Regardless of the problem on which an analytical chemist is working, its solution requires a knowledge of chemistry and the ability to apply that knowledge. For example, an analytical chemist studying the effect of pollution on spruce trees needs to know, or know where to find, the chemical differences between \( p \)-hydroxybenzoic acid and \( p \)-hydroxyacetophenone, two common phenols found in the needles of spruce trees.

Your ability to “think as a chemist” is a product of your experience in the classroom and in the laboratory. The material in this text assumes your familiarity with topics from earlier courses. Because of its importance to analytical chemistry, this chapter provides a review of equilibrium chemistry. Much of the material in this chapter should be familiar to you, although some topics—ladder diagrams and activity, for example—afford you with new ways to look at equilibrium chemistry.
Napoleon’s expedition to Egypt was the first to include a significant scientific presence. The Commission of Sciences and Arts, which included Claude Berthollet, began with 151 members, and operated in Egypt for three years. In addition to Berthollet’s work, other results included a publication on mirages, and detailed catalogs of plant and animal life, mineralogy, and archeology. For a review of the Commission’s contributions, see Gillispie, C. G. “Scientific Aspects of the French Egyptian Expedition, 1798-1801,” *Proc. Am. Phil. Soc.* **1989**, *133*, 447–474.

Natron is another name for the mineral sodium carbonate, \( \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \). In nature, it usually contains impurities of \( \text{NaHCO}_3 \), and \( \text{NaCl} \). In ancient Egypt, natron was mined and used for a variety of purposes, including as a cleaning agent and in mumification.

6A Reversible Reactions and Chemical Equilibria

In 1798, the chemist Claude Berthollet accompanied Napoleon’s military expedition to Egypt. While visiting the Natron Lakes, a series of salt water lakes carved from limestone, Berthollet made an observation that led him to an important discovery. When exploring the lake’s shore Berthollet found deposits of \( \text{Na}_2\text{CO}_3 \), a result he found surprising. Why did Berthollet find this result surprising and how did it contribute to an important discovery? Answering these questions provides an example of chemical reasoning and introduces us to the topic of this chapter.

At the end of the 18th century, chemical reactivity was explained in terms of elective affinities. If, for example, substance A reacts with substance BC to form AB

\[
A + BC \rightarrow AB + C
\]

then A and B were said to have an elective affinity for each other. With elective affinity as the driving force for chemical reactivity, reactions were understood to proceed to completion and to proceed in one direction. Once formed, the compound AB could not revert to A and BC.

\[
AB + C \rightleftharpoons A + BC
\]

From his experience in the laboratory, Berthollet knew that adding solid \( \text{Na}_2\text{CO}_3 \) to a solution of \( \text{CaCl}_2 \) produces a precipitate of \( \text{CaCO}_3 \).

\[
\text{Na}_2\text{CO}_3(s) + \text{CaCl}_2(aq) \rightarrow 2\text{NaCl}(aq) + \text{CaCO}_3(s)
\]

Understanding this, Berthollet was surprised to find solid \( \text{Na}_2\text{CO}_3 \) forming on the edges of the lake, particularly since the deposits formed only when the lake’s salt water was in contact with limestone, \( \text{CaCO}_3 \). Where the lake was in contact with clay soils, there was little or no \( \text{Na}_2\text{CO}_3 \).

Berthollet’s important insight was recognizing that the chemistry leading to the formation of \( \text{Na}_2\text{CO}_3 \) is the reverse of that seen in the laboratory.

\[
2\text{NaCl}(aq) + \text{CaCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CaCl}_2(aq)
\]

Using this insight Berthollet reasoned that the reaction is reversible, and that the relative amounts of \( \text{NaCl}, \text{CaCO}_3, \text{Na}_2\text{CO}_3, \) and \( \text{CaCl}_2 \) determine the direction in which the reaction occurs and the final composition of the reaction mixture. We recognize a reaction’s ability to move in both directions by using a double arrow when writing the reaction.

\[
\text{Na}_2\text{CO}_3(s) + \text{CaCl}_2(aq) \rightleftharpoons 2\text{NaCl}(aq) + \text{CaCO}_3(s)
\]

Berthollet’s reasoning that reactions are reversible was an important step in understanding chemical reactivity. When we mix together solutions of \( \text{Na}_2\text{CO}_3 \) and \( \text{CaCl}_2 \) they react to produce \( \text{NaCl} \) and \( \text{CaCO}_3 \). If during
the reaction we monitor the mass of \(\text{Ca}^{2+}\) remaining in solution and the mass of \(\text{CaCO}_3\) that precipitates, the result looks something like Figure 6.1. At the start of the reaction the mass of \(\text{Ca}^{2+}\) decreases and the mass of \(\text{CaCO}_3\) increases. Eventually the reaction reaches a point after which there is no further change in the amounts of these species. Such a condition is called a state of **equilibrium**.

Although a system at equilibrium appears static on a macroscopic level, it is important to remember that the forward and reverse reactions continue to occur. A reaction at equilibrium exists in a **steady-state**, in which the rate at which a species forms equals the rate at which it is consumed.

## 6B Thermodynamics and Equilibrium Chemistry

Thermodynamics is the study of thermal, electrical, chemical, and mechanical forms of energy. The study of thermodynamics crosses many disciplines, including physics, engineering, and chemistry. Of the various branches of thermodynamics, the most important to chemistry is the study of the change in energy during a chemical reaction.

Consider, for example, the general equilibrium reaction shown in equation 6.1, involving the species \(A, B, C,\) and \(D\), with stoichiometric coefficients \(a, b, c,\) and \(d\).

\[
aA + bB \rightleftharpoons cC + dD
\]

By convention, we identify species on the left side of the equilibrium arrow as reactants, and those on the right side of the equilibrium arrow as products. As Berthollet discovered, writing a reaction in this fashion does not guarantee that the reaction of \(A\) and \(B\) to produce \(C\) and \(D\) is favorable. Depending on initial conditions, the reaction may move to the left, move to the right, or be in a state of equilibrium. Understanding the factors that determine the reaction’s final, equilibrium position is one of the goals of chemical thermodynamics.

The direction of a reaction is that which lowers the overall free energy. At a constant temperature and pressure, typical of many bench-top chemical reactions, a reaction’s free energy is given by the **Gibb’s free energy** function

\[
\Delta G = \Delta H - T\Delta S
\]

where \(T\) is the temperature in kelvin, and \(\Delta G, \Delta H,\) and \(\Delta S\) are the differences in the Gibb’s free energy, the enthalpy, and the entropy between the products and the reactants.

**Enthalpy** is a measure of the flow of energy, as heat, during a chemical reaction. Reactions releasing heat have a negative \(\Delta H\) and are called **exo-thermic**. Endothermic reactions absorb heat from their surroundings and have a positive \(\Delta H\). **Entropy** is a measure of energy that is unavailable for useful, chemical work. The entropy of an individual species is always posi-
Equation 6.2 shows that the sign of $\Delta G$ depends on the signs of $\Delta H$ and $\Delta S$, and the temperature, $T$. The following table summarizes the possibilities.

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>$\Delta G &lt; 0$ at all temperatures</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>$\Delta G &lt; 0$ at low temperatures</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>$\Delta G &lt; 0$ at high temperatures</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>$\Delta G &gt; 0$ at all temperatures</td>
</tr>
</tbody>
</table>

tive and tends to be larger for gases than for solids, and for more complex molecules than for simpler molecules. Reactions producing a large number of simple, gaseous products usually have a positive $\Delta S$.

The sign of $\Delta G$ indicates the direction in which a reaction moves to reach its equilibrium position. A reaction is thermodynamically favorable when its enthalpy, $\Delta H$, decreases and its entropy, $\Delta S$, increases. Substituting the inequalities $\Delta H < 0$ and $\Delta S > 0$ into equation 6.2 shows that a reaction is thermodynamically favorable when $\Delta G$ is negative. When $\Delta G$ is positive the reaction is unfavorable as written (although the reverse reaction is favorable). A reaction at equilibrium has a $\Delta G$ of zero.

As a reaction moves from its initial, non-equilibrium condition to its equilibrium position, the value of $\Delta G$ approaches zero. At the same time, the chemical species in the reaction experience a change in their concentrations. The Gibb’s free energy, therefore, must be a function of the concentrations of reactants and products.

As shown in equation 6.3, we can split the Gibb’s free energy into two terms.

$$\Delta G = \Delta G^o + RT \ln Q$$

6.3

The first term, $\Delta G^o$, is the change in Gibb’s free energy when each species in the reaction is in its **standard state**, which we define as follows: gases with partial pressures of 1 atm, solutes with concentrations of 1 mol/L, and pure solids and pure liquids. The second term, which includes the reaction quotient, $Q$, accounts for non-standard state pressures or concentrations. For reaction 6.1 the reaction quotient is

$$Q = \frac{[C][D]^c}{[A]^c[B]^c}$$

6.4

where the terms in brackets are the concentrations of the reactants and products. Note that we define the reaction quotient with the products are in the numerator and the reactants are in the denominator. In addition, we raise the concentration of each species to a power equivalent to its stoichiometry in the balanced chemical reaction. For a gas, we use partial pressure in place of concentration. Pure solids and pure liquids do not appear in the reaction quotient.

At equilibrium the Gibb’s free energy is zero, and equation 6.3 simplifies to

$$\Delta G^o = -RT \ln K$$

where $K$ is an **equilibrium constant** that defines the reaction’s equilibrium position. The equilibrium constant is just the numerical value of the reaction quotient, $Q$, when substituting equilibrium concentrations into equation 6.4.
Here we include the subscript “eq” to indicate a concentration at equilibrium. Although we usually will omit the “eq” when writing equilibrium constant expressions, it is important to remember that the value of $K$ is determined by equilibrium concentrations.

**6C Manipulating Equilibrium Constants**

We will take advantage of two useful relationships when working with equilibrium constants. First, if we reverse a reaction’s direction, the equilibrium constant for the new reaction is simply the inverse of that for the original reaction. For example, the equilibrium constant for the reaction

$$A + 2B \rightleftharpoons AB_2$$

is the inverse of that for the reaction

$$AB_2 \rightleftharpoons A + 2B$$

$$K_2 = (K_1)^{-1} = \frac{[A][B]^2}{[AB_2]}$$

Second, if we add together two reactions to obtain a new reaction, the equilibrium constant for the new reaction is the product of the equilibrium constants for the original reactions.

$$A + C \rightleftharpoons AC$$

$$K_3 = \frac{[AC]}{[A][C]}$$

$$AC + C \rightleftharpoons AC_2$$

$$K_4 = \frac{[AC_2]}{[AC][C]}$$

$$A + 2C \rightleftharpoons AC_2$$

$$K_5 = K_3 \times K_4 = \frac{[AC]}{[A][C]} \times \frac{[AC_2]}{[AC][C]} = \frac{[AC_2]}{[A][C]^2}$$

**Example 6.1**

Calculate the equilibrium constant for the reaction

$$2A + B \rightleftharpoons C + 3D$$

given the following information.
Another common name for an oxidation-reduction reaction is a redox reaction, where “red” is short for reduction and “ox” is short for oxidation.

Rxn 1: A + B ⇌ D \quad K_1 = 0.40
Rxn 2: A + E ⇌ C + D + F \quad K_2 = 0.10
Rxn 3: C + E ⇌ B \quad K_3 = 2.0
Rxn 4: F + C ⇌ D + B \quad K_4 = 5.0

**Solution**

The overall reaction is equivalent to

\[ \text{Rxn 1} + \text{Rxn 2} - \text{Rxn 3} + \text{Rxn 4} \]

Subtracting a reaction is equivalent to adding the reverse reaction; thus, the overall equilibrium constant is

\[ K = \frac{K_1 \times K_2 \times K_4}{K_3} = \frac{0.40 \times 0.10 \times 5.0}{2.0} = 0.10 \]

**Practice Exercise 6.1**

Calculate the equilibrium constant for the reaction

\[ C + D + F \rightleftharpoons 2A + 3B \]

using the equilibrium constants from Example 6.1.

Click here to review your answer to this exercise.

### 6D Equilibrium Constants for Chemical Reactions

Several types of chemical reactions are important in analytical chemistry, either in preparing a sample for analysis or during the analysis. The most significant of these are: precipitation reactions, acid–base reactions, complexation reactions, and oxidation–reduction reactions. In this section we review these reactions and their equilibrium constant expressions.

#### 6D.1 Precipitation Reactions

In a precipitation reaction, two or more soluble species combine to form an insoluble precipitate. The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. For example, if we add a solution of lead nitrate, Pb(NO\(_3\))\(_2\), to a solution of potassium chloride, KCl, the result is a precipitate of lead chloride, PbCl\(_2\).

We usually write a precipitation reaction as a net ionic equation, showing only the precipitate and those ions forming the precipitate. Thus, the precipitation reaction for PbCl\(_2\) is

\[ \text{Pb}^{2+} (aq) + 2\text{Cl}^- (aq) \rightleftharpoons \text{PbCl}_2 (s) \]
When writing an equilibrium constant for a precipitation reaction, we focus on the precipitate's solubility. Thus, for PbCl$_2$, the solubility reaction is

$$\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$$

and its equilibrium constant, which we call the **solvability product**, $K_{sp}$, is

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5} \quad \text{(6.6)}$$

Even though it does not appear in the $K_{sp}$ expression, it is important to remember that equation 6.6 is valid only if PbCl$_2(s)$ is present and in equilibrium with Pb$^{2+}$ and Cl$^-$. You will find values for selected solubility products in Appendix 10.

### 6D.2 Acid–Base Reactions

A useful definition of acids and bases is that independently introduced in 1923 by Johannes Brønsted and Thomas Lowry. In the Brønsted-Lowry definition, an **acid** is a proton donor and a **base** is a proton acceptor. Note the connection in these definitions—defining a base as a proton acceptor implies that there is an acid available to donate the proton. For example, in reaction 6.7 acetic acid, CH$_3$COOH, donates a proton to ammonia, NH$_3$, which serves as the base.

$$\text{CH}_3\text{COOH}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{CH}_3\text{COO}^-(aq) \quad \text{(6.7)}$$

When an acid and a base react, the products are a new acid and a new base. For example, the acetate ion, CH$_3$COO$^-$, in reaction 6.7 is a base that can accept a proton from the acidic ammonium ion, NH$_4^+$, forming acetic acid and ammonia. We call the acetate ion the conjugate base of acetic acid, and the ammonium ion is the conjugate acid of ammonia.

**Strong and Weak Acids**

The reaction of an acid with its solvent (typically water) is an acid dissociation reaction. We divide acids into two categories—strong and weak—based on their ability to donate a proton to the solvent. A strong acid, such as HCl, almost completely transfers its proton to the solvent, which acts as the base.

$$\text{HCl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)$$

We use a single arrow (→) in place of the equilibrium arrow (⇌) because we treat HCl as if it completely dissociates in aqueous solutions. In water, the common strong acids are hydrochloric acid (HCl), hydroiodic acid (HI), hydrobromic acid (HBr), nitric acid (HNO$_3$), perchloric acid (HClO$_4$), and the first proton of sulfuric acid (H$_2$SO$_4$).
A weak acid, of which aqueous acetic acid is one example, does not completely donate its acidic proton to the solvent. Instead, most of the acid remains undissociated, with only a small fraction present as the conjugate base.

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

The equilibrium constant for this reaction is an acid dissociation constant, \(K_a\), which we write as

\[
K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5}
\]

The magnitude of \(K_a\) provides information about a weak acid’s relative strength, with a smaller \(K_a\) corresponding to a weaker acid. The ammonium ion, \(\text{NH}_4^+\), for example, with a \(K_a\) of \(5.702 \times 10^{-10}\), is a weaker acid than acetic acid.

**Monoprotic** weak acids, such as acetic acid, have only a single acidic proton and a single acid dissociation constant. Other acids, such as phosphoric acid, have more than one acidic proton, each characterized by an acid dissociation constant. We call such acids **polyprotic** weak acids. Phosphoric acid, for example, has three acid dissociation reactions and three acid dissociation constants.

\[
\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{H}_2\text{PO}_4^-(aq)
\]

\[
K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = 7.11 \times 10^{-3}
\]

\[
\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq)
\]

\[
K_{a2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = 6.32 \times 10^{-8}
\]

\[
\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{PO}_4^{3-}(aq)
\]

\[
K_{a3} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} = 4.5 \times 10^{-13}
\]

The decrease in the acid dissociation constants from \(K_{a1}\) to \(K_{a3}\) tells us that each successive proton is harder to remove. Consequently, \(\text{H}_3\text{PO}_4\) is a stronger acid than \(\text{H}_2\text{PO}_4^-\), and \(\text{H}_2\text{PO}_4^-\) is a stronger acid than \(\text{HPO}_4^{2-}\).
Strong and Weak Bases

The most common example of a strong base is an alkali metal hydroxide, such as sodium hydroxide, NaOH, which completely dissociates to produce hydroxide ion.

\[
\text{NaOH}(s) \rightarrow \text{Na}^+ (aq) + \text{OH}^- (aq)
\]

A weak base, such as the acetate ion, CH₃COO⁻, only partially accepts a proton from the solvent, and is characterized by a base dissociation constant, \( K_b \). For example, the base dissociation reaction and the base dissociation constant for the acetate ion are

\[
\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^- (aq) + \text{CH}_3\text{COOH}(aq)
\]

\[
K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.71 \times 10^{-10}
\]

A polyprotic weak base, like a polyprotic acid, has more than one base dissociation reaction and more than one base dissociation constant.

