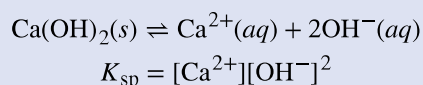
Answer: $1.2 \times 10^{-8} \ M$

Example 15.4

Determination of Molar Solubility from K_{sp}

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$
$$K_{sp} = [Ca^{2+}][OH^-]^2$$

The ICE table for this system is

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

Substituting terms for the equilibrium concentrations into the solubility product expression and solving for x gives

$$K_{sp} = [Ca^{2+}][OH^-]^2$$
$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$
$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 7.0 \times 10^{-3}\ M$$

As defined in the ICE table, x is the molarity of calcium ion in the saturated solution. The dissolution stoichiometry shows a 1:1 relation between moles of calcium ion in solution and moles of compound dissolved, and so, the molar solubility of $Ca(OH)_2$ is $6.9 \times 10^{-3}\ M$.

Check Your Learning

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

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

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 4.6×10^{-6} g/L. Determine the solubility product for $PbCrO_4$.
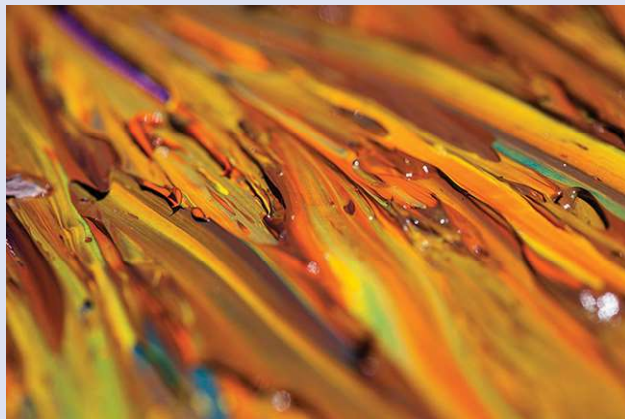
Figure 15.3 Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

Before calculating the solubility product, the provided solubility must be converted to molarity:

$$[PbCrO_4] = \frac{4.6 \times 10^{-6}\,g\ PbCrO_4}{1\,L} \times \frac{1\,mol\ PbCrO_4}{323.2\,g\ PbCrO_4}$$

$$= \frac{1.4 \times 10^{-8}\,mol\ PbCrO_4}{1\,L}$$

$$= 1.4 \times 10^{-8}\,M$$

The dissolution equation for this compound is

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4{}^{2-}(aq)$$
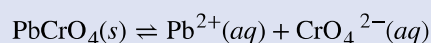
The dissolution stoichiometry shows a 1:1 relation between the molar amounts of compound and its two ions, and so both $[Pb^{2+}]$ and $[CrO_4{}^{2-}]$ are equal to the molar solubility of $PbCrO_4$:

$$[Pb^{2+}] = [CrO_4{}^{2-}] = 1.4 \times 10^{-8}\,M$$

$K_{sp} = [Pb^{2+}][CrO_4{}^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$

Check Your Learning

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.12 grams per liter at 20 °C. What is its solubility product?

Answer: 2.08×10^{-4}

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 has a very low solubility, as suggested by its very small K_{sp}:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 1.1 \times 10^{-18}$$
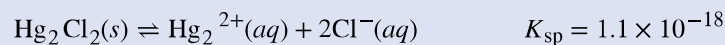
Calculate the molar solubility of Hg_2Cl_2.

Solution

The dissolution stoichiometry shows a 1:1 relation between the amount of compound dissolved and the amount of mercury(I) ions, and so the molar solubility of Hg_2Cl_2 is equal to the concentration of Hg_2^{2+} ions

Following the ICE approach results in

	$Hg_2Cl_2\ (s) \rightleftharpoons Hg_2^{2+}\ (aq)\ +\ 2Cl^-\ (aq)$		
Initial concentration (M)		0	0
Change (M)		$+x$	$+2x$
Equilibrium concentration (M)		x	$2x$

Substituting the equilibrium concentration terms into the solubility product expression and solving for x gives

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$
$$1.1 \times 10^{-18} = (x)(2x)^2$$
$$4x^3 = 1.1 \times 10^{-18}$$
$$x = \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} = 6.5 \times 10^{-7}\ M$$
$$[Hg_2^{2+}] = 6.5 \times 10^{-7}\ M = 6.5 \times 10^{-7}\ M$$
$$[Cl^-] = 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6}\ M$$

The dissolution stoichiometry shows the molar solubility of Hg_2Cl_2 is equal to $[Hg_2^{2+}]$, or 6.5×10^{-7} *M*.

Check Your Learning

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

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

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 2.3×10^{-8}, 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 A suspension of barium sulfate coats the intestinal tract, permitting greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)

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)** 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:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq) \quad K_{sp} = [Ca^{2+}][CO_3{}^{2-}] = 8.7 \times 10^{-9}$$
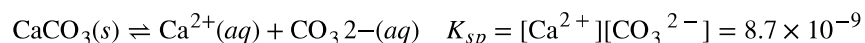
It is important to realize that this equilibrium is established in any aqueous solution containing Ca^{2+} and $CO_3{}^{2-}$ ions, not just in a solution formed by saturating water with calcium carbonate. Consider, for example, mixing aqueous solutions of the soluble compounds sodium carbonate and calcium nitrate. If the concentrations of calcium and carbonate ions in the mixture do not yield a reaction quotient, Q_{sp}, that exceeds the solubility product, K_{sp}, then no precipitation will occur. If the ion concentrations yield a reaction quotient greater than the solubility product, then precipitation will occur, lowering those concentrations until equilibrium is established ($Q_{sp} = K_{sp}$). The comparison of Q_{sp} to K_{sp} to predict precipitation is an example of the general approach to predicting the direction of a reaction first introduced in the chapter on equilibrium. For the specific case of solubility equilibria:

$Q_{sp} < K_{sp}$: the reaction proceeds in the forward direction (solution is not saturated; no precipitation observed)

$Q_{sp} > K_{sp}$: the reaction proceeds in the reverse direction (solution is supersaturated; precipitation will occur)

This predictive strategy and related calculations are demonstrated in the next few example exercises.

Example 15.7

Precipitation of $Mg(OH)_2$

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

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = 8.9 \times 10^{-12}$$
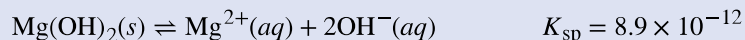
The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 M. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 M?

Solution

Calculation of the reaction quotient under these conditions is shown here:

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

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), the reverse reaction will proceed, precipitating magnesium hydroxide until the dissolved ion concentrations have been sufficiently lowered, so that $Q_{sp} = K_{sp}$.

Check Your Learning

Predict whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}] = 0.0001$ M and $[HPO_4{}^{2-}] = 0.001$ M.

Answer: No precipitation of $CaHPO_4$; $Q = 1 \times 10^{-7}$, which is less than K_{sp} (7×10^{-7})
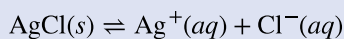
Example 15.8

Precipitation of AgCl

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

Solution

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

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility product is 1.6×10^{-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}. Because the volume doubles when equal volumes of $AgNO_3$ and NaCl solutions are mixed, each concentration is reduced to half its initial value

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

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

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

AgCl will precipitate from the mixture until the dissolution equilibrium is established, 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^-? (Hint: Use the dilution equation to calculate the concentrations of potassium and perchlorate ions in the mixture.)