Amphiprotic Species

Some species can behave as either a weak acid or as a weak base. For example, the following two reactions show the chemical reactivity of the bicarbonate ion, HCO₃⁻, in water.

\[
\text{HCO}_3^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{CO}_3^{2-} (aq) \hspace{1cm} 6.8
\]

\[
\text{HCO}_3^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^- (aq) + \text{H}_2\text{CO}_3(aq) \hspace{1cm} 6.9
\]

A species that is both a proton donor and a proton acceptor is called amphiprotic. Whether an amphiprotic species behaves as an acid or as a base depends on the equilibrium constants for the competing reactions. For bicarbonate, the acid dissociation constant for reaction 6.8

\[
K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11}
\]

is smaller than the base dissociation constant for reaction 6.9.

\[
K_{b2} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = 2.25 \times 10^{-8}
\]

Because bicarbonate is a stronger base than it is an acid, we expect an aqueous solution of HCO₃⁻ to be basic.
**Dissociation of Water**

Water is an amphiprotic solvent because it can serve as an acid or as a base. An interesting feature of an amphiprotic solvent is that it is capable of reacting with itself in an acid–base reaction.

\[
2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]

We identify the equilibrium constant for this reaction as water’s dissociation constant, \(K_w\),

\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}
\]

which has a value of 1.0000 \(\times\) 10\(^{-14}\) at a temperature of 24\(^\circ\)C. The value of \(K_w\) varies substantially with temperature. For example, at 20\(^\circ\)C \(K_w\) is 6.809 \(\times\) 10\(^{-15}\), while at 30\(^\circ\)C \(K_w\) is 1.469 \(\times\) 10\(^{-14}\). At 25\(^\circ\)C, \(K_w\) is 1.008 \(\times\) 10\(^{-14}\), which is sufficiently close to 1.00 \(\times\) 10\(^{-14}\) that we can use the latter value with negligible error.

An important consequence of equation 6.11 is that the concentration of \(\text{H}_3\text{O}^+\) and the concentration of \(\text{OH}^-\) are related. If we know \([\text{H}_3\text{O}^+]\) for a solution, then we can calculate \([\text{OH}^-]\) using equation 6.11.

**Example 6.2**

What is the \([\text{OH}^-]\) if the \([\text{H}_3\text{O}^+]\) is 6.12 \(\times\) 10\(^{-5}\) M?

**Solution**

\[
[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{6.12 \times 10^{-5}} = 1.63 \times 10^{-10}
\]

**The pH Scale**

Equation 6.11 allows us to develop a pH scale that indicates a solution’s acidity. When the concentrations of \(\text{H}_3\text{O}^+\) and \(\text{OH}^-\) are equal a solution is neither acidic nor basic; that is, the solution is neutral. Letting

\[
[\text{H}_3\text{O}^+] = [\text{OH}^-]
\]

substituting into equation 6.11

\[
K_w = [\text{H}_3\text{O}^+]^2 = 1.00 \times 10^{-14}
\]

and solving for \([\text{H}_3\text{O}^+]\) gives

\[
[\text{H}_3\text{O}^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}
\]
A neutral solution has a hydronium ion concentration of $1.00 \times 10^{-7}$ M and a pH of 7.00. For a solution to be acidic the concentration of $\text{H}_3\text{O}^+$ must be greater than that for $\text{OH}^-$, which means that

$$[\text{H}_3\text{O}^+] > 1.00 \times 10^{-7} \text{ M}$$

The pH of an acidic solution, therefore, must be less than 7.00. A basic solution, on the other hand, has a pH greater than 7.00. Figure 6.2 shows the pH scale and pH values for some representative solutions.

**Tabulating Values for $K_a$ and $K_b$**

A useful observation about acids and bases is that the strength of a base is inversely proportional to the strength of its conjugate acid. Consider, for example, the dissociation reactions of acetic acid and acetate.

$$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq) \quad 6.12$$

$$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{CH}_3\text{COOH}(aq) \quad 6.13$$

Adding together these two reactions gives the reaction

$$2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$$

for which the equilibrium constant is $K_w$. Because adding together two reactions is equivalent to multiplying their respective equilibrium constants, we may express $K_w$ as the product of $K_a$ for $\text{CH}_3\text{COOH}$ and $K_b$ for $\text{CH}_3\text{COO}^-$.

$$K_w = K_{a,\text{CH}_3\text{COOH}} \times K_{b,\text{CH}_3\text{COO}^-}$$

For any weak acid, $\text{HA}$, and its conjugate weak base, $\text{A}^-$, we can generalize this to the following equation.

$$K_w = K_{a,\text{HA}} \times K_{b,\text{A}^-} \quad 6.14$$

The relationship between $K_a$ and $K_b$ for a conjugate acid–base pair simplifies our tabulation of acid and base dissociation constants. **Appendix 11** includes acid dissociation constants for a variety of weak acids. To find the value of $K_b$ for a weak base, use equation 6.14 and the $K_a$ value for its corresponding weak acid.

**Example 6.3**

Using **Appendix 11**, calculate values for the following equilibrium constants.

(a) $K_b$ for pyridine, $\text{C}_5\text{H}_5\text{N}$

(b) $K_b$ for dihydrogen phosphate, $\text{H}_2\text{PO}_4^-$
When finding the $K_b$ value for polyprotic weak base, you must be careful to choose the correct $K_a$ value. Remember that equation 6.14 applies only to a conjugate acid–base pair. The conjugate acid of $\text{H}_2\text{PO}_4^−$ is $\text{H}_3\text{PO}_4$, not $\text{HPO}_4^{2−}$.

### Solution

(a) $K_{b, \text{C}_3\text{H}_2\text{N}} = \frac{K_w}{K_{a, \text{C}_3\text{H}_2\text{NH}^+}} = \frac{1.00 \times 10^{-14}}{5.90 \times 10^{-6}} = 1.69 \times 10^{-9}$

(b) $K_{b, \text{H}_3\text{PO}_4^-} = \frac{K_w}{K_{a, \text{H}_3\text{PO}_4}} = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$

### Practice Exercise 6.2

Using Appendix 11, calculate the $K_b$ values for hydrogen oxalate, $\text{HC}_2\text{O}_4^−$, and oxalate, $\text{C}_2\text{O}_4^{2−}$.

Click here to review your answer to this exercise.

### 6D.3 Complexation Reactions

A more general definition of acids and bases was proposed in 1923 by G. N. Lewis. The Brønsted-Lowry definition of acids and bases focuses on an acid’s proton-donating ability and a base’s proton-accepting ability. Lewis theory, on the other hand, uses the breaking and forming of covalent bonds to describe acid–base characteristics. In this treatment, an acid is an electron pair acceptor and a base in an electron pair donor. Although we can apply Lewis theory to the treatment of acid–base reactions, it is more useful for treating complexation reactions between metal ions and ligands.

The following reaction between the metal ion $\text{Cd}^{2+}$ and the ligand $\text{NH}_3$ is typical of a complexation reaction.

$$\text{Cd}^{2+}(aq) + 4:\text{NH}_3(aq) \rightleftharpoons \text{Cd}(:\text{NH}_3)_4^{2+}(aq) \quad 6.15$$

The product of this reaction is a metal–ligand complex. In writing this reaction we show ammonia as $:\text{NH}_3$, using a pair of dots to emphasize the pair of electrons it donates to $\text{Cd}^{2+}$. In subsequent reactions we will omit this notation.

### Metal-Ligand Formation Constants

We characterize the formation of a metal–ligand complex by a formation constant, $K_f$. The complexation reaction between $\text{Cd}^{2+}$ and $\text{NH}_3$, for example, has the following equilibrium constant.

$$K_f = \frac{[\text{Cd}(:\text{NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = 5.5 \times 10^7 \quad 6.16$$

The reverse of reaction 6.15 is a dissociation reaction, which we characterize by a dissociation constant, $K_d$, that is the reciprocal of $K_f$.

Many complexation reactions occur in a stepwise fashion. For example, the reaction between $\text{Cd}^{2+}$ and $\text{NH}_3$ involves four successive reactions.
Cd\(^{2+}\)(aq) + NH\(_3\)(aq) ⇌ Cd(NH\(_3\))\(^{2+}\)(aq) \hspace{1cm} 6.17

Cd(NH\(_3\))\(^{2+}\)(aq) + NH\(_3\)(aq) ⇌ Cd(NH\(_3\))\(_2\)\(^{2+}\)(aq) \hspace{1cm} 6.18

Cd(NH\(_3\))\(_2\)\(^{2+}\)(aq) + NH\(_3\)(aq) ⇌ Cd(NH\(_3\))\(_3\)\(^{2+}\)(aq) \hspace{1cm} 6.19

Cd(NH\(_3\))\(_3\)\(^{2+}\)(aq) + NH\(_3\)(aq) ⇌ Cd(NH\(_3\))\(_4\)\(^{2+}\)(aq) \hspace{1cm} 6.20

To avoid ambiguity, we divide formation constants into two categories. **Stepwise formation constants**, which we designate as \(K_i\) for the \(i\)th step, describe the successive addition of one ligand to the metal–ligand complex from the previous step. Thus, the equilibrium constants for reactions 6.17–6.20 are, respectively, \(K_1\), \(K_2\), \(K_3\), and \(K_4\). Overall, or **cumulative formation constants**, which we designate as \(\beta_i\), describe the addition of \(i\) ligands to the free metal ion. The equilibrium constant in equation 6.16 is correctly identified as \(\beta_4\), where

\[
\beta_4 = K_1 \times K_2 \times K_3 \times K_4
\]

In general

\[
\beta_i = K_1 \times K_2 \times \cdots \times K_i
\]

Stepwise and overall formation constants for selected metal–ligand complexes are in Appendix 12.

**Metal–ligand complexation and solubility**

A formation constant characterizes the addition of one or more ligands to a free metal ion. To find the equilibrium constant for a complexation reaction involving a solid, we combine appropriate \(K_{sp}\) and \(K_f\) expressions. For example, the solubility of AgCl increases in the presence of excess chloride as the result of the following complexation reaction.

\[
AgCl(s) + Cl^-(aq) ⇌ AgCl\(^-\)(aq) \hspace{1cm} 6.21
\]

We can write this reaction as the sum of three other reactions with known equilibrium constants—the solubility of AgCl, described by its \(K_{sp}\)

\[
AgCl(s) ⇌ Ag^+(aq) + Cl^-(aq)
\]

and the stepwise formation of AgCl\(^-\), described by \(K_1\) and \(K_2\).

\[
Ag^+(aq) + Cl^-(aq) ⇌ AgCl(aq)
\]

\[
AgCl(aq) + Cl^-(aq) ⇌ AgCl\(^-\)(aq)
\]

The equilibrium constant for reaction 6.21, therefore, is \(K_{sp} \times K_1 \times K_2\).
Example 6.4

Determine the value of the equilibrium constant for the reaction

$$\text{PbCl}_2(s) \rightleftharpoons \text{PbCl}_2(aq)$$

**Solution**

We can write this reaction as the sum of three other reactions. The first of these reactions is the solubility of PbCl$_2$(s), described by its $K_{sp}$ reaction.

$$\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$$

The remaining two reactions are the stepwise formation of PbCl$_2$(aq), described by $K_1$ and $K_2$.

$$\text{Pb}^{2+}(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{PbCl}^+(aq)$$

$$\text{PbCl}^+(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{PbCl}_2(aq)$$

Using values for $K_{sp}$, $K_1$, and $K_2$ from Appendix 10 and Appendix 12, we find that the equilibrium constant is

$$K = K_{sp} \times K_1 \times K_2 = (1.7 \times 10^{-5}) \times 38.9 \times 1.62 = 1.1 \times 10^{-3}$$

Practice Exercise 6.3

What is the equilibrium constant for the following reaction? You will find appropriate equilibrium constants in Appendix 10 and Appendix 11.

$$\text{AgBr}(s) + 2\text{S}_2\text{O}_3^2-(aq) \rightleftharpoons \text{Ag}^{+}\text{S}_2\text{O}_3^3-(aq) + \text{Br}^-(aq)$$

Click here to review your answer to this exercise.

6D.4 Oxidation–Reduction (Redox) Reactions

An oxidation–reduction reaction occurs when electrons move from one reactant to another reactant. As a result of this electron transfer, these reactants undergo a change in oxidation state. Those reactants that experience an increase in oxidation state undergo oxidation, and those experiencing a decrease in oxidation state undergo reduction. For example, in the following redox reaction between Fe$^{3+}$ and oxalic acid, H$_2$C$_2$O$_4$, iron is reduced because its oxidation state changes from +3 to +2.

$$2\text{Fe}^{3+}(aq) + \text{H}_2\text{C}_2\text{O}_4(aq) + 2\text{H}_2\text{O}(l) \rightleftharpoons 2\text{Fe}^{2+}(aq) + 2\text{CO}_2(g) + 2\text{H}_3\text{O}^+(aq)$$

Oxalic acid, on the other hand, undergoes oxidation because the oxidation state for carbon increases from +3 in H$_2$C$_2$O$_4$ to +4 in CO$_2$. 
We can divide a redox reaction, such as reaction 6.22, into separate \textbf{HALF-REACTIONS} that show the oxidation and the reduction processes.

\[
\text{H}_2\text{C}_2\text{O}_4(aq) + 2\text{H}_2\text{O}(l) \rightleftharpoons 2\text{CO}_2(g) + 2\text{H}_3\text{O}^+(aq) + 2e^-
\]

\[
\text{Fe}^{3+}(aq) + e^- \rightleftharpoons \text{Fe}^{2+}(aq)
\]

It is important to remember, however, that an oxidation reaction and a reduction reaction occur as a pair. We formalize this relationship by identifying as a \textbf{REDUCING AGENT} the reactant undergoing oxidation, because it provides the electrons for the reduction half-reaction. Conversely, the reactant undergoing reduction is an \textbf{OXIDIZING AGENT}. In reaction 6.22, \text{Fe}^{3+} is the oxidizing agent and \text{H}_2\text{C}_2\text{O}_4 is the reducing agent.

The products of a redox reaction also have redox properties. For example, the \text{Fe}^{2+} in reaction 6.22 can be oxidized to \text{Fe}^{3+}, while \text{CO}_2 can be reduced to \text{H}_2\text{C}_2\text{O}_4. Borrowing some terminology from acid–base chemistry, \text{Fe}^{2+} is the conjugate reducing agent of the oxidizing agent \text{Fe}^{3+}, and \text{CO}_2 is the conjugate oxidizing agent of the reducing agent \text{H}_2\text{C}_2\text{O}_4.

\textbf{THERMODYNAMICS OF REDOX REACTIONS}

Unlike precipitation reactions, acid–base reactions, and complexation reactions, we rarely express the equilibrium position of a redox reaction using an equilibrium constant. Because a redox reaction involves a transfer of electrons from a reducing agent to an oxidizing agent, it is convenient to consider the reaction’s thermodynamics in terms of the electron.

For a reaction in which one mole of a reactant undergoes oxidation or reduction, the net transfer of charge, \(Q\), in coulombs is

\[
Q = nF
\]

where \(n\) is the moles of electrons per mole of reactant, and \(F\) is Faraday’s constant (96,485 \text{ C/mol}). The free energy, \(\Delta G\), to move this charge, \(Q\), over a change in \textbf{POTENTIAL}, \(E\), is

\[
\Delta G = EQ
\]

The change in free energy (in kJ/mole) for a redox reaction, therefore, is

\[
\Delta G = -nFE \hspace{1cm} \text{6.23}
\]

where \(\Delta G\) has units of kJ/mol. The minus sign in equation 6.23 is the result of a difference in the conventions for assigning a reaction’s favorable direction. In thermodynamics, a reaction is favored when \(\Delta G\) is negative, but a redox reaction is favored when \(E\) is positive. Substituting equation 6.23 into \textbf{equation 6.3}

\[
-nFE = -nFE^o + RT\ln Q
\]

and dividing by \(-nF\), leads to the well-known \textbf{NERNST EQUATION}
\[ E = E^\circ - \frac{RT}{nF} \ln Q \]

where \( E^\circ \) is the potential under standard-state conditions. Substituting appropriate values for \( R \) and \( F \), assuming a temperature of 25°C (298 K), and switching from \( \ln \) to \( \log \) gives the potential in volts as

\[ E = E^\circ - \frac{0.05916}{n} \log Q \quad 6.24 \]

**Standard Potentials**

A redox reaction’s **standard potential**, \( E^\circ \), provides an alternative way of expressing its equilibrium constant and, therefore, its equilibrium position. Because a reaction at equilibrium has a \( \Delta G \) of zero, the potential, \( E \), also must be zero at equilibrium. Substituting these values into equation 6.24 and rearranging provides a relationship between \( E^\circ \) and \( K \).

\[ E^\circ = \frac{0.05916}{n} \log K \quad 6.25 \]

We generally do not tabulate standard potentials for redox reactions. Instead, we calculate \( E^\circ \) using the standard potentials for the corresponding oxidation half-reaction and reduction half-reaction. By convention, standard potentials are provided for reduction half-reactions. The standard potential for a redox reaction, \( E^\circ \), is

\[ E^\circ = E^\circ_{\text{red}} - E^\circ_{\text{ox}} \]

where \( E^\circ_{\text{red}} \) and \( E^\circ_{\text{ox}} \) are the standard reduction potentials for the reduction half-reaction and the oxidation half-reaction.

Because we cannot measure the potential for a single half-reaction, we arbitrarily assign a standard reduction potential of zero to a reference half-reaction and report all other reduction potentials relative to this reference. The reference half-reaction is

\[ 2\text{H}_3\text{O}^+ (aq) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(l) + \text{H}_2(g) \]

Appendix 13 contains a list of selected standard reduction potentials. The more positive the standard reduction potential, the more favorable the reduction reaction under standard state conditions. Thus, under standard state conditions the reduction of \( \text{Cu}^{2+} \) to \( \text{Cu} \) (\( E^\circ = +0.3419 \text{ V} \)) is more favorable than the reduction of \( \text{Zn}^{2+} \) to \( \text{Zn} \) (\( E^\circ = -0.7618 \text{ V} \)).

**Example 6.5**

Calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential when [\( \text{Ag}^+ \)] = 0.020 M and [\( \text{Cd}^{2+} \)] = 0.050 M, for the following reaction at 25°C.
Cd(s) + 2Ag⁺(aq) ⇌ 2Ag(s) + Cd²⁺(aq)

**Solution**

(a) In this reaction Cd is undergoing oxidation and Ag⁺ is undergoing reduction. The standard cell potential, therefore, is

\[ E^o = E^o_{Ag^+/Ag} - E^o_{Cd^{2+}/Cd} = 0.7996 - (-0.4030) = 1.2026 \text{ V} \]

(b) To calculate the equilibrium constant we substitute appropriate values into equation 6.25.

\[ E^o = 1.2026 \text{ V} = \frac{0.05916 \text{ V}}{2} \log K \]

Solving for \( K \) gives the equilibrium constant as

\[ \log K = 40.6558 \]
\[ K = 4.527 \times 10^{40} \]

(c) To calculate the potential when [Ag⁺] is 0.020 M and [Cd²⁺] is 0.050 M, we use the appropriate relationship for the reaction quotient, \( Q \), in equation 6.24.

\[ E = E^o - \frac{0.05916 \text{ V}}{n} \log \frac{[Cd²⁺]^n}{[Ag⁺]^n} \]

\[ E = 1.2606 \text{ V} - \frac{0.05916 \text{ V}}{2} \log \frac{(0.050)}{(0.020)^2} \]
\[ E = 1.14 \text{ V} \]

**Practice Exercise 6.4**

For the following reaction at 25°C

\[ 5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) ⇌ 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l) \]

calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential under these conditions: \([Fe^{2+}] = 0.50 \text{ M}, [Fe^{3+}] = 0.10 \text{ M}, [MnO_4^-] = 0.025 \text{ M}, [Mn^{2+}] = 0.015 \text{ M}, and a pH of 7.00. See Appendix 13 for standard state reduction potentials.

Click here to review your answer to this exercise.
6E  Le Châtelier’s Principle

At a temperature of 25 °C, acetic acid’s dissociation reaction

\[ \text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)} \]

has an equilibrium constant of

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5} \quad 6.26 \]

Because equation 6.26 has three variables—[CH₃COOH], [CH₃COO⁻], and [H₃O⁺]—it does not have a unique mathematical solution. Nevertheless, although two solutions of acetic acid may have different values for [CH₃COOH], [CH₃COO⁻], and [H₃O⁺], each solution must have the same value of $K_a$.

If we add sodium acetate to a solution of acetic acid, the concentration of CH₃COO⁻ increases, suggesting an apparent increase in the value of $K_a$. Because $K_a$ must remain constant, the concentration of all three species in equation 6.26 must change to restore $K_a$ to its original value. In this case, a partial reaction of CH₃COO⁻ and H₃O⁺ decreases their concentrations, producing additional CH₃COOH and reestablishing the equilibrium.

The observation that a system at equilibrium responds to an external stress by reequilibrating in a manner that diminishes the stress, is formalized as **Le Châtelier’s principle**. One of the most common stresses to a system at equilibrium is to change the concentration of a reactant or product. We already have seen, in the case of adding sodium acetate to acetic acid, that if we add a product to a reaction at equilibrium the system responds by converting some of the products into reactants. Adding a reactant has the opposite effect, resulting in the conversion of reactants to products.

When we add sodium acetate to a solution of acetic acid, we are directly applying the stress to the system. It is also possible to indirectly apply a concentration stress. Consider, for example, the solubility of AgCl.

\[ \text{AgCl}(s) \rightleftharpoons \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \quad 6.27 \]

The effect on the solubility of AgCl of adding AgNO₃ is obvious, but what is the effect of adding a ligand that forms a stable, soluble complex with Ag⁺? Ammonia, for example, reacts with Ag⁺ as shown here

\[ \text{Ag}^+_{(aq)} + 2\text{NH}_3_{(aq)} \rightleftharpoons \text{Ag(NH}_3)^+_{(aq)} \quad 6.28 \]

Adding ammonia decreases the concentration of Ag⁺ as the Ag(NH₃)₂⁺ complex forms. In turn, decreasing the concentration of Ag⁺ increases the solubility of AgCl as reaction 6.27 reestablishes its equilibrium position. Adding together reaction 6.27 and reaction 6.28 clarifies the effect of ammonia on the solubility of AgCl, by showing ammonia as a reactant.

\[ \text{AgCl}(s) + 2\text{NH}_3_{(aq)} \rightleftharpoons \text{Ag(NH}_3)^+_{(aq)} + \text{Cl}^-_{(aq)} \quad 6.29 \]
Example 6.6

What happens to the solubility of AgCl if we add HNO$_3$ to the equilibrium solution defined by reaction 6.29?

**Solution**

Nitric acid is a strong acid, which reacts with ammonia as shown here

\[
\text{HNO}_3(aq) + \text{NH}_3(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{NO}_3^-(aq)
\]

Adding nitric acid lowers the concentration of ammonia. Decreasing ammonia’s concentration causes reaction 6.29 to move from products to reactants, decreasing the solubility of AgCl.

Increasing or decreasing the partial pressure of a gas is the same as increasing or decreasing its concentration. Because the concentration of a gas depends on its partial pressure, and not on the total pressure of the system, adding or removing an inert gas has no effect on a reaction’s equilibrium position.

Most reactions involve reactants and products dispersed in a solvent. If we change the amount of solvent by diluting or concentrating the solution, then the concentrations of all reactants and products either decrease or increase. The effect of simultaneously changing the concentrations of all reactants and products is not as intuitively obvious as when changing the concentration of a single reactant or product. As an example, let’s consider how diluting a solution affects the equilibrium position for the formation of the aqueous silver-amine complex (reaction 6.28). The equilibrium constant for this reaction is

\[
\beta_2 = \frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}
\]

where we include the subscript “eq” for clarification. If we dilute a portion of this solution with an equal volume of water, each of the concentration terms in equation 6.30 is cut in half. The reaction quotient, $Q$, becomes

\[
Q = \frac{0.5[\text{Ag(NH}_3)_2^+]_{eq}}{0.5[\text{Ag}^+]_{eq}(0.5)^2[\text{NH}_3]^2_{eq}} = \frac{0.5}{(0.5)^3} \times \frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2_{eq}} = 4\beta_2
\]

Because $Q$ is greater than $\beta_2$, equilibrium is reestablished by shifting the reaction to the left, decreasing the concentration of Ag(NH$_3$)$_2^+$. Note that the new equilibrium position lies toward the side of the equilibrium reaction having the greatest number of solute particles (one Ag$^+$ ion and two molecules of NH$_3$ versus a single metal-ligand complex). If we concentrate the solution of Ag(NH$_3$)$_2^+$ by evaporating some of the solvent, equilibrium is re-established in the opposite direction. This is a general conclusion that we can apply to any reaction. Increasing volume always favors the direc-
tion producing the greatest number of particles, and decreasing volume always favors the direction producing the fewest particles. If the number of particles is the same on both sides of the reaction, then the equilibrium position is unaffected by a change in volume.

6F  Ladder Diagrams

When developing or evaluating an analytical method, we often need to understand how the chemistry taking place affects our results. Suppose we wish to isolate Ag\(^+\) by precipitating it as AgCl. If we also need to control pH, then we must use a reagent that will not adversely affect the solubility of AgCl. It is a mistake to add NH\(_3\) to the reaction mixture, for example, because it increases the solubility of AgCl (reaction 6.29).

In this section we introduce the LADDER DIAGRAM as a simple graphical tool for evaluating the equilibrium chemistry.\(^2\) Using ladder diagrams we will be able to determine what reactions occur when combining several reagents, estimate the approximate composition of a system at equilibrium, and evaluate how a change to solution conditions might affect an analytical method.

6F.1  Ladder Diagrams for Acid–Base Equilibria

Let’s use acetic acid, CH\(_3\)COOH, to illustrate the process of drawing and interpreting an acid–base ladder diagram. Before drawing the diagram, however, let’s consider the equilibrium reaction in more detail. The equilibrium constant expression for acetic acid’s dissociation reaction

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

is

\[
K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5}
\]

Taking the logarithm of each term in this equation, and multiplying through by −1 gives

\[
-\log K_a = -\log[\text{H}_3\text{O}^+] - \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.76
\]

Replacing the negative log terms with p-functions and rearranging the equation, leaves us with the result shown here.

---

Equation 6.31 tells us a great deal about the relationship between pH and the relative amounts of acetic acid and acetate at equilibrium. If the concentrations of CH₃COOH and CH₃COO⁻ are equal, then equation 6.31 reduces to

$$\text{pH} = pK_a + \log \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right) = 4.76$$

If the concentration of CH₃COO⁻ is greater than that of CH₃COOH, then the log term in equation 6.31 is positive and

$$\text{pH} > pK_a \quad \text{or} \quad \text{pH} > 4.76$$

This is a reasonable result because we expect the concentration of the conjugate base, CH₃COO⁻, to increase as the pH increases. Similar reasoning shows that the concentration of CH₃COOH exceeds that of CH₃COO⁻ when

$$\text{pH} < pK_a \quad \text{or} \quad \text{pH} < 4.76$$

Now we are ready to construct acetic acid’s ladder diagram (Figure 6.3). First, we draw a vertical arrow representing the solution’s pH, with smaller (more acidic) pH levels at the bottom and larger (more basic) pH levels at the top. Second, we draw a horizontal line at a pH equal to acetic acid’s pKₐ value. This line, or step on the ladder, divides the pH axis into regions where either CH₃COOH or CH₃COO⁻ is the predominate species. This completes the ladder diagram.

Using the ladder diagram, it is easy to identify the predominate form of acetic acid at any pH. At a pH of 3.5, for example, acetic acid exists primarily as CH₃COOH. If we add sufficient base to the solution such that the pH increases to 6.5, the predominate form of acetic acid is CH₃COO⁻.

Figure 6.3 Acid–base ladder diagram for acetic acid showing the relative concentrations of CH₃COOH and CH₃COO⁻. A simpler version of this ladder diagram dispenses with the equalities and shows only the predominate species in each region.
Example 6.7

Draw a ladder diagram for the weak base \( p \)-nitrophenolate and identify its predominate form at a pH of 6.00.

**Solution**

To draw a ladder diagram for a weak base, we simply draw the ladder diagram for its conjugate weak acid. From Appendix 12, the \( pK_a \) for \( p \)-nitrophenol is 7.15. The resulting ladder diagram is shown in Figure 6.4. At a pH of 6.00, \( p \)-nitrophenolate is present primarily in its weak acid form.

Practice Exercise 6.5

Draw a ladder diagram for carbonic acid, \( H_2CO_3 \). Because \( H_2CO_3 \) is a diprotic weak acid, your ladder diagram will have two steps. What is the predominate form of carbonic acid when the pH is 7.00? Relevant equilibrium constants are in Appendix 11.

Click [here](#) to review your answer to this exercise.

Ladder diagrams are particularly useful for evaluating the reactivity between a weak acid and a weak base. Figure 6.5 shows a single ladder diagram for acetic acid/acetate and \( p \)-nitrophenol/\( p \)-nitrophenolate. An acid and a base can not co-exist if their respective areas of predominance do not overlap. If we mix together solutions of acetic acid and sodium \( p \)-nitrophenolate, the reaction

\[
O_2N-C-O^- (aq) + CH_3COOH(aq) \rightleftharpoons CH_3COO^- (aq) + O_2N-C-OH(aq)
\]

occurs because the areas of predominance for acetic acid and \( p \)-nitrophenolate do not overlap. The solution's final composition depends on which spe-
cies is the limiting reagent. The following example shows how we can use the ladder diagram in Figure 6.5 to evaluate the result of mixing together solutions of acetic acid and p-nitrophenolate.

**Example 6.8**

Predict the approximate pH and the final composition of mixing together 0.090 moles of acetic acid and 0.040 moles of p-nitrophenolate.

**Solution**

The ladder diagram in Figure 6.5 indicates that the reaction between acetic acid and p-nitrophenolate is favorable. Because acetic acid is in excess, we assume that the reaction of p-nitrophenolate to p-nitrophenol is complete. At equilibrium essentially no p-nitrophenolate remains and there are 0.040 mol of p-nitrophenol. Converting p-nitrophenolate to p-nitrophenol consumes 0.040 moles of acetic acid; thus

\[
\text{moles } CH_3COOH = 0.090 - 0.040 = 0.050 \text{ mol}
\]

\[
\text{moles } CH_3COO^- = 0.040 \text{ mol}
\]

According to the ladder diagram, the pH is 4.76 when there are equal amounts of \( CH_3COOH \) and \( CH_3COO^- \). Because we have slightly more \( CH_3COOH \) than \( CH_3COO^- \), the pH is slightly less than 4.76.

**Practice Exercise 6.6**

Using Figure 6.5, predict the approximate pH and the composition of a solution formed by mixing together 0.090 moles of p-nitrophenolate and 0.040 moles of acetic acid.

Click here to review your answer to this exercise.

If the areas of predominance for an acid and a base overlap, then practically no reaction occurs. For example, if we mix together solutions of \( CH_3COO^- \) and p-nitrophenol, there is no significant change in the moles of either reagent. Furthermore, the pH of the mixture must be between 4.76 and 7.15, with the exact pH depending upon the relative amounts of \( CH_3COO^- \) and p-nitrophenol.

We also can use an acid–base ladder diagram to evaluate the effect of pH on other equilibria. For example, the solubility of \( CaF_2 \)

\[
CaF_2 (s) \rightleftharpoons Ca^{2+} (aq) + 2F^- (aq)
\]

is affected by pH because \( F^- \) is a weak base. Using Le Châtelier’s principle, converting \( F^- \) to HF increases the solubility of \( CaF_2 \). To minimize the solubility of \( CaF_2 \) we need to maintain the solution’s pH so that \( F^- \) is the predominate species. The ladder diagram for HF (Figure 6.6) shows us that maintaining a pH of more than 3.17 minimizes solubility losses.
6F.2 Ladder Diagrams for Complexation Equilibria

We can apply the same principles for constructing and interpreting acid–base ladder diagrams to equilibria involving metal–ligand complexes. For a complexation reaction we define the ladder diagram’s scale using the concentration of uncomplexed, or free ligand, pL. Using the formation of Cd(NH$_3$)$_2^{2+}$ as an example

\[
\text{Cd}^{2+}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{Cd(NH}_3)_2^{2+}(aq)
\]

we can easily show that log $K_1$ is the dividing line between the areas of predominance for Cd$^{2+}$ and Cd(NH$_3$)$_2^{2+}$.

\[
K_1 = \frac{[\text{Cd(NH}_3)_2^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]} = 3.55 \times 10^2
\]

Thus, Cd$^{2+}$ is the predominate species when pNH$_3$ is greater than 2.55 (a concentration of NH$_3$ smaller than 2.82 $\times$ 10$^{-3}$ M) and for pNH$_3$ values less than 2.55, Cd(NH$_3$)$_2^{2+}$ is the predominate species. Figure 6.7 shows a complete metal–ligand ladder diagram for Cd$^{2+}$ and NH$_3$.

**Example 6.9**

Draw a single ladder diagram for the Ca(EDTA)$^{2-}$ and Mg(EDTA)$^{2-}$ metal–ligand complexes. Using your ladder diagram, predict the result of adding 0.080 moles of Ca$^{2+}$ to 0.060 moles of Mg(EDTA)$^{2-}$. EDTA is an abbreviation for the ligand ethylenediaminetetraacetic acid.