Answer: No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$

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, $C_2O_4^{2-}$, for this purpose (**Figure 15.5**). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (calcium oxalate monohydrate). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} *M*. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4 \cdot H_2O$ 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:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$
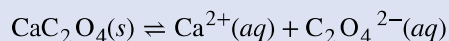
For this reaction:

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^{-8}$$

(see **Appendix J**)

Substitute the provided calcium ion concentration into the solubility product expression and solve for oxalate concentration:

$$Q = K_{sp} = [Ca^{2+}][C_2O_4{}^{2-}] = 1.96 \times 10^{-8}$$
$$(2.2 \times 10^{-3})[C_2O_4{}^{2-}] = 1.96 \times 10^{-8}$$
$$[C_2O_4{}^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6} \ M$$

A concentration of $[C_2O_4{}^{2-}] = 8.9 \times 10^{-6} \ M$ 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: $6.7 \times 10^{-5} \ M$

## Example 15.10

Concentrations Following Precipitation

Clothing washed in water that has a manganese $[Mn^{2+}(aq)]$ concentration exceeding 0.1 mg/L (1.8×10^{-6} M) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be decreased by adding a base to precipitate $Mn(OH)_2$. 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:

$$Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = 2 \times 10^{-13}$$
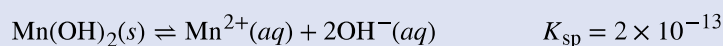
At equilibrium:

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

or

$$(1.8 \times 10^{-6})[OH^-]^2 = 2 \times 10^{-13}$$

so

$$[OH^-] = 3.3 \times 10^{-4} \ M$$

Calculate the pH from the pOH:

$$pOH = -\log[OH^-] = -\log(3.3 \times 10 - 4) = 3.48$$
$$pH = 14.00 - pOH = 14.00 - 3.80 = 10.5$$

(final result rounded to one significant digit, limited by the certainty of the K_{sp})

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 decreased to $1.0 \times 10^{-5} \ M$

Answer: 10.97

In solutions containing two or more ions that may form insoluble compounds with the same counter ion, an experimental strategy called **selective precipitation** may be used to remove individual ions from solution. By increasing the counter ion concentration in a controlled manner, ions in solution may be precipitated individually, assuming their compound solubilities are adequately different. In solutions with equal concentrations of target ions,

the ion forming the least soluble compound will precipitate first (at the lowest concentration of counter ion), with the other ions subsequently precipitating as their compound's solubilities are reached. As an illustration of this technique, the next example exercise describes separation of a two halide ions via precipitation of one as a silver salt.

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 $(PO_4{}^{3-})$ 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, or lime, $Ca(OH)_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3OH$, which then precipitates out of the solution:

$$5Ca^{2+} + 3PO_4{}^{3-} + OH^- \rightleftharpoons Ca_5(PO_4)_3 \cdot OH(s)$$

Because the amount of calcium ion added does not result in exceeding the solubility products for other calcium salts, the anions of those salts remain behind in the wastewater. 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/l/16Wastewater)** for more information on how phosphorus is removed from wastewater.
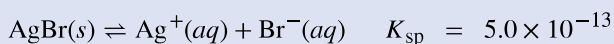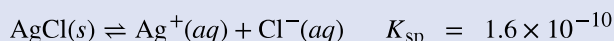
Example 15.11

Precipitation of Silver Halides

A solution contains 0.00010 mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

Solution

The two equilibria involved are:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.6 \times 10^{-10}$$

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad K_{sp} = 5.0 \times 10^{-13}$$

If the solution contained about *equal* concentrations of Cl^- and Br^-, then the silver salt with the smaller K_{sp} (AgBr) would precipitate first. The concentrations are not equal, however, so the $[Ag^+]$ at which AgCl begins to precipitate and the $[Ag^+]$ at which AgBr begins to precipitate must be calculated. The salt that forms at the lower $[Ag^+]$ precipitates first.

AgBr precipitates when Q equals K_{sp} for AgBr

$$Q = [Ag^+][Br^-] = [Ag^+](0.00010) = 5.0 \times 10^{-13}$$

$$[Ag^+] = \frac{5.0 \times 10^{-13}}{0.00010} = 5.0 \times 10^{-9} \ M$$

AgI begins to precipitate when $[Ag^+]$ is $5.0 \times 10^{-9} \ M$.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10^{-10}). When $[Cl^-] = 0.10 \ M$:

$$Q_{sp} = [Ag^+][Cl^-] = [Ag^+](0.10) = 1.6 \times 10^{-10}$$

$$[Ag^+] = \frac{1.6 \times 10^{-10}}{0.10} = 1.6 \times 10^{-9} \ M$$

AgCl begins to precipitate when $[Ag^+]$ is $1.6 \times 10^{-9} \ M$.

AgCl begins to precipitate at a lower $[Ag^+]$ than AgBr, so AgCl begins to precipitate first. Note the chloride ion concentration of the initial mixture was significantly greater than the bromide ion concentration, and so silver chloride precipitated first despite having a K_{sp} greater than that of silver bromide.

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: $[Ag^+] = 1.0 \times 10^{-11} \ M$; AgBr precipitates first

Common Ion Effect

Compared with pure water, the solubility of an ionic compound is less in aqueous solutions containing a *common ion* (one also produced by dissolution of the ionic compound). This is an example of a phenomenon known as the **common ion effect**, which is a consequence of the law of mass action that may be explained using Le ChÂtelier's principle. Consider the dissolution of silver iodide:

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$
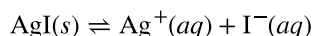
This solubility equilibrium may be shifted left by the addition of either silver(I) or iodide ions, resulting in the precipitation of AgI and lowered concentrations of dissolved Ag^+ and I^-. In solutions that already contain either of these ions, less AgI may be dissolved than in solutions without these ions.

This effect may also be explained in terms of mass action as represented in the solubility product expression:

$$K_{sp} = [Ag^+][I^-]$$

The mathematical product of silver(I) and iodide ion molarities is constant in an equilibrium mixture *regardless of the source of the ions*, and so an increase in one ion's concentration must be balanced by a proportional decrease in the other.

Link to Learning

View this **simulation (http://openstaxcollege.org/l/16solublesalts)** to explore various aspects of the common ion effect.

Link to Learning

View this **simulation (http://openstax.org/l/16commonion)** to see how the common ion effect works with different concentrations of salts.
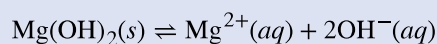
Example 15.12

Common Ion Effect on Solubility

What is the effect on the amount of solid $Mg(OH)_2$ and the concentrations of Mg^{2+} and OH^- when each of the following are added to a saturated solution of $Mg(OH)_2$?

(a) $MgCl_2$

(b) KOH

(c) $NaNO_3$

(d) $Mg(OH)_2$

Solution

The solubility equilibrium is

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

(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, $[OH^-]$ is less and $[Mg^{2+}]$ 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, $[OH^-]$ is greater and $[Mg^{2+}]$ 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

(a) Adding a common ion, Mg^{2+}, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of hydroxide ion and increasing the amount of undissolved magnesium hydroxide.

(b) Adding a common ion, OH^-, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of magnesium ion and increasing the amount of undissolved magnesium hydroxide.

(c) The added compound does not contain a common ion, and no effect on the magnesium hydroxide solubility equilibrium is expected.

(d) Adding more solid magnesium hydroxide will increase the amount of undissolved compound in the mixture. The solution is already saturated, though, so the concentrations of dissolved magnesium and hydroxide ions will remain the same.

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

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 $NiCO_3$ and the concentrations of Ni^{2+} and $CO_3{}^{2-}$ when each of the following are added to a saturated solution of $NiCO_3$

(a) $Ni(NO_3)_2$

(b) $KClO_4$

(c) $NiCO_3$

(d) K_2CO_3

　　Answer:　(a) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ increases, $[CO_3{}^{2-}]$ decreases; (b) no appreciable effect;
(c) no effect except to increase the amount of solid $NiCO_3$; (d) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ decreases, $[CO_3{}^{2-}]$ increases;
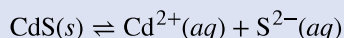
Example 15.13

Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide (CdBr$_2$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

This calculation can be performed using the ICE approach:

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

	CdS (s) $\rightleftharpoons$ **Cd^{2+} (aq)**	+	**S^{2-} (aq)**
Initial concentration (M)	0.010		0
Change (M)	+x		+x
Equilibrium concentration (M)	0.010 + x		x

$$K_{sp} = [Cd^{2+}][S^{2-}] = 1.0 \times 10^{-28}$$
$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

Because K_{sp} is very small, assume $x \ll 0.010$ and solve the simplified equation for x:

$$(0.010)(x) = 1.0 \times 10^{-28}$$
$$x = 1.0 \times 10^{-26} \; M$$

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,

$Al(NO_3)_3$. The K_{sp} of $Al(OH)_3$ is 2×10^{-32}.

Answer: $4 \times 10^{-11}\ M$

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.
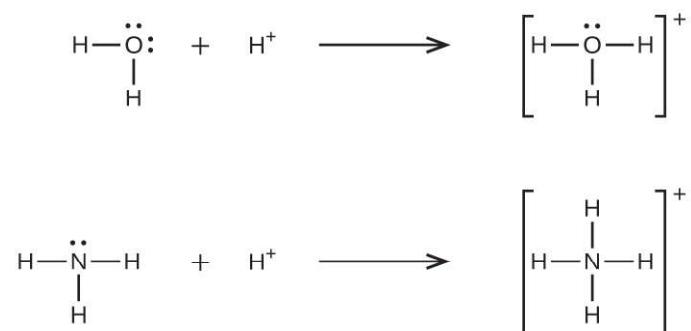

Reactions involving the formation of coordinate covalent bonds are classified as **Lewis acid-base chemistry**. The species donating the electron pair that compose the bond is a **Lewis base**, the species accepting the electron pair is a **Lewis acid**, and the product of the reaction is a **Lewis acid-base adduct**. As the two examples above illustrate, Brønsted-Lowry acid-base reactions represent a subcategory of Lewis acid reactions, specifically, those in which the acid species is H^+. A few examples involving other Lewis acids and bases are described below.