**Solution**

Figure 6.8 shows the ladder diagram for this system of metal–ligand complexes. Because the predominance regions for Ca$^{2+}$ and Mg(EDTA)$^{2-}$ do not overlap, the reaction

\[
\text{Ca}^{2+}(aq) + \text{Mg(EDTA)}^{2-}(aq) \rightleftharpoons \text{Ca(EDTA)}^{2-}(aq) + \text{Mg}^{2+}(aq)
\]

takes place. Because Ca$^{2+}$ is the excess reagent, the composition of the final solution is approximately

\[
\text{moles } \text{Ca}^{2+} = 0.080 - 0.060 = 0.020 \text{ mol}
\]
mol Ca(EDTA)$^{2-}$ = 0.060 mol
mol Mg$^{2+}$ = 0.060 mol
mol Mg(EDTA)$^{2-}$ = 0 mol

The metal–ligand ladder diagram in Figure 6.7 uses stepwise formation constants. We can also construct ladder diagrams using cumulative formation constants. The first three stepwise formation constants for the reaction of Zn$^{2+}$ with NH$_3$

$$
\text{Zn}^{2+}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{Zn(NH}_3)_2^{2+}(aq) \quad K_1 = 1.6 \times 10^2
$$

$$
\text{Zn(NH}_3)_2^{2+}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{Zn(NH}_3)_3^{2+}(aq) \quad K_2 = 1.95 \times 10^2
$$

$$
\text{Zn(NH}_3)_3^{2+}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{Zn(NH}_3)_3^{3+}(aq) \quad K_3 = 2.3 \times 10^2
$$

show that the formation of Zn(NH$_3$)$_3^{2+}$ is more favorable than the formation of Zn(NH$_3$)$_2^{2+}$ or Zn(NH$_3$)$_2^{2+}$. For this reason, the equilibrium is best represented by the cumulative formation reaction shown here.

$$
\text{Zn}^{2+}(aq) + 3\text{NH}_3(aq) \rightleftharpoons \text{Zn(NH}_3)_3^{3+}(aq) \quad \beta_3 = 7.2 \times 10^6
$$

To see how we incorporate this cumulative formation constant into a ladder diagram, we begin with the reaction’s equilibrium constant expression.

Because $K_3$ is greater than $K_2$, which is greater than $K_1$, the formation of the metal-ligand complex Zn(NH$_3$)$_3^{2+}$ is more favorable than the formation of the other metal ligand complexes. For this reason, at lower values of pNH$_3$ the concentration of Zn(NH$_3$)$_3^{2+}$ is larger than that for Zn(NH$_3$)$_2^{2+}$ and Zn(NH$_3$)$_2^{2+}$. The value of $\beta_3$ is

$$
\beta_3 = K_1 \times K_2 \times K_3
$$
Taking the log of each side gives

\[
\log \beta_3 = \log \frac{[\text{Zn}(\text{NH}_3)_3^{2+}]}{[\text{Zn}^{2+}][\text{NH}_3]^3} - 3 \log [\text{NH}_3]
\]

or

\[
p\text{NH}_3 = \frac{1}{3} \log \beta_3 + \frac{1}{3} \log \frac{[\text{Zn}]}{[\text{Zn}(\text{NH}_3)_3^{2+}]}
\]

When the concentrations of \(\text{Zn}^{2+}\) and \(\text{Zn} (\text{NH}_3)_3^{2+}\) are equal, then

\[
p\text{NH}_3 = \frac{1}{3} \log \beta_3 = 2.29
\]

In general, for the metal–ligand complex \(\text{ML}_n\), the step for a cumulative formation constant is

\[
pL = \frac{1}{n} \log \beta_n
\]

Figure 6.9 shows the complete ladder diagram for the \(\text{Zn}^{2+}–\text{NH}_3\) system.

### 6F.3 Ladder Diagram for Oxidation/Reduction Equilibria

We also can construct ladder diagrams to help evaluate redox equilibria. Figure 6.10 shows a typical ladder diagram for two half-reactions in which the scale is the potential, \(E\). The Nernst equation defines the areas of predominance. Using the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) half-reaction as an example, we write

\[
E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.771 \text{V}
\]

\[
E^0_{\text{Sn}^{4+}/\text{Sn}^{2+}} = +0.154 \text{V}
\]
\[ E = E^\circ - \frac{RT}{nF} \ln \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) = +0.771 - 0.05916 \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) \]

At potentials more positive than the standard state potential, the predominant species is \( \text{Fe}^{3+} \), whereas \( \text{Fe}^{2+} \) predominates at potentials more negative than \( E^\circ \). When coupled with the step for the \( \text{Sn}^{4+}/\text{Sn}^{2+} \) half-reaction we see that \( \text{Sn}^{2+} \) is a useful reducing agent for \( \text{Fe}^{3+} \). If \( \text{Sn}^{2+} \) is in excess, the potential of the resulting solution is near +0.151 V.

Because the steps on a redox ladder diagram are standard state potentials, complications arise if solutes other than the oxidizing agent and reducing agent are present at non-standard state concentrations. For example, the potential for the half-reaction

\[ \text{UO}_2^{2+}(aq) + 4\text{H}_2\text{O}^+(aq) + 2e^- \rightleftharpoons \text{U}^{4+}(aq) + 6\text{H}_2\text{O}(l) \]

depends on the solution’s pH. To define areas of predominance in this case we begin with the Nernst equation

\[ E = +0.327 - \frac{0.05916}{2} \log \left( \frac{[\text{U}^{4+}]}{[\text{UO}_2^{2+}][\text{H}_3\text{O}^+]^4} \right) \]

and factor out the concentration of \( \text{H}_3\text{O}^+ \).

\[ E = +0.327 + \frac{0.05916}{2} \log[\text{H}_3\text{O}^+]^4 - \frac{0.05916}{2} \log \left( \frac{[\text{U}^{4+}]}{[\text{UO}_2^{2+}]} \right) \]

From this equation we see that the area of predominance for \( \text{UO}_2^{2+} \) and \( \text{U}^{4+} \) is defined by a step whose potential is

\[ E = +0.327 + \frac{0.05916}{2} \log[\text{H}_3\text{O}^+]^4 = +0.327 - 0.1183\text{pH} \]

Figure 6.11 shows how pH affects the step for the \( \text{UO}_2^{2+}/\text{U}^{4+} \) half-reaction.

### 6G Solving Equilibrium Problems

Ladder diagrams are a useful tool for evaluating chemical reactivity, usually providing a reasonable approximation of a chemical system’s composition at equilibrium. If we need a more exact quantitative description of the equilibrium condition, then a ladder diagram is insufficient. In this case we need to find an algebraic solution. In this section we will learn how to set-up and solve equilibrium problems. We will start with a simple problem and work toward more complex problems.
6G.1 A Simple Problem—Solubility of Pb(IO$_3$)$_2$

If we place an insoluble compound such as Pb(IO$_3$)$_2$ in deionized water, the solid dissolves until the concentrations of Pb$^{2+}$ and IO$_3^−$ satisfy the solubility product for Pb(IO$_3$)$_2$. At equilibrium the solution is saturated with Pb(IO$_3$)$_2$, which simply means that no more solid can dissolve. How do we determine the equilibrium concentrations of Pb$^{2+}$ and IO$_3^−$, and what is the molar solubility of Pb(IO$_3$)$_2$ in this saturated solution?

We begin by writing the equilibrium reaction and the solubility product expression for Pb(IO$_3$)$_2$.

$$\text{Pb(IO}_3\text{)}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{IO}_3^−(aq)$$

$$K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^−]^2 = 2.5 \times 10^{-13} \quad 6.33$$

As Pb(IO$_3$)$_2$ dissolves, two IO$_3^−$ ions are produced for each ion of Pb$^{2+}$. If we assume that the change in the molar concentration of Pb$^{2+}$ at equilibrium is $x$, then the change in the molar concentration of IO$_3^-$ is $2x$. The following table helps us keep track of the initial concentrations, the change in concentrations, and the equilibrium concentrations of Pb$^{2+}$ and IO$_3^−$.

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>Pb(IO$_3$)$_2$(s)</th>
<th>Pb$^{2+}$ (aq)</th>
<th>2IO$_3^−$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>solid</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>solid</td>
<td>$+x$</td>
<td>$+2x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>solid</td>
<td>$x$</td>
<td>$2x$</td>
</tr>
</tbody>
</table>

Substituting the equilibrium concentrations into equation 6.33 and solving gives

$$(x)(2x)^2 = 4x^3 = 2.5 \times 10^{-13}$$

$$x = 3.97 \times 10^{-5}$$

Substituting this value of $x$ back into the equilibrium concentration expressions for Pb$^{2+}$ and IO$_3^−$ gives their concentrations as

$$[\text{Pb}^{2+}] = x = 4.0 \times 10^{-5} \text{ M}$$

$$[\text{IO}_3^−] = 2x = 7.9 \times 10^{-5} \text{ M}$$

Because one mole of Pb(IO$_3$)$_2$ contains one mole of Pb$^{2+}$, the molar solubility of Pb(IO$_3$)$_2$ is equal to the concentration of Pb$^{2+}$, or $4.0 \times 10^{-5}$ M.

**Practice Exercise 6.7**

Calculate the molar solubility and the mass solubility for Hg$_2$Cl$_2$, given the following solubility reaction and $K_{sp}$ value.

$$\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}^{2+}(aq) + 2\text{Cl}^−(aq) \quad K_{sp} = 1.2 \times 10^{-18}$$

Click [here](#) to review your answer to this exercise.
6G.2 A More Complex Problem—The Common Ion Effect

Calculating the solubility of Pb(IO$_3$)$_2$ in deionized water is a straightforward problem since the solid’s dissolution is the only source of Pb$^{2+}$ and IO$_3^−$. But what if we add Pb(IO$_3$)$_2$ to a solution of 0.10 M Pb(NO$_3$)$_2$, which provides a second source of Pb$^{2+}$? Before we set up and solve this problem algebraically, think about the system’s chemistry and decide whether the solubility of Pb(IO$_3$)$_2$ will increase, decrease or remain the same.

We begin by setting up a table to help us keep track of the concentrations of Pb$^{2+}$ and IO$_3^−$ as this system moves toward and reaches equilibrium.

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>Pb(IO$_3$)$_2$(s)</th>
<th>⇌</th>
<th>Pb$^{2+}$ (aq)</th>
<th>+</th>
<th>2IO$_3^−$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>solid</td>
<td></td>
<td>0.10</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>solid</td>
<td>+x</td>
<td>solid</td>
<td>+2x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>solid</td>
<td>0.10 + x</td>
<td>2x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Substituting the equilibrium concentrations into equation 6.33

\[(0.10 + x)(2x)^2 = 2.5 \times 10^{-13}\]

and multiplying out the terms on the equation’s left side leaves us with

\[4x^3 + 0.40x^2 = 2.5 \times 10^{-13}\] 6.34

This is a more difficult equation to solve than that for the solubility of Pb(IO$_3$)$_2$ in deionized water, and its solution is not immediately obvious. We can find a rigorous solution to equation 6.34 using available computer software packages and spreadsheets, some of which are described in Section 6.J.

How might we solve equation 6.34 if we do not have access to a computer? One approach is to use our understanding of chemistry to simplify the problem. From Le Châtelier’s principle we know that a large initial concentration of Pb$^{2+}$ significantly decreases the solubility of Pb(IO$_3$)$_2$. One reasonable assumption is that the equilibrium concentration of Pb$^{2+}$ is very close to its initial concentration. If this assumption is correct, then the following approximation is reasonable

\[[\text{Pb}^{2+}] = 0.10 + x \approx 0.10 \text{ M}\]

Substituting our approximation into equation 6.33 and solving for $x$ gives

\[(0.1)(2x)^2 = 2.5 \times 10^{-13}\]

\[0.4x^2 = 2.5 \times 10^{-13}\]

\[x = 7.91 \times 10^{-7}\]

Before accepting this answer, we must verify that our approximation is reasonable. The difference between the calculated concentration of Pb$^{2+}$, 0.10 + $x$ M, and our assumption that it is 0.10 M is $7.9 \times 10^{-7}$, or $7.9 \times 10^{-4}$% of
the assumed concentration. This is a negligible error. Accepting the result of our calculation, we find that the equilibrium concentrations of Pb\(^{2+}\) and IO\(_3^-\) are

\[
\begin{align*}
\text{[Pb}^{2+}\text{]} &= 0.10 + x \approx 0.10 \text{ M} \\
\text{[IO}_3^-\text{]} &= 2x = 1.6 \times 10^{-6} \text{ M}
\end{align*}
\]

The molar solubility of Pb(IO\(_3\))\(_2\) is equal to the additional concentration of Pb\(^{2+}\) in solution, or \(7.9 \times 10^{-4}\) mol/L. As expected, Pb(IO\(_3\))\(_2\) is less soluble in the presence of a solution that already contains one of its ions. This is known as the **COMMON ION EFFECT**.

As outlined in the following example, if an approximation leads to an unacceptably large error we can extend the process of making and evaluating approximations.

**Example 6.10**

Calculate the solubility of Pb(IO\(_3\))\(_2\) in \(1.0 \times 10^{-4}\) M Pb(NO\(_3\))\(_2\).

**Solution**

Letting \(x\) equal the change in the concentration of Pb\(^{2+}\), the equilibrium concentrations of Pb\(^{2+}\) and IO\(_3^-\) are

\[
\begin{align*}
\text{[Pb}^{2+}\text{]} &= 1.0 \times 10^{-4} + x \\
\text{[IO}_3^-\text{]} &= 2x
\end{align*}
\]

Substituting these concentrations into equation 6.33 leaves us with

\[
(1.0 \times 10^{-4} + x)(2x)^2 = 2.5 \times 10^{-13}
\]

To solve this equation for \(x\), we make the following assumption

\[
\text{[Pb}^{2+}\text{]} = 1.0 \times 10^{-4} + x \approx 1.0 \times 10^{-4} \text{ M}
\]

obtaining a value for \(x\) of \(2.50 \times 10^{-4}\). Substituting back, gives the calculated concentration of Pb\(^{2+}\) at equilibrium as

\[
\text{[Pb}^{2+}\text{]} = 1.0 \times 10^{-4} + 2.50 \times 10^{-5} = 1.25 \times 10^{-4} \text{ M}
\]

a value that differs by 25% from our assumption that the equilibrium concentration is \(1.0 \times 10^{-4}\) M. This error seems unreasonably large. Rather than shouting in frustration, we make a new assumption. Our first assumption—that the concentration of Pb\(^{2+}\) is \(1.0 \times 10^{-4}\) M—was too small. The calculated concentration of \(1.25 \times 10^{-4}\) M, therefore, is probably a bit too large. For our second approximation, let’s assume that

\[
\text{[Pb}^{2+}\text{]} = 1.0 \times 10^{-4} + x \approx 1.25 \times 10^{-4}
\]

Substituting into equation 6.33 and solving for \(x\) gives its value as \(2.24 \times 10^{-5}\). The resulting concentration of Pb\(^{2+}\) is
\[
\text{[Pb}^{2+}\text{]} = 1.0 \times 10^{-4} + 2.24 \times 10^{-5} = 1.22 \times 10^{-4} \text{ M}
\]

which differs from our assumption of \(1.25 \times 10^{-4}\) M by 2.4%. Because the original concentration of \(\text{Pb}^{2+}\) is given to two significant figures, this is a more reasonable error. Our final solution, to two significant figures, is

\[
\text{[Pb}^{2+}\text{]} = 1.2 \times 10^{-4} \text{ M} \quad \text{[IO}_3^-\text{]} = 4.5 \times 10^{-5} \text{ M}
\]

and the molar solubility of \(\text{Pb(IO}_3\text{)}_2\) is \(2.2 \times 10^{-5}\) mol/L. This iterative approach to solving an equation is known as the **METHOD OF SUCCESSIVE APPROXIMATIONS**.

**Practice Exercise 6.8**

Calculate the molar solubility for \(\text{Hg}_2\text{Cl}_2\) in 0.10 M NaCl and compare your answer to its molar solubility in deionized water (see **Practice Exercise 6.7**).

Click **here** to review your answer to this exercise.

### 6G.3 A Systematic Approach to Solving Equilibrium Problems

Calculating the solubility of \(\text{Pb(IO}_3\text{)}_2\) in a solution of \(\text{Pb(NO}_3\text{)}_2\) is more complicated than calculating its solubility in deionized water. The calculation, however, is still relatively easy to organize, and the simplifying assumption fairly obvious. This problem is reasonably straightforward because it involves only one equilibrium reaction and one equilibrium constant.

Determining the equilibrium composition of a system with multiple equilibrium reactions is more complicated. In this section we introduce a systematic approach to setting-up and solving equilibrium problems. As shown in Table 6.1, this approach involves four steps.