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:
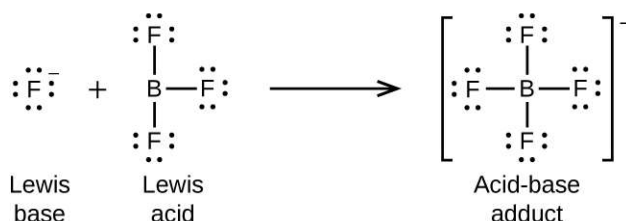

In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:
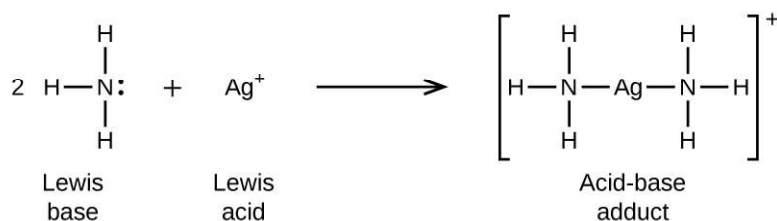
Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:
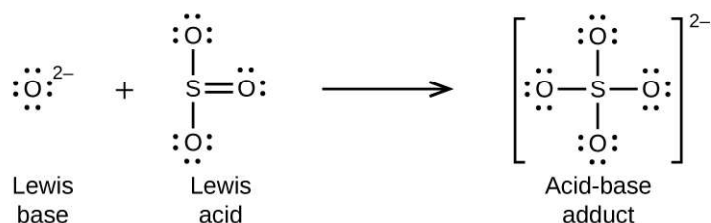
Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:
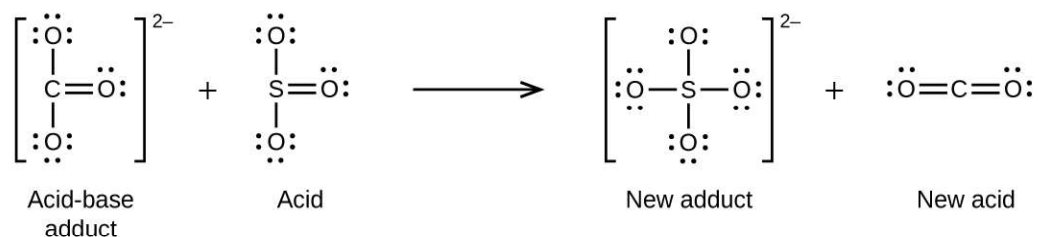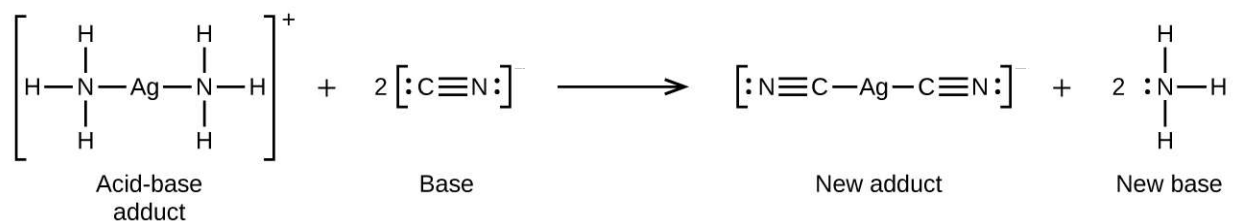
Another type of Lewis acid-base chemistry involves the formation of a complex ion (or a coordination complex) comprising a central atom, typically a transition metal cation, surrounded by ions or molecules called **ligands**. These ligands can be neutral molecules like H_2O or NH_3, or ions such as CN^- or OH^-. Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. These types of Lewis acid-base reactions are examples of a broad subdiscipline called *coordination chemistry*—the topic of another chapter in this text.

The equilibrium constant for the reaction of a metal ion with one or more ligands to form a coordination complex is called a **formation constant (K_f)** (sometimes called a stability constant). For example, the complex ion $Cu(CN)_2{}^-$
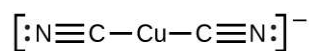
is produced by the reaction

$$Cu^+(aq) + 2CN^-(aq) \rightleftharpoons Cu(CN)_2{}^-(aq)$$
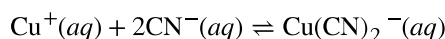
The formation constant for this reaction is

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

Alternatively, the reverse reaction (decomposition of the complex ion) can be considered, in which case the equilibrium constant is a **dissociation constant (K_d)**. Per the relation between equilibrium constants for reciprocal

reactions described, the dissociation constant is the mathematical inverse of the formation constant, $K_d = K_f^{-1}$. A tabulation of formation constants is provided in **Appendix K**.

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^+ ([Ag^+] = 1.3×10^{-5} M):

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
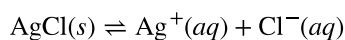
However, if NH_3 is present in the water, the complex ion, $Ag(NH_3)_2{}^+$, can form according to the equation:

Example 15.14

Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 M with respect to $Ag(NH_3)_2{}^+$.

Solution

Applying the standard ICE approach to this reaction yields the following:

	Ag^+ +	$2NH_3$ $\rightleftharpoons$	$Ag(NH_3)_2{}^+$
Initial concentration (M)	0	0	0.10
Change (M)	$+x$	$+2x$	$-x$
Equilibrium concentration (M)	x	$2x$	$0.10 - x$

Substituting these equilibrium concentration terms into the K_f expression gives

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

$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2}$$

The very large equilibrium constant means the amount of the complex ion that will dissociate, x, will be very small. Assuming $x \ll 0.1$ permits simplifying the above equation:

$$1.7 \times 10^7 = \frac{0.10}{(x)(2x)^2}$$

$$x^3 = \frac{0.10}{4(1.7 \times 10^7)} = 1.5 \times 10^{-9}$$

$$x = \sqrt[3]{1.5 \times 10^{-9}} = 1.1 \times 10^{-3}$$

Because only 1.1% of the $Ag(NH_3)_2{}^+$ dissociates into Ag^+ and NH_3, the assumption that x is small is justified.

Using this value of x and the relations in the above ICE table allows calculation of all species' equilibrium concentrations:

$$[Ag^+] = 0 + x = 1.1 \times 10^{-3} \ M$$

$$[NH_3] = 0 + 2x = 2.2 \times 10^{-3} \ M$$

$$[Ag(NH_3)_2{}^+] = 0.10 - x = 0.10 - 0.0011 = 0.099$$

The concentration of free silver ion in the solution is 0.0011 M.

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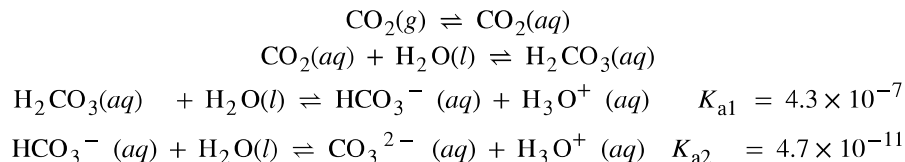
By the end of this section, you will be able to:

- Describe examples of systems involving two (or more) coupled chemical equilibria
- Calculate reactant and product concentrations for coupled equilibrium systems

As discussed in preceding chapters on equilibrium, *coupled equilibria* involve two or more separate chemical reactions that share one or more reactants or products. This section of this chapter will address solubility equilibria coupled with acid-base and complex-formation reactions.

An environmentally relevant example illustrating the coupling of solubility and acid-base equilibria is the impact of ocean acidification on the health of the ocean's coral reefs. These reefs are built upon skeletons of sparingly soluble calcium carbonate excreted by colonies of corals (small marine invertebrates). The relevant dissolution equilibrium is

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{-2}(aq) \qquad K_{sp} = 8.7 \times 10^{-9}$$
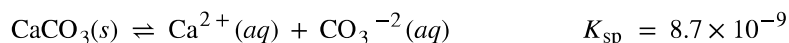
Rising concentrations of atmospheric carbon dioxide contribute to an increased acidity of ocean waters due to the dissolution, hydrolysis, and acid ionization of carbon dioxide:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

Inspection of these equilibria shows the carbonate ion is involved in the calcium carbonate dissolution and the acid hydrolysis of bicarbonate ion. Combining the dissolution equation with the reverse of the acid hydrolysis equation yields

$$CaCO_3(s) + H_3O^+(aq) \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq) + H_2O(l) \qquad K = K_{sp}/K_{a2} = 180$$
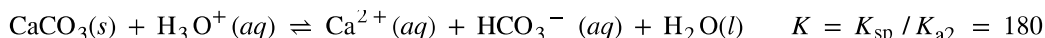
The equilibrium constant for this net reaction is much greater than the K_{sp} for calcium carbonate, indicating its solubility is markedly increased in acidic solutions. As rising carbon dioxide levels in the atmosphere increase the acidity of ocean waters, the calcium carbonate skeletons of coral reefs become more prone to dissolution and subsequently less healthy (**Figure 15.7**).
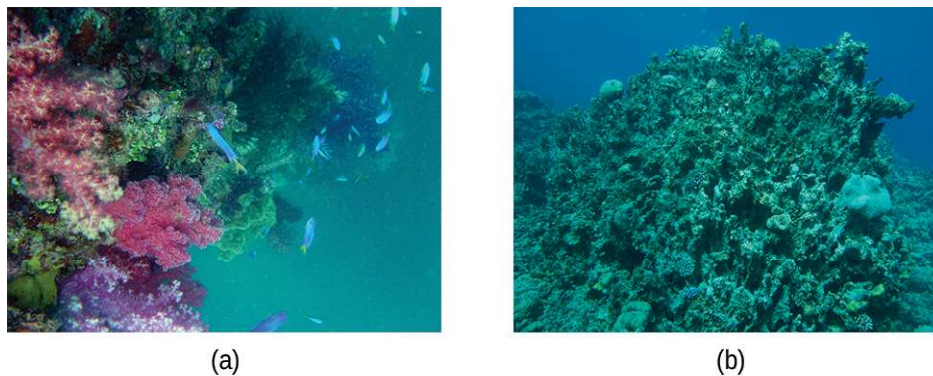
Figure 15.7   Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonate skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small 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)

Link to Learning

Learn more about ocean **acidification (http://openstaxcollege.org/l/16acidicocean)** and how it affects other marine creatures.

This **site (http://openstaxcollege.org/l/16coralreef)** has detailed information about how ocean acidification specifically affects coral reefs.

The dramatic increase in solubility with increasing acidity described above for calcium carbonate is typical of salts containing basic anions (e.g., carbonate, fluoride, hydroxide, sulfide). Another familiar example is the formation of dental cavities in tooth enamel. The major mineral component of enamel is calcium hydroxyapatite (**Figure 15.8**), a sparingly soluble ionic compound whose dissolution equilibrium is

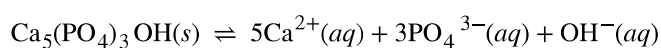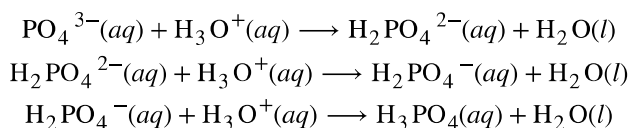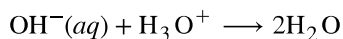$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4{}^{3-}(aq) + OH^-(aq)$$

Figure 15.8   Crystal of the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$, is shown here. The pure compound is white, but like many other minerals, this sample is colored because of the presence of impurities.

This compound dissolved to yield two different basic ions: triprotic phosphate ions

$$PO_4{}^{3-}(aq) + H_3O^+(aq) \longrightarrow H_2PO_4{}^{2-}(aq) + H_2O(l)$$
$$H_2PO_4{}^{2-}(aq) + H_3O^+(aq) \longrightarrow H_2PO_4{}^{-}(aq) + H_2O(l)$$
$$H_2PO_4{}^{-}(aq) + H_3O^+(aq) \longrightarrow H_3PO_4(aq) + H_2O(l)$$

and monoprotic hydroxide ions:

$$OH^-(aq) + H_3O^+ \longrightarrow 2H_2O$$

Of the two basic productions, the hydroxide is, of course, by far the stronger base (it's the strongest base that can exist in aqueous solution), and so it is the dominant factor providing the compound an acid-dependent solubility. Dental cavities form when the acid waste of bacteria growing on the surface of teeth hastens the dissolution of tooth enamel by reacting completely with the strong base hydroxide, shifting the hydroxyapatite solubility equilibrium to the right. Some toothpastes and mouth rinses contain added NaF or SnF_2 that make enamel more acid resistant by replacing the strong base hydroxide with the weak base fluoride:

$$NaF + Ca_5(PO_4)_3OH \rightleftharpoons Ca_5(PO_4)_3F + Na^+ + OH^-$$

The weak base fluoride ion reacts only partially with the bacterial acid waste, resulting in a less extensive shift in the solubility equilibrium and an increased resistance to acid dissolution. 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, $Ca_5(PO_4)_3F$. 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**).
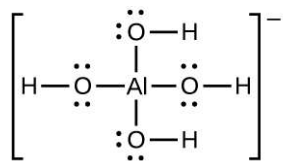

Figure 15.9   Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

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.

The solubility of ionic compounds may also be increased when dissolution is coupled to the formation of a complex

ion. For example, aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion $Al(OH)_4{}^-$.

$$
\left[
\begin{array}{c}
\ddot{\mathrm{O}}{-}\mathrm{H} \\
|\\
\mathrm{H}{-}\ddot{\mathrm{O}}{-}\mathrm{Al}{-}\ddot{\mathrm{O}}{-}\mathrm{H} \\
|\\
\ddot{\mathrm{O}}{-}\mathrm{H}
\end{array}
\right]^{-}
$$

The equations for the dissolution of aluminum hydroxide, the formation of the complex ion, and the combined (net) equation are shown below. As indicated by the relatively large value of K for the net reaction, coupling complex formation with dissolution drastically increases the solubility of $Al(OH)_3$.
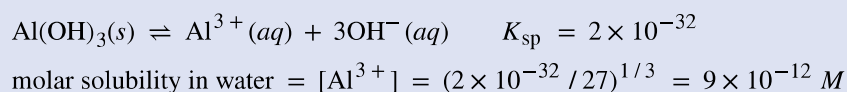
$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = 2 \times 10^{-32}$$

$$Al^{3+}(aq) + 4OH^-(aq) \rightleftharpoons Al(OH)_4{}^-(aq) \qquad K_f = 1.1 \times 10^{33}$$

$$\text{Net: } Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4{}^-(aq) \quad K = K_{sp} K_f = 22$$
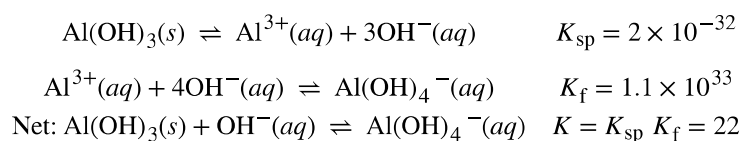
Example 15.15

Increased Solubility in Acidic Solutions

Compute and compare the molar solublities for aluminum hydroxide, $Ca(OH)_2$, dissolved in (a) pure water and (b) a buffer containing 0.100 M acetic acid and 0.100 M sodium acetate.

Solution

(a) The molar solubility of calcium fluoride in water is computed considering the dissolution equilibrium only as demonstrated in several previous examples:

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = 2 \times 10^{-32}$$

$$\text{molar solubility in water} = [Al^{3+}] = (2 \times 10^{-32}/27)^{1/3} = 9 \times 10^{-12} \ M$$

(b) The concentration of hydroxide ion of the buffered solution is conveniently calculated by the Henderson-Hasselbalch equation:

$$pH = pK_a + \log[CH_3COO^-]/[CH_3COOH]$$

$$pH = 4.74 + \log(0.100/0.100) = 4.74$$

At this pH, the concentration of hydroxide ion is

$$pOH = 14.00 - 4.74 = 9.26$$

$$[OH^-] = 10^{-9.26} = 5.5 \times 10^{-10}$$

The solubility of $Al(OH)_3$ in this buffer is then calculated from its solubility product expressions:

$$K_{sp} = [Al^{3+}][OH^-]^3$$

$$\text{molar solubility in buffer} = \left[Al^{2+}\right] = K_{sp}/[OH^-]^3 = (2 \times 10^{-32})/(5.5 \times 10^{-10})^3 = 1.2 \times 10^{-4} \ M$$

Compared to pure water, the solubility of aluminum hydroxide in this mildly acidic buffer is approximately ten million times greater (though still relatively low).