#### Table 6.1 Systematic Approach to Solving Equilibrium Problems

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>Write all relevant equilibrium reactions and equilibrium constant expressions.</td>
</tr>
<tr>
<td>Step 2</td>
<td>Count the unique species appearing in the equilibrium constant expressions; these are your unknowns. You have enough information to solve the problem if the number of unknowns equals the number of equilibrium constant expressions. If not, add a mass balance equation and/or a charge balance equation. Continue adding equations until the number of equations equals the number of unknowns.</td>
</tr>
<tr>
<td>Step 3</td>
<td>Combine your equations and solve for one unknown. Whenever possible, simplify the algebra by making appropriate assumptions. If you make an assumption, set a limit for its error. This decision influences your evaluation of the assumption.</td>
</tr>
<tr>
<td>Step 4</td>
<td>Check your assumptions. If any assumption proves invalid, return to the previous step and continue solving. The problem is complete when you have an answer that does not violate any of your assumptions.</td>
</tr>
</tbody>
</table>
In addition to equilibrium constant expressions, two other equations are important to the systematic approach for solving equilibrium problems. The first of these is a **MASS BALANCE EQUATION**, which is simply a statement that matter is conserved during a chemical reaction. In a solution of a acetic acid, for example, the combined concentrations of the conjugate weak acid, $\text{CH}_3\text{COOH}$, and the conjugate weak base, $\text{CH}_3\text{COO}^-$, must equal acetic acid’s initial concentration, $C_{\text{CH}_3\text{COOH}}$:

\[
C_{\text{CH}_3\text{COOH}} = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]
\]

The second equation is a **CHARGE BALANCE EQUATION**, which requires that total charge from the cations equal the total charge from the anions. Mathematically, the charge balance equation is

\[
\sum_i [(z^+)_i] [C^{z+}_i] = \sum_j [(z^-)_j] [A^{z-}_j]
\]

where $[C^{z+}_i]$ and $[A^{z-}_j]$ are, respectively, the concentrations of the $i$th cation and the $j$th anion, and $|(z^+_i)|$ and $|(z^-_j)|$ are the absolute values of the $i$th cation’s charge and the $j$th anion’s charge. Every ion in solution, even if it does not appear in an equilibrium reaction, must appear in the charge balance equation. For example, the charge balance equation for an aqueous solution of $\text{Ca(NO}_3)_2$ is

\[
2 \times [\text{Ca}^{2+}] + [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{NO}_3^-]
\]

Note that we multiply the concentration of $\text{Ca}^{2+}$ by two, and that we include the concentrations of $\text{H}_3\text{O}^+$ and $\text{OH}^-$.

**Example 6.11**

Write mass balance equations and a charge balance equation for a 0.10 M solution of $\text{NaHCO}_3$.

**Solution**

It is easier to keep track of the species in solution if we write down the reactions controlling the solution’s composition. These reactions are the dissolution of a soluble salt

\[
\text{NaHCO}_3(s) \rightarrow \text{Na}^+(aq) + \text{HCO}_3^-(aq)
\]

and the acid–base dissociation reactions of $\text{HCO}_3^-$ and $\text{H}_2\text{O}$

\[
\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq)
\]

\[
\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{CO}_3(aq)
\]

\[
2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]
The mass balance equations are

\[
0.10 \, \text{M} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

\[
0.10 \, \text{M} = [\text{Na}^+]
\]

and the charge balance equation is

\[
[\text{Na}^+] + [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}]
\]

**Practice Exercise 6.9**

Write appropriate mass balance and charge balance equations for a solution containing 0.10 M KH$_2$PO$_4$ and 0.050 M Na$_2$HPO$_4$.

Click [here](#) to review your answer to this exercise.

### 6G.4 pH of a Monoprotic Weak Acid

To illustrate the systematic approach to solving equilibrium problems, let’s calculate the pH of 1.0 M HF. Two equilibrium reactions affect the pH. The first, and most obvious, is the acid dissociation reaction for HF

\[
\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{F}^- (aq)
\]

for which the equilibrium constant expression is

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4}
\]

6.35

The second equilibrium reaction is the dissociation of water, which is an obvious yet easily neglected reaction

\[
2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq)
\]

\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}
\]

6.36

Counting unknowns, we find four: [HF], [F$^-$], [H$_3$O$^+$], and [OH$^-$]. To solve this problem we need two additional equations. These equations are a mass balance equation on hydrofluoric acid

\[
C_{\text{HF}} = [\text{HF}] + [\text{F}^-]
\]

6.37

and a charge balance equation

\[
[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{F}^-]
\]

6.38

With four equations and four unknowns, we are ready to solve the problem. Before doing so, let’s simplify the algebra by making two assumptions.
Assumption One. Because HF is a weak acid, the solution must be acidic. For an acidic solution it is reasonable to assume that

$$[\text{H}_3\text{O}^+] \gg [\text{OH}^-]$$

which simplifies the charge balance equation to

$$[\text{H}_3\text{O}^+] = [\text{F}^-] \quad 6.39$$

Assumption Two. Because HF is a weak acid, very little dissociation occurs. Most of the HF remains in its conjugate weak acid form and it is reasonable to assume that

$$[\text{HF}] \gg [\text{F}^-]$$

which simplifies the mass balance equation to

$$C_{\text{HF}} = [\text{HF}] \quad 6.40$$

For this exercise let’s accept an assumption if it introduces an error of less than ±5%.

Substituting equation 6.39 and equation 6.40 into equation 6.35, and solving for the concentration of H$_3$O$^+$ gives us

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_3\text{O}^+]}{C_{\text{HF}}} = \frac{[\text{H}_3\text{O}^+]^2}{C_{\text{HF}}} = 6.8 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C_{\text{HF}}} = \sqrt{(6.8 \times 10^{-4})(1.0)} = 2.6 \times 10^{-2}$$

Before accepting this answer, we must verify our assumptions. The first assumption is that [OH$^-$] is significantly smaller than [H$_3$O$^+$]. Using equation 6.36, we find that

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{2.6 \times 10^{-2}} = 3.8 \times 10^{-13}$$

Clearly this assumption is acceptable. The second assumption is that [F$^-$] is significantly smaller than [HF]. From equation 6.39 we have

$$[\text{F}^-] = 2.6 \times 10^{-2} \text{ M}$$

Because [F$^-$] is 2.60% of $C_{\text{HF}}$, this assumption is also acceptable. Given that [H$_3$O$^+$] is 2.6 × 10$^{-2}$ M, the pH of 1.0 M HF is 1.59.

How does the calculation change if we limit an assumption’s error to less than ±1%? In this case we can no longer assume that [HF] >> [F$^-]$ and we cannot simplify the mass balance equation. Solving the mass balance equation for [HF]

$$[\text{HF}] = C_{\text{HF}} - [\text{F}^-] = C_{\text{HF}} - [\text{H}_3\text{O}^+]$$

and substituting into the $K_a$ expression along with equation 6.39 gives

Step 3: Combine your equations and solve for one unknown. Whenever possible, simplify the algebra by making appropriate assumptions. If you make an assumption, set a limit for its error. This decision influences your evaluation the assumption.

Step 4: Check your assumptions. If any assumption proves invalid, return to the previous step and continue solving. The problem is complete when you have an answer that does not violate any of your assumptions.
Chapter 6 Equilibrium Chemistry

\[ K_a = \frac{[H_3O^+]^2}{C_{HF} - [H_3O^+]} \]

Rearranging this equation leaves us with a quadratic equation

\[ [H_3O^+]^2 + K_a[H_3O^+] - K_a C_{HF} = 0 \]

which we solve using the quadratic formula

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

where \( a, b, \) and \( c \) are the coefficients in the quadratic equation

\[ ax^2 + bx + c = 0 \]

Solving a quadratic equation gives two roots, only one of which has chemical significance. For our problem, the equation's roots are

\[ x = \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 - (4)(1)(6.8 \times 10^{-4})}}{2}(1) \]

\[ x = \frac{-6.8 \times 10^{-4} \pm 5.22 \times 10^{-2}}{2} \]

\[ x = 2.57 \times 10^{-2} \text{ or } -2.63 \times 10^{-2} \]

Only the positive root is chemically significant because the negative root gives a negative concentration for \( H_3O^+ \). Thus, \([H_3O^+]\) is \( 2.6 \times 10^{-2} \) M and the pH is 1.59.

You can extend this approach to calculating the pH of a monoprotic weak base by replacing \( K_a \) with \( K_b \), replacing \( C_{HF} \) with the weak base's concentration, and solving for \([OH^-]\) in place of \([H_3O^+]\).

**Practice Exercise 6.10**

Calculate the pH of 0.050 M NH₃. State any assumptions you make in solving the problem, limiting the error for any assumption to ±5%. The \( K_b \) value for NH₃ is \( 1.75 \times 10^{-5} \).

Click here to review your answer to this exercise.

### 6G.5 pH of a Polyprotic Acid or Base

A more challenging problem is to find the pH of a solution containing a polyprotic weak acid or one of its conjugate species. As an example, consider the amino acid alanine, whose structure is shown in Figure 6.12. The ladder diagram in Figure 6.13 shows alanine's three acid–base forms and their respective areas of predominance. For simplicity, we identify these species as \( H_2L^+ \), HL, and \( L^- \).

![Figure 6.12](image_url) Structure of the amino acid alanine, which has \( pK_a \) values of 2.348 and 9.867.
**pH of 0.10 M Alanine Hydrochloride (H₂L⁺)**

Alanine hydrochloride is a salt of the diprotic weak acid H₂L⁺ and Cl⁻. Because H₂L⁺ has two acid dissociation reactions, a complete systematic solution to this problem is more complicated than that for a monoprotic weak acid. The ladder diagram in Figure 6.13 helps us simplify the problem. Because the areas of predominance for H₂L⁺ and L⁻ are so far apart, we can assume that a solution of H₂L⁺ is not likely to contain significant amounts of L⁻. As a result, we can treat H₂L⁺ as though it is a monoprotic weak acid. Calculating the pH of 0.10 M alanine hydrochloride, which is 1.72, is left to the reader as an exercise.

**pH of 0.10 M Sodium Alaninate (L⁻)**

The alaninate ion is a diprotic weak base. Because L⁻ has two base dissociation reactions, a complete systematic solution to this problem is more complicated than that for a monoprotic weak base. Once again, the ladder diagram in Figure 6.13 helps us simplify the problem. Because the areas of predominance for H₂L⁺ and L⁻ are so far apart, we can assume that a solution of L⁻ is not likely to contain significant amounts of H₂L⁺. As a result, we can treat L⁻ as though it is a monoprotic weak base. Calculating the pH of 0.10 M sodium alaninate, which is 11.42, is left to the reader as an exercise.

**pH of 0.1 M Alanine (HL)**

Finding the pH of a solution of alanine is more complicated than our previous two examples because we cannot ignore the presence of both H₂L⁺ and L⁻. To calculate the solution's pH we must consider alanine's acid dissociation reaction

\[
\text{HL}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + L^-(aq)
\]

and its base dissociation reaction

\[
\text{HL}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2L^+(aq)
\]

As always, we must also consider the dissociation of water

\[
2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)
\]

This leaves us with five unknowns—[H₂L⁺], [HL], [L⁻], [H₃O⁺], and [OH⁻]—for which we need five equations. These equations are \(K_{a2}\) and \(K_{b2}\) for alanine

\[
K_{a2} = \frac{[H_3O^+][L^-]}{[HL]}
\]
The $K_w$ equation

$$K_w = [H_3O^+][OH^-]$$

A mass balance equation for alanine

$$C_{HL} = [H_2L^+] + [HL] + [L^-]$$

And a charge balance equation

$$[H_2L^+] + [H_3O^+] = [OH^-] + [L^-]$$

Because HL is a weak acid and a weak base, it seems reasonable to assume that

$$[HL] >> [H_2L^+] + [L^-]$$

Which allows us to simplify the mass balance equation to

$$C_{HL} = [HL]$$

Next we solve $K_{b2}$ for $[H_2L^+]$

$$[H_2L^+] = \frac{K_w[HL]}{K_{a1}[OH^-]} = \frac{[H_3O^+][HL]}{K_{a1}} = \frac{C_{HL}[H_3O^+]}{K_{a1}}$$

And $K_{a2}$ for $[L^-]$

$$[L^-] = \frac{K_{a2}[HL]}{[H_3O^+]} = \frac{K_{a2}C_{HL}}{[H_3O^+]}

Substituting these equations for $[H_2L^+]$ and $[L^-]$, along with the equation for $K_w$, into the charge balance equation give us

$$\frac{C_{HL}[H_3O^+]}{K_{a1}} + [H_3O^+] = \frac{K_w}{[H_3O^+]} + \frac{K_{a2}C_{HL}}{[H_3O^+]}$$

Which we simplify to

$$[H_3O^+] \frac{C_{HL}}{K_{a1}} + 1 = \frac{1}{[H_3O^+]}(K_w + K_{a2}C_{HL})$$

$$[H_3O^+]^2 = \frac{K_{a2}C_{HL} + K_w}{C_{HL} + 1} = \frac{K_{a1}(K_{a2}C_{HL} + K_w)}{(C_{HL} + K_{a1})}$$
\[ [\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a1}K_{a2}C_{\text{HL}} + K_{a1}K_w}{C_{\text{HL}} + K_{a1}}} \]

We can further simplify this equation if \( K_{a1}K_w << K_{a1}K_{a2}C_{\text{HL}} \), and if \( K_{a1} << C_{\text{HL}} \), leaving us with

\[
[\text{H}_3\text{O}^+] = \sqrt{K_{a1}K_{a2}}
\]

For a solution of 0.10 M alanine the \([\text{H}_3\text{O}^+]\) is

\[
[\text{H}_3\text{O}^+] = \sqrt{(4.487 \times 10^{-3})(1.358 \times 10^{-10})} = 7.807 \times 10^{-7} \text{ M}
\]

or a pH of 6.11.

**Practice Exercise 6.11**

Verify that each assumption in our solution for the pH of 0.10 M alanine is reasonable, using ±5% as the limit for the acceptable error.

Click [here](#) to review your answer to this exercise.

### 6G.6 Effect of Complexation on Solubility

One method for increasing a precipitate’s solubility is to add a ligand that forms soluble complexes with one of the precipitate’s ions. For example, the solubility of AgI increases in the presence of NH\(_3\) due to the formation of the soluble Ag(NH\(_3\))\(_2^+\) complex. As a final illustration of the systematic approach to solving equilibrium problems, let’s calculate the molar solubility of AgI in 0.10 M NH\(_3\).

We begin by writing the relevant equilibrium reactions, which includes the solubility of AgI, the acid–base chemistry of NH\(_3\) and H\(_2\)O, and the metal-ligand complexation chemistry between Ag\(^+\) and NH\(_3\).

\[
\text{AgI}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{I}^{-}(aq)
\]

\[
\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^{-}(aq) + \text{NH}_4^+(aq)
\]

\[
2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^{-}(aq)
\]

\[
\text{Ag}^{+}(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)
\]

This leaves us with seven unknowns—[Ag\(^+\)], [I\(^-\)], [NH\(_3\)], [NH\(_4^+\)], [OH\(^-\)], [H\(_3\)O\(^+\)], and [Ag(NH\(_3\))\(_2^+\)]—and a need for seven equations. Four of the equations we need to solve this problem are the equilibrium constant expressions

\[
K_{sp} = [\text{Ag}^{+}][\text{I}^{-}] = 8.3 \times 10^{-17}
\]

6.41
\[ K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5} \quad 6.42 \]

\[ K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \quad 6.43 \]

\[ \beta_2 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7 \quad 6.44 \]

We still need three additional equations. The first of these equation is a mass balance for NH\textsubscript{3},

\[ C_{\text{NH}_3} = [NH_3] + [NH_4^+] + 2 \times [\text{Ag(NH}_3)_2^+] \quad 6.45 \]

In writing this mass balance equation we multiply the concentration of Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+} by two since there are two moles of NH\textsubscript{3} per mole of Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}. The second additional equation is a mass balance between iodide and silver. Because AgI is the only source of I\textsuperscript{-} and Ag\textsuperscript{+}, each iodide in solution must have an associated silver ion, which may be Ag\textsuperscript{+} or Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}; thus

\[ [I^-] = [Ag^+] + [Ag(NH_3)_2^+] \quad 6.46 \]

Finally, we include a charge balance equation.

\[ [Ag^+] + [Ag(NH_3)_2^+] + [NH_4^+] + [H_3O^+] = [OH^-] + [I^-] \quad 6.47 \]

Although the problem looks challenging, three assumptions greatly simplify the algebra.

**Assumption One.** Because the formation of the Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+} complex is so favorable (β\textsubscript{2} is 1.7 \times 10\textsuperscript{7}), there is very little free Ag\textsuperscript{+} and it is reasonable to assume that

\[ [Ag^+] << [Ag(NH_3)_2^+] \]

**Assumptions Two.** Because NH\textsubscript{3} is a weak base we may reasonably assume that most uncomplexed ammonia remains as NH\textsubscript{3}; thus

\[ [NH_4^+] << [NH_3] \]

**Assumption Three.** Because \( K_{sp} \) for AgI is significantly smaller than β\textsubscript{2} for Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}, the solubility of AgI is probably small enough that very little ammonia is needed for metal–ligand complexation; thus

\[ [Ag(NH_3)_2^+] << [NH_3] \]

As we use these assumptions to simplify the algebra, let’s set ±5% as the limit for error.

Assumption two and assumption three suggest that the concentration of NH\textsubscript{3} is much larger than the concentrations of either NH\textsubscript{4}\textsuperscript{+} or Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}, allowing us to simplify the mass balance equation for NH\textsubscript{3} to
Finally, using assumption one, which suggests that the concentration of Ag(NH$_3$)$_2^+$ is much larger than the concentration of Ag$^+$, we simplify the mass balance equation for $I^-$ to

$$[I^-] = [\text{Ag(NH}_3\text{)}_2^+]$$

6.49

Now we are ready to combine equations and solve the problem. We begin by solving equation 6.41 for [Ag$^+$] and substitute it into $\beta_2$ (equation 6.44), leaving us with

$$\beta_2 = \frac{[\text{Ag(NH}_3\text{)}_2^+][I^-]}{K_{sp}\text{[NH}_3\text{]}^2}$$

6.50

Next we substitute equation 6.48 and equation 6.49 into equation 6.50, obtaining

$$\beta_2 = \frac{[I^-]^2}{K_{sp}(C_{\text{NH}_3})^2}$$

6.51

Solving equation 6.51 for [I$-$] gives

$$[I^-] = C_{\text{NH}_3} \sqrt{\beta_2 K_{sp}} = (0.10)\sqrt{(1.7 \times 10^7)(8.3 \times 10^{-17})} = 3.76 \times 10^{-6} \text{ M}$$

Because one mole of AgI produces one mole of I$^-$, the molar solubility of AgI is the same as the [I$^-$], or $3.8 \times 10^{-6}$ mol/L.

Before accepting this answer we need to check our assumptions. Substituting [I$^-$] into equation 6.41, we find that the concentration of Ag$^+$ is

$$[\text{Ag}^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \times 10^{-17}}{3.76 \times 10^{-6}} = 2.2 \times 10^{-11} \text{ M}$$

Substituting the concentrations of I$^-$ and Ag$^+$ into the mass balance equation for iodide (equation 6.46), gives the concentration of Ag(NH$_3$)$_2^+$ as

$$[\text{Ag(NH}_3\text{)}_2^+] = [I^-] - [\text{Ag}^+] = 3.76 \times 10^{-6} - 2.2 \times 10^{-11} = 3.8 \times 10^{-6} \text{ M}$$

Our first assumption that [Ag$^+$] is significantly smaller than the [Ag(NH$_3$)$_2^+$] is reasonable.

Substituting the concentrations of Ag$^+$ and Ag(NH$_3$)$_2^+$ into equation 6.44 and solving for [NH$_3$], gives

$$[\text{NH}_3] = \sqrt{\frac{[\text{Ag(NH}_3\text{)}_2^+]}{[\text{Ag}^+]\beta_2}} = \sqrt{\frac{3.8 \times 10^{-6}}{(2.2 \times 10^{-11})(1.7 \times 10^7)}} = 0.10 \text{ M}$$

From the mass balance equation for NH$_3$ (equation 6.44) we see that [NH$_4^+$] is negligible, verifying our second assumption that [NH$_4^+$] is sig-
significantly smaller than \([\text{NH}_3]\). Our third assumption that \([\text{Ag(NH}_3)_2]^+\) is significantly smaller than \([\text{NH}_3]\) also is reasonable.

### 6H Buffer Solutions

Adding as little as 0.1 mL of concentrated HCl to a liter of \(\text{H}_2\text{O}\) shifts the pH from 7.0 to 3.0. Adding the same amount of HCl to a liter of a solution that is 0.1 M in acetic acid and 0.1 M in sodium acetate, however, results in a negligible change in pH. Why do these two solutions respond so differently to the addition of HCl?

A mixture of acetic acid and sodium acetate is one example of an acid–base buffer. To understand how this buffer works to limit the change in pH, we need to consider its acid dissociation reaction

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

and its corresponding acid dissociation constant

\[
K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5}
\]

Taking the negative log of the terms in equation 6.52 and solving for pH leaves us with the result shown here.

\[
pH = pK_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.76 + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad 6.53
\]

Buffering occurs because of the logarithmic relationship between pH and the ratio of the concentrations of acetate and acetic acid. Here is an example to illustrate this point. If the concentrations of acetic acid and acetate are equal, the buffer’s pH is 4.76. If we convert 10% of the acetate to acetic acid, by adding a strong acid, the ratio \([\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]\) changes from 1.00 to 0.818, and the pH decreases from 4.76 to 4.67—a decrease of only 0.09 pH units.

### 6H.1 Systematic Solution to Buffer Problems

Equation 6.53 is written in terms of the equilibrium concentrations of \(\text{CH}_3\text{COOH}\) and \(\text{CH}_3\text{COO}^-\). A more useful relationship relates a buffer’s pH to the initial concentrations of the weak acid and the weak base. We can derive a general buffer equation by considering the following reactions for a weak acid, HA, and the salt of its conjugate weak base, NaA.

\[
\text{NaA}(aq) \rightarrow \text{Na}^+(aq) + \text{A}^-(aq)
\]

\[
\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)
\]

\[
2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]
Because the concentrations of Na\(^+\), A\(^-\), HA, H\(_3\)O\(^+\), and OH\(^-\) are unknown, we need five equations to uniquely define the solution's composition. Two of these equations are the equilibrium constant expressions for HA and H\(_2\)O.

\[
K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad 6.54
\]

\[
K_w = [H_3O^+][OH^-]
\]

The remaining three equations are mass balance equations for HA and for Na\(^+\)

\[
C_{HA} + C_{NaA} = [HA] + [A^-] \quad 6.55
\]

\[
C_{NaA} = [Na^+] \quad 6.56
\]

and a charge balance equation

\[
[H_3O^+] + [Na^+] = [OH^-] + [A^-] \quad 6.57
\]

Substituting equation 6.56 into equation 6.57 and solving for [A\(^-\)] gives

\[
[A^-] = C_{NaA} - [OH^-] + [H_3O^+] \quad 6.58
\]

Next, we substitute equation 6.58 into equation 6.55, which gives the concentration of HA as

\[
[HA] = C_{HA} + [OH^-] - [H_3O^+] \quad 6.59
\]

Finally, substituting equations 6.58 and 6.59 into equation 6.54 and solving for pH gives a general equation for a buffer's pH.

\[
pH = pK_a + \log \frac{C_{NaA} - [OH^-] + [H_3O^+]}{C_{HA} + [OH^-] - [H_3O^+]} \quad 6.60
\]

If the initial concentrations of the weak acid, C\(_{HA}\), and the weak base, C\(_{NaA}\), are greater than [H\(_3\)O\(^+\)] and [OH\(^-\)], then we can simplify the general equation to the HENDERSON–HASSELBALCH EQUATION.

\[
pH = pK_a + \log \frac{C_{NaA}}{C_{HA}} \quad 6.60
\]

As outlined below, the Henderson–Hasselbalch equation provides a simple way to calculate the pH of a buffer, and to determine the change in pH upon adding a strong acid or strong base.
Example 6.12

Calculate the pH of a buffer that is 0.020 M in NH₃ and 0.030 M in NH₄Cl. What is the pH after adding 1.0 mL of 0.10 M NaOH to 0.10 L of this buffer?

Solution

The acid dissociation constant for NH₄⁺ is $5.70 \times 10^{-10}$, or a pKₐ of 9.24. Substituting the initial concentrations of NH₃ and NH₄Cl into equation 6.60 and solving, we find that the buffer’s pH is

$$\text{pH} = 9.24 + \log \frac{0.020}{0.030} = 9.06$$

Adding NaOH converts a portion of the NH₄⁺ to NH₃ as a result of the following reaction

$$\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3$$

Because this reaction’s equilibrium constant is so large (it is $5.7 \times 10^{4}$), we may treat the reaction as if it goes to completion. The new concentrations of NH₄⁺ and NH₃ are

$$C_{\text{NH}_4^+} = \frac{\text{mol NH}_4^+ - \text{mol OH}^-}{V_{\text{total}}} = \frac{(0.030 \text{ M})(0.10 \text{ L}) - (0.10 \text{ M})(1.0 \times 10^{-3} \text{ L})}{0.10 \text{ L} + 1.0 \times 10^{-3} \text{ L}} = 0.029 \text{ M}$$

$$C_{\text{NH}_3} = \frac{\text{mol NH}_3 + \text{mol OH}^-}{V_{\text{total}}} = \frac{(0.020 \text{ M})(0.10 \text{ L}) + (0.10 \text{ M})(1.0 \times 10^{-3} \text{ L})}{0.10 \text{ L} + 1.0 \times 10^{-3} \text{ L}} = 0.021 \text{ M}$$

Substituting these concentrations into the equation 6.60 gives a pH of

$$\text{pH} = 9.24 + \log \frac{0.021}{0.029} = 9.10$$

Practice Exercise 6.12

Calculate the pH of a buffer that is 0.10 M in KH₂PO₄ and 0.050 M in Na₂HPO₄. What is the pH after adding 5.0 mL of 0.20 M HCl to 0.10 L of this buffer. Use Appendix 1 to find the appropriate $K_a$ value.

Click here to review your answer to this exercise.
We can use a multiprotic weak acid to prepare buffers at as many different pH’s as there are acidic protons, with the Henderson–Hasselbalch equation applying in each case. For example, using malonic acid ($pK_a = 2.85$ and $pK_a = 5.70$) we can prepare buffers with pH values of

$$\text{pH} = 2.85 + \log \frac{C_{\text{HM}^-}}{C_{\text{H}_2\text{M}}}$$

$$\text{pH} = 5.70 + \log \frac{C_{\text{M}^{2-}}}{C_{\text{HM}^-}}$$

where $\text{H}_2\text{M}$, $\text{HM}^-$ and $\text{M}^{2-}$ are malonic acid’s different acid–base forms.

Although our treatment of buffers relies on acid–base chemistry, we can extend the use of buffers to equilibria involving complexation or redox reactions. For example, the Nernst equation for a solution containing $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ is similar in form to the Henderson–Hasselbalch equation.

$$E = E^{o}_{\text{Fe}^{2+/3+}} - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

A solution containing similar concentrations of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ is buffered to a potential near the standard state reduction potential for $\text{Fe}^{3+}$. We call such solutions redox buffers. Adding a strong oxidizing agent or a strong reducing agent to a redox buffer results in a small change in potential.

### 6H.2 Representing Buffer Solutions with Ladder Diagrams

A ladder diagram provides a simple graphical description of a solution’s predominate species as a function of solution conditions. It also provides a convenient way to show the range of solution conditions over which a buffer is effective. For example, an acid–base buffer exists when the concentrations of the weak acid and its conjugate weak base are similar. For convenience, let’s assume that an acid–base buffer exists when

$$\frac{1}{10} \leq \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \leq 10$$

Substituting these ratios into the Henderson–Hasselbalch equation

$$\text{pH} = pK_a + \log \frac{1}{10} = pK_a - 1$$

$$\text{pH} = pK_a + \log \frac{10}{1} = pK_a + 1$$

shows that an acid–base buffer works over a pH range of $pK_a \pm 1$.

Using the same approach, it is easy to show that a metal-ligand complexation buffer for $\text{ML}_n$ exists when
where $K_n$ or $\beta_n$ is the relevant stepwise or overall formation constant. For an oxidizing agent and its conjugate reducing agent, a redox buffer exists when

$$E = E^\circ \pm \frac{1}{n} \frac{RT}{F} = E^\circ \pm \frac{0.05916}{n} \text{ (at 25°C)}$$

Ladder diagrams showing buffer regions for several equilibria are shown in Figure 6.14.

### 6H.3 Preparing Buffers

**Buffer capacity** is the ability of a buffer to resist a change in pH when adding a strong acid or a strong base. A buffer’s capacity to resist a change in pH is a function of the concentrations of the weak acid and the weak base, as well as their relative proportions. The importance of the weak acid’s concentration and the weak base’s concentration is obvious. The more moles of weak acid and weak base a buffer has, the more strong base or strong acid it can neutralize without significantly changing its pH.

The relative proportions of a weak acid and a weak base also affects how much the pH changes when adding a strong acid or a strong base. Buffers that are equimolar in weak acid and weak base require a greater amount of strong acid or strong base to bring about a one unit change in pH. Consequently, a buffer is most effective against the addition of strong acids or strong bases when its pH is near the weak acid’s $pK_a$ value.

Although higher concentrations of buffering agents provide greater buffer capacity, there are reasons for using smaller concentrations, including the formation of unwanted precipitates and the tolerance of cells for high concentrations of dissolved salts.

A good “rule of thumb” when choosing a buffer is to select one whose reagents have a $pK_a$ value close to your desired pH.
Buffer solutions are often prepared using standard “recipes” found in the chemical literature. In addition, there are computer programs and online calculators to aid in preparing buffers. Perhaps the simplest way to make a buffer, however, is to prepare a solution containing an appropriate conjugate weak acid and weak base and measure its pH. You can then adjust the pH to the desired value by adding small portions of either a strong acid or a strong base.

### 6.1 Activity Effects

Careful measurements on the metal–ligand complex Fe(SCN)$^{2+}$ suggest that its stability decreases in the presence of inert ions. We can demonstrate this by adding an inert salt to an equilibrium mixture of Fe$^{3+}$ and SCN$^{-}$. Figure 6.15a shows the result of mixing together equal volumes of 1.0 mM FeCl$_3$ and 1.5 mM KSCN, both of which are colorless. The solution’s reddish–orange color is due to the formation of Fe(SCN)$^{2+}$.

$$\text{Fe}^{3+}(aq) + \text{SCN}^{-}(aq) \rightleftharpoons \text{Fe(SCN)}^{2+}(aq) \quad 6.61$$

Adding 10 g of KNO$_3$ to the solution and stirring to dissolve the solid, produces the result shown in Figure 6.15b. The solution's lighter color suggests that adding KNO$_3$ shifts reaction 6.61 to the left, decreasing the concentration of Fe(SCN)$^{2+}$ and increasing the concentrations of Fe$^{3+}$ and SCN$^{-}$. The result is a decrease in the complex's formation constant, $K_1$.

$$K_1 = \frac{[\text{Fe(SCN)}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} \quad 6.62$$

---

**Figure 6.15** The effect of a inert salt on a reaction's equilibrium position is shown by the solutions in these two beakers. The beaker on the left contains equal volumes of 1.0 mM FeCl$_3$ and 1.5 mM KSCN. The solution's color is due to the formation of the metal–ligand complex Fe(SCN)$^{2+}$. Adding 10 g of KNO$_3$ to the beaker on the left produces the result shown on the right. The lighter color suggests that there is less Fe(SCN)$^{2+}$ as a result of the equilibrium in reaction 6.61 shifting to the left.

---


Why should adding an inert electrolyte affect a reaction's equilibrium position? We can explain the effect of KNO$_3$ on the formation of Fe(SCN)$_{2+}$ by considering the reaction on a microscopic scale. The solution in Figure 6.15b contains a variety of cations and anions—Fe$^{3+}$, SCN$^-$, K$^+$, NO$_3^-$, H$_3$O$^+$, and OH$^-$. Although the solution is homogeneous, on average, there are slightly more anions in regions near Fe$^{3+}$ ions, and slightly more cations in regions near SCN$^-$ ions. As shown in Figure 6.16, each Fe$^{3+}$ ion and SCN$^-$ ion is surrounded by an ionic atmosphere of opposite charge ($\delta^-$ and $\delta^+$) that partially screen the ions from each other. Because each ion's apparent charge at the edge of its ionic atmosphere is less than its actual charge, the force of attraction between the two ions is smaller. As a result, the formation of the Fe(SCN)$_{2+}$ is slightly less favorable and the formation constant in equation 6.62 is slightly smaller. Higher concentrations of KNO$_3$ increase $\delta^-$ and $\delta^+$, resulting in even smaller values for the formation constant.

**Ionic Strength**

To factor the concentration of ions into the formation constant for Fe(SCN)$_{2+}$, we need a way to express that concentration in a meaningful way. Because both an ion's concentration and its charge are important, we define the solution's ionic strength, $\mu$ as

$$\mu = \frac{1}{2} \sum_i c_i z_i^2$$

where $c_i$ and $z_i$ are the concentration and charge of the $i$th ion.
Example 6.13

Calculate the ionic strength for a solution of 0.10 M NaCl. Repeat the calculation for a solution of 0.10 M Na$_2$SO$_4$.

**Solution**

The ionic strength for 0.10 M NaCl is

$$I = \frac{1}{2} \left\{ [\text{Na}^+] \times (+1)^2 + [\text{Cl}^-] \times (-1)^2 \right\}$$

$$= \frac{1}{2} \left\{ (0.10) \times (+1)^2 + (0.10) \times (-1)^2 \right\}$$

$$= 0.10 \text{ M}$$

For 0.10 M Na$_2$SO$_4$ the ionic strength is

$$I = \frac{1}{2} \left\{ [\text{Na}^+] \times (+1)^2 + [\text{SO}_4^{2-}] \times (-2)^2 \right\}$$

$$= \frac{1}{2} \left\{ (0.10) \times (+1)^2 + (0.20) \times (-2)^2 \right\}$$

$$= 0.30 \text{ M}$$

Note that the unit for ionic strength is molarity, but that a salt’s ionic strength need not match its molar concentration. For a 1:1 salt, such as NaCl, ionic strength and molar concentration are identical. The ionic strength of a 2:1 electrolyte, such as Na$_2$SO$_4$, is three times larger than the electrolyte’s molar concentration.