Check Your Learning
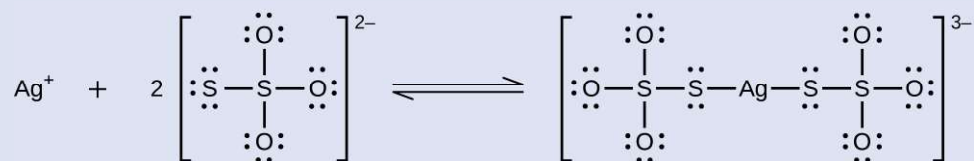
What is the solubility of aluminum hydroxide in a buffer comprised of 0.100 M formic acid and 0.100 M sodium formate?
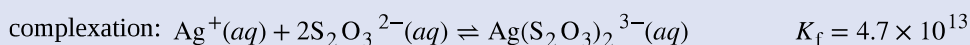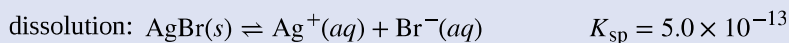
Answer: 0.1 M

Example 15.16

Multiple Equilibria

Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($Na_2S_2O_3$, called hypo) to form the complex ion $Ag(S_2O_3)_2{}^{3-}$ ($K_f = 4.7 \times 10^{13}$).

$$Ag^+ \quad + \quad 2\left[\begin{array}{c} :\overset{..}{O}: \\ | \\ :\overset{..}{S}-S-\overset{..}{O}: \\ | \\ :\overset{..}{O}: \end{array}\right]^{2-} \rightleftharpoons \left[\begin{array}{c} :\overset{..}{O}: \qquad :\overset{..}{O}: \\ | \qquad | \\ :\overset{..}{O}-S-\overset{..}{S}-Ag-\overset{..}{S}-S-\overset{..}{O}: \\ | \qquad | \\ :\overset{..}{O}: \qquad :\overset{..}{O}: \end{array}\right]^{3-}$$

What mass of $Na_2S_2O_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $Ag(S_2O_3)_2{}^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $S_2O_3{}^{2-}$ ion:

dissolution: $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ $K_{sp} = 5.0 \times 10^{-13}$

complexation: $Ag^+(aq) + 2S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq)$ $K_f = 4.7 \times 10^{13}$

First, calculate the concentration of bromide that will result when the 1.00 g of AgBr is completely dissolved via the cited complexation reaction:

$$1.00 \text{ g AgBr} / (187.77 \text{ g/mol})(1 \text{ mol Br}^- / 1 \text{ mol AgBr}) = 0.00532 \text{ mol Br}_-$$
$$0.00521 \text{ mol Br}^- / 1.00 \text{ L} = 0.00521 \, M \text{ Br}^-$$

Next, use this bromide molarity and the solubility product for silver bromide to calculate the silver ion molarity in the solution:

$$[Ag^+] = K_{sp} / [Br^-] = 5.0 \times 10^{-13} / 0.00521 = 9.6 \times 10^{-11} \, M$$

Based on the stoichiometry of the complex ion formation, the concentration of complex ion produced is

$$0.00521 - 9.6 \times 10^{-11} = 0.00521 \, M$$

Use the silver ion and complex ion concentrations and the formation constant for the complex ion to compute the concentration of thiosulfate ion.

$$[S_2O_{32}^-]^2 = [Ag(S_2O_3)^2]/[Ag^+]K_f = 0.00521/(9.6 \times 10^{-11})(4.7 \times 10^{13}) = 1.15 \times 10^{-6}$$
$$[S_2O_{32}^-] = 1.1 \times 10^{-3} \, M$$

Finally, use this molar concentration to derive the required mass of sodium thiosulfate:

$$(1.1 \times 10^{-3} \text{ mol } S_2O_{32}^- / L)(1 \text{ mol } NaS_2O_3 / 1 \text{ mol } S_2O_{32}^-)(158.1 \text{ g } NaS_2O_3 / \text{mol}) = 1.7 \text{ g}$$

Thus, 1.00 L of a solution prepared from 1.7 g $Na_2S_2O_3$ dissolves 1.0 g of AgBr.

Check Your Learning

AgCl(s), silver chloride, has a very low solubility: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, $K_{sp} = 1.6 \times 10^{-10}$. 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 4.81 g NH_3 dissolves 2.0 g of AgCl.

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 central atom surrounding molecules or ions called ligands via coordinate covalent bonds

coordinate covalent bond (also, dative bond) covalent bond in which both electrons originated from the same atom

coupled equilibria system characterized the simultaneous establishment of two or more equilibrium reactions sharing one or more reactant or product

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

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

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 acid-base chemistry reactions involving the formation of coordinate covalent bonds

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

ligand molecule or ion acting as a Lewis base in complex ion formation; bonds to the central atom of the complex

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

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

**solubility product constant (K_{sp})** equilibrium constant for the dissolution of an ionic compound

Key Equations

- $M_p X_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$ $\qquad K_{sp} = [M^{m+}]^p[X^{n-}]^q$
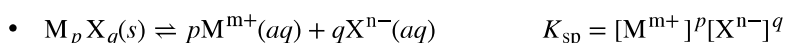
Summary

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. For a heterogeneous equilibrium involving the slightly soluble solid M_pX_q and its ions M^{m+} and X^{n-}:

$$M_p X_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$$
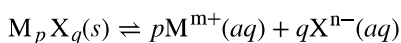
the solubility product expression is:

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

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.

15.2 Lewis Acids and Bases

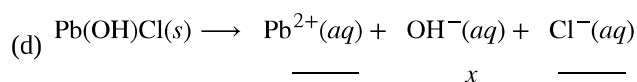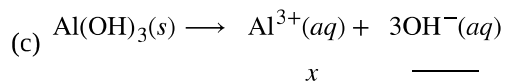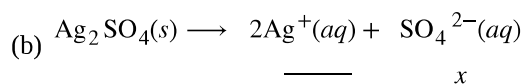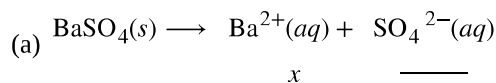A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts and comprise central metal atoms or ions acting as Lewis acids bonded to molecules or ions called ligands that act as Lewis bases. The equilibrium constant for the reaction between a metal ion and ligands produces a complex ion called a formation constant; for the reverse reaction, it is called a dissociation constant.

15.3 Coupled Equilibria

Systems involving two or more chemical equilibria that share one or more reactant or product are called coupled equilibria. Common examples of coupled equilibria include the increased solubility of some compounds in acidic solutions (coupled dissolution and neutralization equilibria) and in solutions containing ligands (coupled dissolution and complex formation). The equilibrium tools from other chapters may be applied to describe and perform calculations on these systems.

Exercises

15.1 Precipitation and Dissolution

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

(a)
$$AgI(s) \longrightarrow Ag^+(aq) + I^-(aq)$$
$$\quad\quad\quad\quad x \quad\quad \underline{\quad\quad}$$

(b)
$$CaCO_3(s) \longrightarrow Ca^{2+}(aq) + CO_3{}^{2-}(aq)$$
$$\quad\quad\quad\quad \underline{\quad\quad} \quad\quad x$$

(c)
$$Mg(OH)_2(s) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$
$$\quad\quad\quad\quad x \quad\quad \underline{\quad\quad}$$

(d)
$$Mg_3(PO_4)_2(s) \longrightarrow 3Mg^{2+}(aq) + 2PO_4{}^{3-}(aq)$$
$$\quad\quad\quad\quad x\underline{\quad\quad}$$

(e)
$$Ca_5(PO_4)_3OH(s) \longrightarrow 5Ca^{2+}(aq) + 3PO_4{}^{3-}(aq) + OH^-(aq)$$
$$\quad\quad\quad\quad \underline{\quad\quad} \quad\quad \underline{\quad\quad} \quad\quad x$$

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

(a)
$$BaSO_4(s) \longrightarrow Ba^{2+}(aq) + SO_4{}^{2-}(aq)$$
$$ x \qquad\qquad \underline{}$$

(b)
$$Ag_2SO_4(s) \longrightarrow 2Ag^+(aq) + SO_4{}^{2-}(aq)$$
$$ \underline{} \qquad\qquad x$$

(c)
$$Al(OH)_3(s) \longrightarrow Al^{3+}(aq) + 3OH^-(aq)$$
$$ x \qquad\qquad \underline{}$$

(d)
$$Pb(OH)Cl(s) \longrightarrow Pb^{2+}(aq) + OH^-(aq) + Cl^-(aq)$$
$$ \underline{} \qquad x \qquad\qquad \underline{}$$

(e)
$$Ca_3(AsO_4)_2(s) \longrightarrow 3Ca^{2+}(aq) + 2AsO_4{}^{3-}(aq)$$
$$ 3x \qquad\qquad \underline{}$$

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?
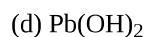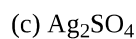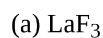
6. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: $CoSO_3$, CuI, $PbCO_3$, $PbCl_2$, Tl_2S, $KClO_4$?