**Activity and Activity Coefficients**

Figure 6.15 shows that adding KNO$_3$ to a mixture of Fe$^{3+}$ and SCN$^-$ decreases the formation constant for Fe(SCN)$_2^+$. This creates a contradiction. Earlier in this chapter we showed that there is a relationship between a reaction’s standard-state free energy, $\Delta G^o$, and its equilibrium constant, $K$.

$$\Delta G^o = -RT \ln K$$

Because a reaction has only one standard-state, its equilibrium constant must be independent of solution conditions. Although ionic strength affects the apparent formation constant for Fe(SCN)$_2^+$, reaction 6.61 must have an underlying thermodynamic formation constant that is independent of ionic strength.

The apparent formation constant for Fe(SCN)$_2^+$, as shown in equation 6.62, is a function of concentrations. In place of concentrations, we define the true thermodynamic equilibrium constant using activities. The activity of species A, $a_A$, is the product of its concentration, [A], and a solution-dependent activity coefficient, $\gamma_A$. 

In calculating the ionic strengths of these solutions we are ignoring the presence of H$_3$O$^+$ and OH$^-$, and, in the case of Na$_2$SO$_4$, the presence of HSO$_4^-$ from the base dissociation reaction of SO$_4^{2-}$.

In the case of 0.10 M NaCl, the concentrations of H$_3$O$^+$ and OH$^-$ are 1.0 $\times$ 10$^{-7}$, which is significantly smaller than the concentrations of Na$^+$ and Cl$^-$. Because SO$_4^{2-}$ is a very weak base ($K_b = 1.0 \times 10^{-12}$), the solution is only slightly basic (pH = 7.5), and the concentrations of H$_3$O$^+$, OH$^-$, and HSO$_4^-$ are negligible.

Although we can ignore the presence of H$_3$O$^+$, OH$^-$, and HSO$_4^-$ when calculating the ionic strength of these two solutions, be aware that an equilibrium reaction may well generate ions that affect the solution’s ionic strength.
The true thermodynamic formation constant for Fe(SCN)$^{2+}$, therefore, is

$$K_1 = \frac{a_{\text{Fe(SCN)}^{2+}}}{a_{\text{Fe}^{3+}}a_{\text{SCN}^-}} = \frac{[\text{Fe(SCN)}^{2+}]\gamma_{\text{Fe(SCN)}^{2+}}}{[\text{Fe}^{3+}]\gamma_{\text{Fe}^{3+}}[\text{SCN}^-]\gamma_{\text{SCN}^-}}$$

The **activity coefficient** for a species corrects for any deviation between its physical concentration and its ideal value. For a gas, a pure solid, a pure liquid, or a non-ionic solute, the activity coefficient is approximately one under most reasonable experimental conditions. For reactions involving only these species, the difference between activity and concentration is negligible. The activity coefficient for an ion, however, depends on the solution's ionic strength, the ion's charge, and the ion's size. It is possible to calculate activity coefficients using the **extended debye-hückel equation**

$$\log \gamma_A = \frac{-0.51 \times z_A^2 \times \sqrt{\mu}}{1 + 3.3 \times \alpha_A \times \sqrt{\mu}}$$

where $z_A$ is the ion's charge, $\alpha_A$ is the effective diameter of the hydrated ion in nanometers (Table 6.2), $\mu$ is the solution's ionic strength, and 0.51 and 3.3 are constants appropriate for an aqueous solution at 25°C. An ion's effective hydrated radius is the radius of the ion plus those water molecules closely bound to the ion. The effective radius is greater for smaller, more highly charged ions than it is for larger, less highly charged ions.

### Table 6.2 Effective Diameters (a) for Selected Ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Effective Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$O$^+$</td>
<td>0.9</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.6</td>
</tr>
<tr>
<td>Na$^+$, IO$_3^-$, HSO$_3^-$, HCO$_3^-$, H$_2$PO$_4^-$</td>
<td>0.45</td>
</tr>
<tr>
<td>OH$^-$, F$^-$, SCN$^-$, HS$^-$, ClO$_3^-$, ClO$_4^-$, MnO$_4^-$</td>
<td>0.35</td>
</tr>
<tr>
<td>K$^+$, Cl$^-$, Br$^-$, I$^-$, CN$^-$, NO$_2^-$, NO$_3^-$</td>
<td>0.3</td>
</tr>
<tr>
<td>Cs$^+$, Tl$^+$, Ag$^+$, NH$_4^+$</td>
<td>0.25</td>
</tr>
<tr>
<td>Mg$^{2+}$, Be$^{2+}$</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Sn$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Co$^{2+}$</td>
<td>0.6</td>
</tr>
<tr>
<td>Sr$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, S$^{2-}$</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb$^{2+}$, CO$_3^{2-}$, SO$_3^{2-}$</td>
<td>0.45</td>
</tr>
<tr>
<td>Hg$_2^{2+}$, SO$_4^{2-}$, S$_2$O$_3^{2-}$, CrO$_4^{2-}$, HPO$_4^{2-}$</td>
<td>0.40</td>
</tr>
<tr>
<td>Al$^{3+}$, Fe$^{3+}$, Cr$^{3+}$</td>
<td>0.9</td>
</tr>
<tr>
<td>PO$_4^{3-}$, Fe(CN)$_6^{3-}$</td>
<td>0.4</td>
</tr>
<tr>
<td>Zr$^{4+}$, Ce$^{4+}$, Sn$^{4+}$</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe(CN)$_6^{4-}$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Several features of equation 6.63 deserve mention. First, as the ionic strength approaches zero an ion’s activity coefficient approaches a value of one. In a solution where \( \mu = 0 \), an ion’s activity and its concentration are identical. We can take advantage of this fact to determine a reaction’s thermodynamic equilibrium constant by measuring the apparent equilibrium constant for several increasingly smaller ionic strengths and extrapolating back to an ionic strength of zero. Second, an activity coefficient is smaller, and the effect of activity is more important, for an ion with a higher charge and a smaller effective radius. Finally, the extended Debye-Hückel equation provides a reasonable value for an ion’s activity coefficient when the ionic strength is less than 0.1. Modifications to equation 6.63 extend the calculation of activity coefficients to higher ionic strengths.⁶

**Including Activity Coefficients When Solving Equilibrium Problems**

Earlier in this chapter we calculated the solubility of Pb(IO₃)₂ in deionized water, obtaining a result of \( 4.0 \times 10^{-5} \) mol/L. Because the only significant source of ions is from the solubility reaction, the ionic strength is very low and we can assume that \( \gamma \approx 1 \) for both Pb²⁺ and IO₃⁻. In calculating the solubility of Pb(IO₃)₂ in deionized water, we do not need to account for ionic strength.

But what if the we need to know the solubility of Pb(IO₃)₂ in a solution containing other, inert ions? In this case we need to include activity coefficients in our calculation.

**Example 6.14**

Calculate the solubility of Pb(IO₃)₂ in a matrix of 0.020 M Mg(NO₃)₂.

**Solution**

We begin by calculating the solution’s ionic strength. Since Pb(IO₃)₂ is only sparingly soluble, we will assume that we can ignore its contribution to the ionic strength; thus

\[
[\text{ionic strength}] = \frac{1}{2} \left\{ (0.020 \text{ M})(+2)^{2} + (0.040 \text{ M})(-1)^{2} \right\} = 0.060 \text{ M}
\]

Next, we use equation 6.63 to calculate the activity coefficients for Pb²⁺ and IO₃⁻.

\[
\log \gamma_{\text{Pb}^{2+}} = \frac{-0.51 \times (+2)^{2} \times \sqrt{0.060}}{1 + 3.3 \times 0.45 \times \sqrt{0.060}} = -0.366
\]

\[
\gamma_{\text{Pb}^{2+}} = 0.431
\]

---

\[
\log \gamma_{\text{IO}_3^-} = \frac{-0.51 \times (-1)^2 \times \sqrt{0.060}}{1 + 3.3 \times 0.45 \times \sqrt{0.060}} = -0.0916
\]

\[\gamma_{\text{IO}_3^-} = 0.810\]

Defining the equilibrium concentrations of \(\text{Pb}^{2+}\) and \(\text{IO}_3^-\) in terms of the variable \(x\)

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>(\text{Pb} (\text{IO}_3)_2 (s))</th>
<th>(\text{Pb}^{2+} (aq))</th>
<th>(2\text{IO}_3^- (aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>solid</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>solid</td>
<td>(+x)</td>
<td>(+2x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>solid</td>
<td>(x)</td>
<td>(2x)</td>
</tr>
</tbody>
</table>

and substituting into the thermodynamic solubility product for \(\text{Pb} (\text{IO}_3)_2\) leaves us with

\[
K_{\varphi} = a_{\text{Pb}^{2+}} a_{\text{IO}_3^-}^2 = \gamma_{\text{Pb}^{2+}}^2 \gamma_{\text{IO}_3^-}^2 = 2.5 \times 10^{-13}
\]

\[
K_{\varphi} = (0.431)(0.810)^2(2x)^2 = 2.5 \times 10^{-13}
\]

\[
K_{\varphi} = 1.131x^3 = 2.5 \times 10^{-13}
\]

Solving for \(x\) gives \(6.0 \times 10^{-5}\), or a molar solubility of \(6.0 \times 10^{-5}\) mol/L. Ignoring activity, as we did in our earlier calculation, gives the molar solubility as \(4.0 \times 10^{-5}\) mol/L. Failing to account for activity in this case underestimates the molar solubility of \(\text{Pb} (\text{IO}_3)_2\) by 33%.

As this example shows, failing to correct for the effect of ionic strength can lead to a significant error in an equilibrium calculation. Nevertheless, it is not unusual to ignore activities and to assume that the equilibrium constant is expressed in terms of concentrations. There is a practical reason for this—in an analysis we rarely know the exact composition, much less the ionic strength of aqueous samples or of solid samples brought into solution. Equilibrium calculations are a useful guide when developing an analytical method; however, only by completing an analysis and evaluating the results can we judge whether our theory matches reality. In the end, our work in the laboratory is the most critical step in developing a reliable analytical method.

Practice Exercise 6.13

Calculate the molar solubility of \(\text{Hg}_2\text{Cl}_2\) in 0.10 M NaCl, taking into account the effect of ionic strength. Compare your answer to that from Practice Exercise 6.8 in which you ignored the effect of ionic strength.

Click here to review your answer to this exercise.

The solution's equilibrium composition is

- \([\text{Pb}^{2+}] = 6.0 \times 10^{-5}\) M
- \([\text{IO}_3^-] = 1.2 \times 10^{-4}\) M
- \([\text{Mg}^{2+}] = 0.020\) M
- \([\text{NO}_3^-] = 0.040\) M

Because the concentrations of \(\text{Pb}^{2+}\) and \(\text{IO}_3^-\) are much smaller than the concentrations of \(\text{Mg}^{2+}\) and \(\text{NO}_3^-\), our decision to ignore the contribution of \(\text{Pb}^{2+}\) and \(\text{IO}_3^-\) to the ionic strength is reasonable.

How do we handle the calculation if we cannot ignore the concentrations of \(\text{Pb}^{2+}\) and \(\text{IO}_3^-\)? One approach is to use the method of successive approximations. First, we recalculate the ionic strength using the concentrations of all ions, including \(\text{Pb}^{2+}\) and \(\text{IO}_3^-\). Next, we recalculate the activity coefficients for \(\text{Pb}^{2+}\) and \(\text{IO}_3^-\), and then recalculate the molar solubility. We continue this cycle until two successive calculations yield the same molar solubility within an acceptable margin of error.

This is a good place to revisit the meaning of pH. In Chapter 2 we defined pH as

\[
pH = -\log [\text{H}_3\text{O}^+]\]

Now we see that the correct definition is

\[
pH = -\log a_{\text{H}_3\text{O}^+} = -\log \gamma_{\text{H}_3\text{O}^+} [\text{H}_3\text{O}^+]\]

Failing to account for the effect of ionic strength can lead to a significant error in the reported concentration of \(\text{H}_3\text{O}^+\). For example, if the pH of a solution is 7.00 and the activity coefficient for \(\text{H}_3\text{O}^+\) is 0.90, then the concentration of \(\text{H}_3\text{O}^+\) is \(1.11 \times 10^{-7}\) M, not \(1.00 \times 10^{-7}\) M, an error of +11%. Fortunately, in developing and carrying out analytical methods, we are more interested in controlling pH than in calculating \([\text{H}_3\text{O}^+]\). As a result, the difference between the two definitions of pH is rarely a significant concern.
6J Using Excel and R to Solve Equilibrium Problems

In solving equilibrium problems we typically make one or more assumptions to simplify the algebra. These assumptions are important because they allow us to reduce the problem to an equation in \( x \) that we can solve by simply taking a square-root, a cube-root, or by using the quadratic equation. Without these assumptions, most equilibrium problems result in a cubic equation (or a higher-order equation) that is harder to solve. Both Excel and R are useful tools for solving such equations.

6J.1 Excel

Excel offers a useful tool—the Solver function—for finding a polynomial equation’s chemically significant root. In addition, it is easy to solve a system of simultaneous equations by constructing a spreadsheet that allows you to test and evaluate multiple solutions. Let’s work through two examples.

Example 1: Solubility of \( \text{Pb(IO}_3\text{)}_2 \) in 0.10 M \( \text{Pb(NO}_3\text{)}_2 \)

In our earlier treatment of this problem we arrived at the following cubic equation

\[
4x^3 + 0.40x^2 = 2.5 \times 10^{-13}
\]

where \( x \) is the equilibrium concentration of \( \text{Pb}^{2+} \). Although there are several approaches for solving cubic equations, none are computationally easy. One approach is to iterate in on the answer by finding two values of \( x \), one of which leads to a result larger than \( 2.5 \times 10^{-13} \) and one of which gives a result smaller than \( 2.5 \times 10^{-13} \). Having established boundaries for the value of \( x \), we then shift the upper limit and the lower limit until the precision of our answer is satisfactory. Without going into details, this is how Excel’s Solver function works.

To solve this problem, we first rewrite the cubic equation so that its right-side equals zero.

\[
4x^3 + 0.40x^2 - 2.5 \times 10^{-13} = 0
\]

Next, we set up the spreadsheet shown in Figure 6.17a, placing the formula for the cubic equation in cell B2, and entering our initial guess for \( x \) in

![Figure 6.17 Spreadsheet demonstrating the use of Excel’s Solver function to find the root of a cubic equation. The spreadsheet in (a) shows the cubic equation in cell B2 and the initial guess for the value of \( x \) in cell B1; Excel replaces the formula with its equivalent value. The spreadsheet in (b) shows the results of running Excel’s Solver function.](image-url)
cell B1. We expect $x$ to be small—because $\text{Pb(IO}_3\text{)}_2$ is not very soluble—so setting our initial guess to 0 seems reasonable. Finally, we access the Solver function by selecting **Solver...** from the **Tools** menu, which opens the **Solver Parameters** window.

To define the problem, place the cursor in the box for **Set Target Cell** and then click on cell B2. Select the **Value of:** radio button and enter 0 in the box. Place the cursor in the box for **By Changing Cells:** and click on cell B1. Together, these actions instruct the Solver function to change the value of $x$, which is in cell B1, until the cubic equation in cell B2 equals zero.

Before we actually solve the function, we need to consider whether there are any limitations for an acceptable result. For example, we know that $x$ cannot be smaller than 0 because a negative concentration is not possible. We also want to ensure that the solution’s precision is acceptable. Click on the button labeled **Options...** to open the **Solver Options** window. Checking the option for **Assume Non-Negative** forces the Solver to maintain a positive value for the contents of cell B1, meeting one of our criteria. Setting the precision takes a bit more thought. The Solver function uses the precision to decide when to stop its search, doing so when

$$\left| \frac{\text{expected value} - \text{calculated value}}{\text{calculated value}} \right| \times 100 \leq \text{precision (\%)}$$

where expected value is the target cell’s desired value (0 in this case), calculated value is the function’s current value (cell B1 in this case), and precision is the value we enter in the box for **Precision**. Because our initial guess of $x=0$ gives a calculated result of $2.5 \times 10^{-13}$, accepting the Solver’s default precision of $1 \times 10^{-6}$ stops the search after one cycle. To be safe, set the precision to $1 \times 10^{-18}$. Click **OK** and then **Solve**. When the Solver function finds a solution, the results appear in your spreadsheet (see **Figure 6.17b**). Click **OK** to keep the result, or **Cancel** to return to the original values. Note that the answer here agrees with our earlier result of $7.91 \times 10^{-7}$ M for the solubility of $\text{Pb(IO}_3\text{)}_2$.