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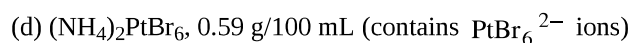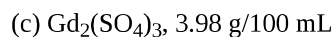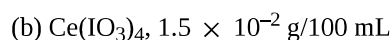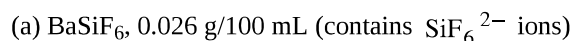
8. Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:

(a) $PbCl_2$

(b) Ag_2S

(c) $Sr_3(PO_4)_2$

(d) $SrSO_4$
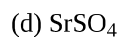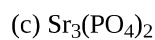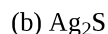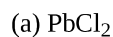
9. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

(a) LaF_3

(b) $CaCO_3$

(c) Ag_2SO_4

(d) $Pb(OH)_2$

10. The *Handbook of Chemistry and Physics (http://openstaxcollege.org/l/16Handbook)* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

(a) $BaSiF_6$, 0.026 g/100 mL (contains $SiF_6{}^{2-}$ ions)

(b) $Ce(IO_3)_4$, 1.5×10^{-2} g/100 mL

(c) $Gd_2(SO_4)_3$, 3.98 g/100 mL

(d) $(NH_4)_2PtBr_6$, 0.59 g/100 mL (contains $PtBr_6{}^{2-}$ ions)

11. The *Handbook of Chemistry and Physics (http://openstaxcollege.org/l/16Handbook)* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

(a) $BaSeO_4$, 0.0118 g/100 mL

(b) $Ba(BrO_3)_2 \cdot H_2O$, 0.30 g/100 mL

(c) $NH_4MgAsO_4 \cdot 6H_2O$, 0.038 g/100 mL

(d) $La_2(MoO_4)_3$, 0.00179 g/100 mL

12. Use solubility products and predict which of the following salts is the most soluble, in terms of moles per liter, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.

13. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

(a) $KHC_4H_4O_6$

(b) PbI_2

(c) $Ag_4[Fe(CN)_6]$, a salt containing the $Fe(CN)_4^-$ ion

(d) Hg_2I_2

14. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

(a) Ag_2SO_4

(b) $PbBr_2$

(c) AgI

(d) $CaC_2O_4 \cdot H_2O$

15. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

(a) $AgCl(s)$ in 0.025 *M* NaCl

(b) $CaF_2(s)$ in 0.00133 *M* KF

(c) $Ag_2SO_4(s)$ in 0.500 L of a solution containing 19.50 g of K_2SO_4

(d) $Zn(OH)_2(s)$ in a solution buffered at a pH of 11.45

16. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

(a) $TlCl(s)$ in 1.250 *M* HCl

(b) $PbI_2(s)$ in 0.0355 *M* CaI_2

(c) $Ag_2CrO_4(s)$ in 0.225 L of a solution containing 0.856 g of K_2CrO_4

(d) $Cd(OH)_2(s)$ in a solution buffered at a pH of 10.995

17. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.

(a) TlCl(*s*) in 0.025 *M* TlNO$_3$

(b) BaF$_2$(*s*) in 0.0313 *M* KF

(c) MgC$_2$O$_4$ in 2.250 L of a solution containing 8.156 g of Mg(NO$_3$)$_2$

(d) Ca(OH)$_2$(*s*) in an unbuffered solution initially with a pH of 12.700

18. Explain why the changes in concentrations of the common ions in **Exercise 15.17** can be neglected.

19. Explain why the changes in concentrations of the common ions in **Exercise 15.18** cannot be neglected.

20. Calculate the solubility of aluminum hydroxide, Al(OH)$_3$, in a solution buffered at pH 11.00.

21. Refer to **Appendix J** for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per liter and which is most soluble in grams per liter.

22. Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract (**Figure 15.4**). This use of BaSO$_4$ is possible because of its low solubility. Calculate the molar solubility of BaSO$_4$ and the mass of barium present in 1.00 L of water saturated with BaSO$_4$.

23. Public Health Service standards for drinking water set a maximum of 250 mg/L (2.60 $\times$ 10^{-3} *M*) of SO$_4{}^{2-}$ because of its cathartic action (it is a laxative). Does natural water that is saturated with CaSO$_4$ ("gyp" water) as a result or passing through soil containing gypsum, CaSO$_4$·2H$_2$O, meet these standards? What is the concentration of SO$_4{}^{2-}$ in such water?

24. Perform the following calculations:

(a) Calculate [Ag$^+$] in a saturated aqueous solution of AgBr.

(b) What will [Ag$^+$] be when enough KBr has been added to make [Br$^-$] = 0.050 *M*?

(c) What will [Br$^-$] be when enough AgNO$_3$ has been added to make [Ag$^+$] = 0.020 *M*?

25. The solubility product of CaSO$_4$·2H$_2$O is 2.4 $\times$ 10^{-5}. What mass of this salt will dissolve in 1.0 L of 0.010 *M* SO4^{2-}?

26. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see **Appendix J** for solubility products).

(a) TlCl

(b) BaF$_2$

(c) Ag$_2$CrO$_4$

(d) CaC$_2$O$_4$·H$_2$O

(e) the mineral anglesite, PbSO$_4$

27. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see **Appendix J** for solubility products):

(a) AgI

(b) Ag$_2$SO$_4$

(c) Mn(OH)$_2$

(d) Sr(OH)$_2$·8H$_2$O

(e) the mineral brucite, Mg(OH)$_2$

28. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

(a) AgBr: $[Ag^+] = 5.7 \times 10^{-7}\ M$, $[Br^-] = 5.7 \times 10^{-7}\ M$

(b) CaCO$_3$: $[Ca^{2+}] = 5.3 \times 10^{-3}\ M$, $[CO_3{}^{2-}] = 9.0 \times 10^{-7}\ M$

(c) PbF$_2$: $[Pb^{2+}] = 2.1 \times 10^{-3}\ M$, $[F^-] = 4.2 \times 10^{-3}\ M$

(d) Ag$_2$CrO$_4$: $[Ag^+] = 5.3 \times 10^{-5}\ M$, $3.2 \times 10^{-3}\ M$

(e) InF$_3$: $[In^{3+}] = 2.3 \times 10^{-3}\ M$, $[F^-] = 7.0 \times 10^{-3}\ M$

29. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

(a) TlCl: $[Tl^+] = 1.21 \times 10^{-2}\ M$, $[Cl^-] = 1.2 \times 10^{-2}\ M$

(b) Ce(IO$_3$)$_4$: $[Ce^{4+}] = 1.8 \times 10^{-4}\ M$, $[IO_3{}^-] = 2.6 \times 10^{-13}\ M$

(c) Gd$_2$(SO$_4$)$_3$: $[Gd^{3+}] = 0.132\ M$, $[SO_4{}^{2-}] = 0.198\ M$

(d) Ag$_2$SO$_4$: $[Ag^+] = 2.40 \times 10^{-2}\ M$, $[SO_4{}^{2-}] = 2.05 \times 10^{-2}\ M$

(e) BaSO$_4$: $[Ba^{2+}] = 0.500\ M$, $[SO_4{}^{2-}] = 4.6 \times 10^{-8}\ M$

30. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See **Appendix J** for K_{sp} values.)

(a) KClO$_4$: $[K^+] = 0.01\ M$, $[ClO_4{}^-] = 0.01\ M$

(b) K$_2$PtCl$_6$: $[K^+] = 0.01\ M$, $[PtCl_6{}^{2-}] = 0.01\ M$

(c) PbI$_2$: $[Pb^{2+}] = 0.003\ M$, $[I^-] = 1.3 \times 10^{-3}\ M$

(d) Ag$_2$S: $[Ag^+] = 1 \times 10^{-10}\ M$, $[S^{2-}] = 1 \times 10^{-13}\ M$

31. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See **Appendix J** for K_{sp} values.)

(a) CaCO$_3$: $[Ca^{2+}] = 0.003\ M$, $[CO_3{}^{2-}] = 0.003\ M$

(b) Co(OH)$_2$: $[Co^{2+}] = 0.01\ M$, $[OH^-] = 1 \times 10^{-7}\ M$

(c) CaHPO$_4$: $[Ca^{2+}] = 0.01\ M$, $[HPO_4{}^{2-}] = 2 \times 10^{-6}\ M$

(d) Pb$_3$(PO$_4$)$_2$: $[Pb^{2+}] = 0.01\ M$, $[PO_4{}^{3-}] = 1 \times 10^{-13}\ M$

32. Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 M in Cl^-.

33. Calculate the concentration of sulfate ion when BaSO$_4$ just begins to precipitate from a solution that is 0.0758 M in Ba^{2+}.

34. Calculate the concentration of Sr^{2+} when SrF$_2$ starts to precipitate from a solution that is 0.0025 M in F^-.

35. Calculate the concentration of $PO_4{}^{3-}$ when Ag$_3$PO$_4$ starts to precipitate from a solution that is 0.0125 M in Ag^+.

36. Calculate the concentration of F^- required to begin precipitation of CaF$_2$ in a solution that is 0.010 M in Ca^{2+}.

37. Calculate the concentration of Ag^+ required to begin precipitation of Ag$_2$CO$_3$ in a solution that is 2.50×10^{-6} M in $CO_3{}^{2-}$.
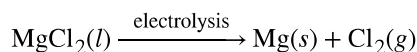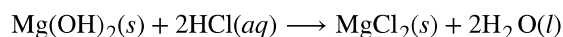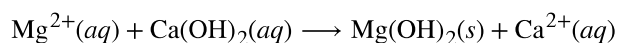
38. What $[Ag^+]$ is required to reduce $[CO_3{}^{2-}]$ to $8.2 \times 10^{-4}\ M$ by precipitation of Ag$_2$CO$_3$?

39. What $[F^-]$ is required to reduce $[Ca^{2+}]$ to $1.0 \times 10^{-4}\ M$ by precipitation of CaF$_2$?

40. A volume of 0.800 L of a 2×10^{-4}-M Ba(NO$_3$)$_2$ solution is added to 0.200 L of $5 \times 10^{-4}\ M$ Li$_2$SO$_4$. Does BaSO$_4$ precipitate? Explain your answer.

41. Perform these calculations for nickel(II) carbonate. (a) With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ (K_{sp} = 1.36 × 10^{-7}).

(b) If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ (K_{sp} = 1.0 × 10^{-12}), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.

42. Iron concentrations greater than 5.4 × 10^{-6} M in water used for laundry purposes can cause staining. What $[OH^-]$ is required to reduce $[Fe^{2+}]$ to this level by precipitation of $Fe(OH)_2$?

43. A solution is 0.010 M in both Cu^{2+} and Cd^{2+}. What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide?

44. A solution is 0.15 M in both Pb^{2+} and Ag^+. If Cl^- is added to this solution, what is $[Ag^+]$ when $PbCl_2$ begins to precipitate?

45. What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 M with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in **Appendix J**.)

(a) $Hg_2{}^{2+}$ and Cu^{2+}

(b) $SO_4{}^{2-}$ and Cl^-

(c) Hg^{2+} and Co^{2+}

(d) Zn^{2+} and Sr^{2+}

(e) Ba^{2+} and Mg^{2+}

(f) $CO_3{}^{2-}$ and OH^-

46. A solution contains 1.0 × 10^{-5} mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

47. A solution contains 1.0 × 10^{-2} 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?

48. The calcium ions in human blood serum are necessary for coagulation (**Figure 15.5**). Potassium oxalate, $K_2C_2O_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $CaC_2O_4·H_2O$. It is necessary to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $K_2C_2O_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)

49. About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form?

50. The pH of normal urine is 6.30, and the total phosphate concentration $([PO_4{}^{3-}] + [HPO_4{}^{2-}] + [H_2PO_4{}^-] + [H_3PO_4])$ is 0.020 M. What is the minimum concentration of Ca^{2+} necessary to induce kidney stone formation? (See **Exercise 15.49** for additional information.)

51. Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

$$Mg^{2+}(aq) + Ca(OH)_2(aq) \longrightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(s) + 2H_2O(l)$$

$$MgCl_2(l) \xrightarrow{\text{electrolysis}} Mg(s) + Cl_2(g)$$

Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as Mg^{2+}(aq) by mass. What mass, in kilograms, of Ca(OH)$_2$ is required to precipitate 99.9% of the magnesium in 1.00 × 10^3 L of sea water?

52. Hydrogen sulfide is bubbled into a solution that is 0.10 M in both Pb^{2+} and Fe^{2+} and 0.30 M in HCl. After the solution has come to equilibrium it is saturated with H$_2$S ([H$_2$S] = 0.10 M). What concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H$_2$S we can use the equilibrium:

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$
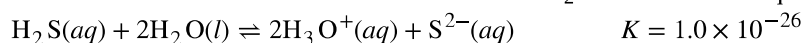
(Hint: The [H$_3$O$^+$] changes as metal sulfides precipitate.)

53. Perform the following calculations involving concentrations of iodate ions:

(a) The iodate ion concentration of a saturated solution of La(IO$_3$)$_3$ was found to be 3.1 × 10^{-3} mol/L. Find the K_{sp}.

(b) Find the concentration of iodate ions in a saturated solution of Cu(IO$_3$)$_2$ (K_{sp} = 7.4 × 10^{-8}).

54. Calculate the molar solubility of AgBr in 0.035 M NaBr (K_{sp} = 5 × 10^{-13}).

55. How many grams of Pb(OH)$_2$ will dissolve in 500 mL of a 0.050-M PbCl$_2$ solution (K_{sp} = 1.2 × 10^{-15})?

56. Use the **simulation (http://openstaxcollege.org/l/16solublesalts)** from the earlier Link to Learning to complete the following exercise. Using 0.01 g CaF$_2$, give the K$_{sp}$ values found in a 0.2-M solution of each of the salts. Discuss why the values change as you change soluble salts.

57. How many grams of Milk of Magnesia, Mg(OH)$_2$ (s) (58.3 g/mol), would be soluble in 200 mL of water. K_{sp} = 7.1 × 10^{-12}. Include the ionic reaction and the expression for K_{sp} in your answer. (K_w = 1 × 10^{-14} = [H$_3$O$^+$][OH$^-$])

58. Two hypothetical salts, LM$_2$ and LQ, have the same molar solubility in H$_2$O. If K_{sp} for LM$_2$ is 3.20 × 10^{-5}, what is the K_{sp} value for LQ?

59. The carbonate ion concentration is gradually increased in a solution containing divalent cations of magnesium, calcium, strontium, barium, and manganese. Which of the following carbonates will form first? Which of the following will form last? Explain.

(a) MgCO$_3$ $\qquad K_{sp} = 3.5 \times 10^{-8}$

(b) CaCO$_3$ $\qquad K_{sp} = 4.2 \times 10^{-7}$

(c) SrCO$_3$ $\qquad K_{sp} = 3.9 \times 10^{-9}$

(d) BaCO$_3$ $\qquad K_{sp} = 4.4 \times 10^{-5}$

(e) MnCO$_3$ $\qquad K_{sp} = 5.1 \times 10^{-9}$

**60.** How many grams of Zn(CN)$_2$(s) (117.44 g/mol) would be soluble in 100 mL of H$_2$O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for Zn(CN)$_2$(s) is 3.0 × 10^{-16}.

15.2 Lewis Acids and Bases

61. Even though Ca(OH)$_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of Ca(OH)$_2$?

62. Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?
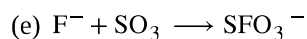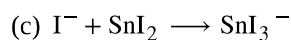
63. Explain why the addition of NH_3 or HNO_3 to a saturated solution of Ag_2CO_3 in contact with solid Ag_2CO_3 increases the solubility of the solid.

64. Calculate the cadmium ion concentration, $[Cd^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 *M* $Cd(NO_3)_2$ with 1.150 L of 0.100 $NH_3(aq)$.

65. Explain why addition of NH_3 or HNO_3 to a saturated solution of $Cu(OH)_2$ in contact with solid $Cu(OH)_2$ increases the solubility of the solid.

66. Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d. For the complex ion $AlF_6{}^{3-}$ the dissociation reaction is:
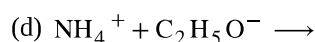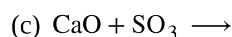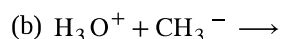
$$AlF_6{}^{3-} \rightleftharpoons Al^{3+} + 6F^- \text{ and } K_d = \frac{[Al^{3+}][F^-]^6}{[AlF_6{}^{3-}]} = 2 \times 10^{-24}$$
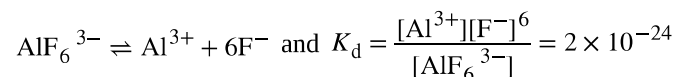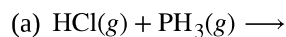
Calculate the value of the formation constant, K_f, for $AlF_6{}^{3-}$.

67. Using the value of the formation constant for the complex ion $Co(NH_3)_6{}^{2+}$, calculate the dissociation constant.

68. Using the dissociation constant, $K_d = 7.8 \times 10^{-18}$, calculate the equilibrium concentrations of Cd^{2+} and CN^- in a 0.250-*M* solution of $Cd(CN)_4{}^{2-}$.

69. Using the dissociation constant, $K_d = 3.4 \times 10^{-15}$, calculate the equilibrium concentrations of Zn^{2+} and OH^- in a 0.0465-*M* solution of $Zn(OH)_4{}^{2-}$.

70. Using the dissociation constant, $K_d = 2.2 \times 10^{-34}$, calculate the equilibrium concentrations of Co^{3+} and NH_3 in a 0.500-*M* solution of $Co(NH_3)_6{}^{3+}$.

71. Using the dissociation constant, $K_d = 1 \times 10^{-44}$, calculate the equilibrium concentrations of Fe^{3+} and CN^- in a 0.333 M solution of $Fe(CN)_6{}^{3-}$.

72. Calculate the mass of potassium cyanide ion that must be added to 100 mL of solution to dissolve 2.0×10^{-2} mol of silver cyanide, AgCN.

73. Calculate the minimum concentration of ammonia needed in 1.0 L of solution to dissolve 3.0×10^{-3} mol of silver bromide.

74. A roll of 35-mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass of $Na_2S_2O_3·5H_2O$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as $Ag(S_2O_3)_2{}^{3-}$ ($K_f = 4.7 \times 10^{13}$)?

75. We have seen an introductory definition of an acid: An acid is a compound that reacts with water and increases the amount of hydronium ion present. In the chapter on acids and bases, we saw two more definitions of acids: a compound that donates a proton (a hydrogen ion, H^+) to another compound is called a Brønsted-Lowry acid, and a Lewis acid is any species that can accept a pair of electrons. Explain why the introductory definition is a macroscopic definition, while the Brønsted-Lowry definition and the Lewis definition are microscopic definitions.

76. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

(a) $CO_2 + OH^- \longrightarrow HCO_3{}^-$

(b) $B(OH)_3 + OH^- \longrightarrow B(OH)_4{}^-$

(c) $I^- + I_2 \longrightarrow I_3{}^-$

(d) $AlCl_3 + Cl^- \longrightarrow AlCl_4{}^-$ (use Al-Cl single bonds)

(e) $O^{2-} + SO_3 \longrightarrow SO_4{}^{2-}$

77. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

(a) $CS_2 + SH^- \longrightarrow HCS_3{}^-$

(b) $BF_3 + F^- \longrightarrow BF_4{}^-$

(c) $I^- + SnI_2 \longrightarrow SnI_3{}^-$

(d) $Al(OH)_3 + OH^- \longrightarrow Al(OH)_4{}^-$

(e) $F^- + SO_3 \longrightarrow SFO_3{}^-$

78. Using Lewis structures, write balanced equations for the following reactions:

(a) $HCl(g) + PH_3(g) \longrightarrow$

(b) $H_3O^+ + CH_3{}^- \longrightarrow$

(c) $CaO + SO_3 \longrightarrow$

(d) $NH_4{}^+ + C_2H_5O^- \longrightarrow$

79. Calculate $[HgCl_4{}^{2-}]$ in a solution prepared by adding 0.0200 mol of NaCl to 0.250 L of a 0.100-*M* $HgCl_2$ solution.

80. In a titration of cyanide ion, 28.72 mL of 0.0100 *M* $AgNO_3$ is added before precipitation begins. [The reaction of Ag^+ with CN^- goes to completion, producing the $Ag(CN)_2{}^-$ complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of $Ag(CN)_2{}^-$. How many grams of NaCN were in the original sample?

81. What are the concentrations of Ag^+, CN^-, and $Ag(CN)_2{}^-$ in a saturated solution of AgCN?

82. In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides that are Lewis acids and accept F^- ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3.

83. The simplest amino acid is glycine, $H_2NCH_2CO_2H$. The common feature of amino acids is that they contain the functional groups: an amine group, $-NH_2$, and a carboxylic acid group, $-CO_2H$. An amino acid can function as either an acid or a base. For glycine, the acid strength of the carboxyl group is about the same as that of acetic acid, CH_3CO_2H, and the base strength of the amino group is slightly greater than that of ammonia, NH_3.

(a) Write the Lewis structures of the ions that form when glycine is dissolved in 1 *M* HCl and in 1 *M* KOH.

(b) Write the Lewis structure of glycine when this amino acid is dissolved in water. (Hint: Consider the relative base strengths of the $-NH_2$ and $-CO_2{}^-$ groups.)

84. Boric acid, H_3BO_3, is not a Brønsted-Lowry acid but a Lewis acid.

(a) Write an equation for its reaction with water.

(b) Predict the shape of the anion thus formed.

(c) What is the hybridization on the boron consistent with the shape you have predicted?

15.3 Coupled Equilibria

85. A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?
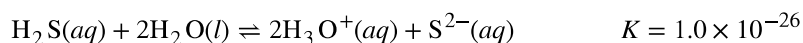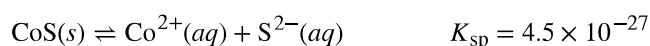
86. Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$.

87. Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of $Zn(CN)_4{}^{2-}$.
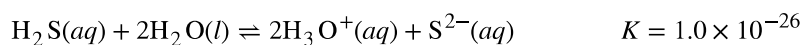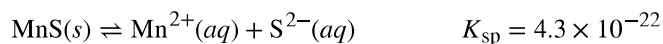
88. Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3.

89. Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^-.

90. Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 M CN^-.

91. Calculate the Co^{2+} equilibrium concentration when 0.100 mole of $[Co(NH_3)_6](NO_3)_2$ is added to a solution with 0.025 M NH_3. Assume the volume is 1.00 L.

92. Calculate the molar solubility of $Sn(OH)_2$ in a buffer solution containing equal concentrations of NH_3 and $NH_4{}^+$.

93. Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 M NH_3 and 0.400 M $NH_4{}^+$.

94. What is the molar solubility of CaF_2 in a 0.100-M solution of HF? K_a for HF = 6.4×10^{-4}.

95. What is the molar solubility of $BaSO_4$ in a 0.250-M solution of $NaHSO_4$? K_a for $HSO_4{}^-$ = 1.2×10^{-2}.

96. What is the molar solubility of $Tl(OH)_3$ in a 0.10-M solution of NH_3?

97. What is the molar solubility of $Pb(OH)_2$ in a 0.138-M solution of CH_3NH_2?

98. A solution of 0.075 M $CoBr_2$ is saturated with H_2S ($[H_2S] = 0.10$ M). What is the minimum pH at which CoS begins to precipitate?

$$CoS(s) \rightleftharpoons Co^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = 4.5 \times 10^{-27}$$

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$

99. A 0.125-M solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S] = 0.10$ M). At what pH does MnS begin to precipitate?

$$MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = 4.3 \times 10^{-22}$$

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$
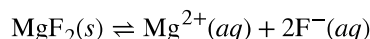
100. Both AgCl and AgI dissolve in NH_3.

(a) What mass of AgI dissolves in 1.0 L of 1.0 M NH_3?

(b) What mass of AgCl dissolves in 1.0 L of 1.0 M NH_3?

101. The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Solve the following problem:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is 1.21×10^{-3} M. The equilibrium is represented by the preceding equation.

(a) Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.

(b) Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.

(c) Predict whether a precipitate of MgF_2 will form when 100.0 mL of a 3.00×10^{-3}-M solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a 2.00×10^{-3}-M solution of NaF at 18 °C. Show the calculations to support your prediction.

(d) At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is 1.17×10^{-3} M. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

102. Which of the following compounds, when dissolved in a 0.01-M solution of $HClO_4$, has a solubility greater than in pure water: CuCl, $CaCO_3$, MnS, $PbBr_2$, CaF_2? Explain your answer.

103. Which of the following compounds, when dissolved in a 0.01-M solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_2$, ZnS, PbI_2? Explain your answer.

104. 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 $Mg(OH)_2$ and water at equilibrium?

(a) $MgCl_2$

(b) KOH

(c) $HClO_4$

(d) $NaNO_3$

(e) $Mg(OH)_2$

105. What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and HPO_4^- when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?

(a) $CaCl_2$

(b) HCl

(c) $KClO_4$

(d) NaOH

(e) $CaHPO_4$

106. Identify all chemical species present in an aqueous solution of $Ca_3(PO_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the PO_4^{3-} ion is a weak base.)