**Example 2: pH of 1.0 M HF**

In developing our solution to this problem we began by identifying four unknowns and writing out the following four equations.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

$$C_{\text{HF}} = [\text{HF}] + [\text{F}^-]$$

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{F}^-]$$

Be sure to evaluate the reasonableness of Solver’s answer. If necessary, repeat the process using a smaller value for the precision.
From this point, we made two assumptions, simplifying the problem to one that was easy to solve.

\[ [\text{H}_3\text{O}^+] = \sqrt{K_a C_{\text{HF}}} = \sqrt{(6.8 \times 10^{-4})(1.0)} = 2.6 \times 10^{-2} \]

Although we did not note this at the time, without making assumptions the solution to our problem is a cubic equation

\[ [\text{H}_3\text{O}^+] + K_a [\text{H}_3\text{O}^+]^2 - (K_a C_{\text{HA}} + K_w) [\text{H}_3\text{O}^+] - K_a K_w = 0 \]

that we can solve using Excel’s Solver function. Of course, this assumes that we successfully complete the derivation!

Another option is to use Excel to solve the equations simultaneously by iterating in on values for [HF], [F\(^-\)], [H\(_3\)O\(^+\)], and [OH\(^-\)]. Figure 6.18 shows a spreadsheet for this purpose. The cells in the first row contain our initial guesses for the equilibrium pH. Using the ladder diagram in Figure 6.14, choosing pH values between 1 and 3 seems reasonable. You can add additional columns if you wish to include more pH values. The formulas in rows 2–5 use the definition of pH to calculate [H\(_3\)O\(^+\)], \(K_w\) to calculate [OH\(^-\)], the charge balance equation to calculate [F\(^-\)], and \(K_a\) to calculate [HF]. To evaluate the initial guesses, we use the mass balance expression for HF, rewriting it as

\[ [\text{HF}] + [\text{F}^-] - C_{\text{HF}} = [\text{HF}] + [\text{F}^-] - 1.0 = 0 \]

and entering it in the last row. This cell gives the calculation’s error.

Figure 6.18b shows the actual values for the spreadsheet in Figure 6.18a. The negative value in cells B6 and C6 means that the combined concentrations of HF and F\(^-\) are too small, and the positive value in cell D6 means that the combined concentrations are too large. The actual pH, therefore, must lie between 2.00 and 1.00. Using these pH values as new limits for the spreadsheet’s first row, we continue to narrow the range for the actual pH. Figure 6.18c shows a final set of guesses, with the actual pH falling between 1.59 and 1.58. Because the error for 1.59 is smaller than that for 1.58, we will accept a pH of 1.59 as the answer. Note that this is an agreement with our earlier result.

**Practice Exercise 6.14**

Using Excel, calculate the solubility of AgI in 0.10 M NH\(_3\) without making any assumptions. See our earlier treatment of this problem for the relevant equilibrium reactions and constants.

Click here to review your answer to this exercise.
## 6J.2 R

R has a simple command—`uniroot`—for finding the chemically significant root of a polynomial equation. In addition, it is easy to write a function to solve a set of simultaneous equations by iterating in on a solution. Let's work through two examples.

### Example 1: Solubility of Pb(IO₃)₂ in 0.10 M Pb(NO₃)₂

In our earlier treatment of this problem we arrived at the following cubic equation

\[ 4x^3 + 0.40x^2 = 2.5 \times 10^{-13} \]
where \( x \) is the equilibrium concentration of \( \text{Pb}^{2+} \). Although there are several approaches for solving cubic equations, none are computationally easy. One approach to solving the problem is to iterate in on the answer by finding two values of \( x \), one of which leads to a result larger than \( 2.5 \times 10^{-13} \) and one of which gives a result smaller than \( 2.5 \times 10^{-13} \). Having established boundaries for the value of \( x \), we then shift the upper limit and the lower limit until the precision of our answer is satisfactory. Without going into details, this is how the \textit{uniroot} command works.

The general form of the \textit{uniroot} command is

\[
\text{uniroot}(\text{function}, \text{lower}, \text{upper}, \text{tol})
\]

where \textit{function} is an object containing the equation whose root we are seeking, \textit{lower} and \textit{upper} and boundaries for the root, and \textit{tol} is the desired accuracy for the root. To create an object containing the equation, we must rewrite it so that its right-side equals zero.

\[
4x^3 + 0.40x^2 - 2.5 \times 10^{-13} = 0
\]

Next, we enter the following code, which defines our cubic equation as a function with the name \textit{eqn}.

\[
> \text{eqn} = \text{function}(x) \ 4 \times x^3 + 0.4 \times x^2 - 2.5 \times 10^{-13}
\]

Because our equation is a function, the \textit{uniroot} command can send a value of \( x \) to \textit{eqn} and receive back the equation’s corresponding value. Finally, we use the \textit{uniroot} command to find the root.

\[
> \text{uniroot(eqn, lower = 0, upper = 0.1, tol = 1 \times 10^{-18})}
\]

We expect \( x \) to be small—because \( \text{Pb}(\text{IO}_3)_2 \) is not very soluble—so setting the lower limit to 0 is a reasonable choice. The choice for the upper limit is less critical. To ensure that the solution has sufficient precision, the tolerance should be smaller than the expected root. Figure 6.19 shows the resulting output. The value \$\text{root} \ is the equation's root, which is in good agreement with our earlier result of \( 7.91 \times 10^{-7} \) for the molar solubility of \( \text{Pb}(\text{IO}_3)_2 \). The other results are the equation's value for the root, the number of iterations needed to find the root, and the root’s estimated precision.

**Example 2: pH of 1.0 M HF**

In developing our solution to this problem we began by identifying four unknowns and writing out the following four equations.

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4}
\]

\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}
\]

\[
C_{\text{HF}} = [\text{HF}] + [\text{F}^-]
\]
\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{F}^-] \]

From this point, we made two assumptions, simplifying the problem to one that was easy to solve.

\[ [\text{H}_3\text{O}^+] = \sqrt{K_a C_{\text{HF}}} = \sqrt{(6.8 \times 10^{-4})(1.0)} = 2.6 \times 10^{-2} \]

Although we did not note this at the time, without making assumptions the solution to our problem is a cubic equation

\[
[\text{H}_3\text{O}^+]^3 + K_a [\text{H}_3\text{O}^+]^2 \quad - (K_a C_{\text{HA}} + K_w)[\text{H}_3\text{O}^+] - K_w K_a \times 10^4 = 0
\]

that we can solve using the \texttt{uniroot} command. Of course, this assumes that we successfully complete the derivation!

Another option is to use write a function to solve simultaneously the four equations for the variables [HF], [F\textsuperscript{−}], [H\textsubscript{3}O\textsuperscript{+}], and [OH\textsuperscript{−}]. Here is the code for this function, which we will call \texttt{eval}.

\[
\begin{align*}
  &> \texttt{eval = function(pH)\{} \\
  &+ \quad \texttt{h3o = 10}^{-\texttt{pH}} \\
  &+ \quad \texttt{oh = 1e}^{-14/\texttt{h3o}} \\
  &+ \quad \texttt{hf = (h3o*f)/6.8e}^{-4} \\
  &+ \quad \texttt{error = hf + f} - 1 \\
  &+ \quad \texttt{output = data.frame(pH, error)} \\
  &+ \quad \texttt{print(output)} \\
  &+ \}\n\end{align*}
\]

Let’s examine more closely how this function works. The function accepts a guess for the pH and uses the definition of pH to calculate [H\textsubscript{3}O\textsuperscript{+}], \(K_w\) to calculate [OH\textsuperscript{−}], the charge balance equation to calculate [F\textsuperscript{−}], and \(K_a\) to calculate [HF]. The function then evaluates the solution using the mass balance expression for HF, rewriting it as

\[
[\text{HF}] + [\text{F}^-] - C_{\text{HF}} = [\text{HF}] + [\text{F}^-] - 1.0 = 0
\]

The function then gathers together the initial guess for the pH and the error and prints them as a table.

The beauty of this function is that the object we pass to it, \(\text{pH}\), can contain many values, allowing us to easily search for a solution. Because HF is an acid, we know that the solution must be acidic. This sets a lower limit of 7 for the pH. We also know that the pH of 1.0 M HF can be no larger than 1.0 M as this would be the upper limit if HF was a strong acid. For our first pass, let’s enter the following code

\[
\begin{align*}
  &> \texttt{pH = c(7, 6, 5, 4, 3, 2, 1)} \\
  &> \texttt{func(pH)}
\end{align*}
\]
which varies the pH within these limits. The result, which is shown in Figure 6.20a, indicates that the pH must be less than 2 and greater than 1 because it is in this interval that the error changes sign.

For our second pass, we explore pH values between 2.0 and 1.0 to further narrow down the problem's solution.

> pH = c(2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0)
> func(pH)

The result in Figure 6.20b show that the pH must be less than 1.6 and greater than 1.5. A third pass between these limits gives the result shown in Figure 6.20c, which is consistent with our earlier result of a pH 1.59.

**Practice Exercise 6.15**

Using R, calculate the solubility of AgI in 0.10 M NH₃ without making any assumptions. See our earlier treatment of this problem for the relevant equilibrium reactions and constants.

Click [here](#) to review your answer to this exercise.

### 6K Some Final Thoughts on Equilibrium Calculations

In this chapter we have developed several tools for evaluating the composition of a system at equilibrium. These tools differ in how accurately they allow us to answer questions involving equilibrium chemistry. They also differ in their ease of use. An important part of having several tools available to you is knowing when to use them. If you need to know whether a reaction is favorable, or to estimate the pH of a solution, then a ladder diagram will meet your needs. On the other hand, if you require a more
accurate estimate of a compound’s solubility, then a rigorous calculation that includes activity coefficients is necessary.

A critical part of solving an equilibrium problem is knowing what equilibrium reactions to include. The importance of including all relevant reactions is obvious, and at first glance this does not appear to be a significant problem—it is, however, a potential source of significant errors. The tables of equilibrium constants in this textbook, although extensive, are a small subset of all known equilibrium constants, making it easy to overlook an important equilibrium reaction. Commercial and freeware computational programs with extensive databases are available for equilibrium modeling. Two excellent freeware programs are Visual Minteq (Windows only) and ChemEQL (Windows, Mac, Linux, and Solaris). These programs also include the ability to account for ionic strength.

Finally, a consideration of equilibrium chemistry can only help us decide if a reaction is favorable. It does not, however, guarantee that the reaction occurs. How fast a reaction approaches its equilibrium position does not depend on the equilibrium constant. The rate of a chemical reaction is a kinetic, not a thermodynamic, phenomenon. We will consider kinetic effects and their application in analytical chemistry in Chapter 13.

### 6L Key Terms

- **acid**
- **activity coefficient**
- **base dissociation constant**
- **charge balance equation**
- **dissociation constant**
- **equilibrium**
- **formation constant**
- **Henderson–Hasselbalch equation**
- **Le Châtelier’s principle**
- **metal–ligand complex**
- **Nernst equation**
- **pH scale**
- **precipitate**
- **reduction**
- **steady state**
- **acid dissociation constant**
- **amphiprotic**
- **buffer**
- **buffer capacity**
- **common ion effect**
- **cumulative formation constant**
- **enhalpy**
- **entropy**
- **equilibrium constant**
- **Gibb’s free energy**
- **ionic strength**
- **half-reaction**
- **ladder diagram**
- **ligand**
- **method of successive approximations**
- **oxidation**
- **polyprotic**
- **redox reaction**
- **standard-state**
- **stepwise formation constant**
- **activity**
- **base**
- **buffer capacity**
- **cumulative formation constant**
- **entropy**
- **extended Debye-Hückel equation**
- **Gibb’s free energy**
- **half-reaction**
- **ladder diagram**
- **mass balance equation**
- **monoprotic**
- **oxidizing agent**
- **potential**
- **reducing agent**
- **standard potential**
- **solubility product**

As you review this chapter, try to define a key term in your own words. Check your answer by clicking on the key term, which will take you to the page where it was first introduced. Clicking on the key term there, will bring you back to this page so that you can continue with another key term.
6M Chapter Summary

Analytical chemistry is more than a collection of techniques; it is the application of chemistry to the analysis of samples. As we will see in later chapters, almost all analytical methods use chemical reactivity to accomplish one or more of the following: dissolve the sample, separate analytes from interferents, transform the analyte to a more useful form, or provide a signal. Equilibrium chemistry and thermodynamics provide us with a means for predicting which reactions are likely to be favorable.

The most important types of reactions are precipitation reactions, acid–base reactions, metal–ligand complexation reactions, and redox reactions. In a precipitation reaction two or more soluble species combine to produce an insoluble product called a precipitate, which we characterize using a solubility product.

An acid–base reaction occurs when an acid donates a proton to a base. The reaction’s equilibrium position is described using either an acid dissociation constant, $K_a$, or a base dissociation constant, $K_b$. The product of $K_a$ and $K_b$ for an acid and its conjugate base is the dissociation constant for water, $K_w$.

When a ligand donates one or more pairs of electron to a metal ion, the result is a metal–ligand complex. Two types of equilibrium constants are used to describe metal–ligand complexation—stepwise formation constants and overall formation constants. There are two stepwise formation constants for the metal–ligand complex $ML_2$, each describing the addition of one ligand; thus, $K_1$ represents the addition of the first ligand to $M$, and $K_2$ represents the addition of the second ligand to $ML$. Alternatively, we can use a cumulative, or overall formation constant, $\beta_2$, for the metal–ligand complex $ML_2$, in which both ligands are added to $M$.

In a redox reaction, one of the reactants undergoes oxidation and another reactant undergoes reduction. Instead of using an equilibrium constants to characterize a redox reactions, we use the potential, positive values of which indicate a favorable reaction. The Nernst equation relates this potential to the concentrations of reactants and products.

Le Châtelier’s principle provides a means for predicting how a system at equilibrium responds to a change in conditions. If we apply a stress to a system at equilibrium—by adding a reactant or product, by adding a reagent that reacts with one of the reactants or products, or by changing the volume—the system responds by moving in the direction that relieves the stress.

You should be able to describe a system at equilibrium both qualitatively and quantitatively. You can develop a rigorous solution to an equilibrium problem by combining equilibrium constant expressions with appropriate mass balance and charge balance equations. Using this systematic approach, you can solve some quite complicated equilibrium problems. If a less rigor-
ous answer is acceptable, then a ladder diagram may help you estimate the equilibrium system's composition.

Solutions containing relatively similar amounts of a weak acid and its conjugate base experience only a small change in pH upon adding a small amount of a strong acid or a strong base. We call these solutions buffers. A buffer can also be formed using a metal and its metal–ligand complex, or an oxidizing agent and its conjugate reducing agent. Both the systematic approach to solving equilibrium problems and ladder diagrams are useful tools for characterizing buffers.

A quantitative solution to an equilibrium problem may give an answer that does not agree with experimental results if we do not consider the effect of ionic strength. The true, thermodynamic equilibrium constant is a function of activities, $a$, not concentrations. A species' activity is related to its molar concentration by an activity coefficient, $\gamma$. Activity coefficients can be calculated using the extended Debye–Hückel equation, making possible a more rigorous treatment of equilibria.

6N Problems

1. Write equilibrium constant expressions for the following reactions. What is the value for each reaction's equilibrium constant?
   a. $\text{NH}_3(aq) + \text{HCl}(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{Cl}^-(aq)$
   b. $\text{PbI}_2(s) + S^{2-}(aq) \rightleftharpoons \text{PbS}(s) + 2\Gamma(aq)$
   c. $\text{Cd}($EDTA$)^2-(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Cd}($CN$)^2-(aq) + $EDTA$^4-(aq)$
   d. $\text{AgCl}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}($NH$_3$)$_2^+(aq) + \text{Cl}^-(aq)$
   e. $\text{BaCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)$

2. Using a ladder diagram, explain why the first reaction is favorable and the second reaction is unfavorable.
   $$\text{H}_3\text{PO}_4(aq) + \text{F}^-(aq) \rightleftharpoons \text{HF}(aq) + \text{H}_2\text{PO}_4^-(aq)$$
   $$\text{H}_3\text{PO}_4(aq) + 2\text{F}^-(aq) \rightleftharpoons 2\text{HF}(aq) + \text{HPO}_4^{2-}(aq)$$

   Determine the equilibrium constant for these reactions and verify that they are consistent with your ladder diagram.

3. Calculate the potential for the following redox reaction for a solution in which $[\text{Fe}^{3+}] = 0.050$ M, $[\text{Fe}^{2+}] = 0.030$ M, $[\text{Sn}^{2+}] = 0.015$ M and $[\text{Sn}^{4+}] = 0.020$ M.
   $$2\text{Fe}^{3+}(aq) + \text{Sn}^{2+}(aq) \rightleftharpoons \text{Sn}^{4+}(aq) + 2\text{Fe}^{2+}(aq)$$

Most of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants.

Appendix 10: Solubility Products
Appendix 11: Acid Dissociation Constants
Appendix 12: Metal-Ligand Formation Constants
Appendix 13: Standard State Reduction Potentials
4. Calculate the standard state potential and the equilibrium constant for each of the following redox reactions. Assume that \([H_3O^+]\) is 1.0 M for acidic solutions, and that \([OH^-]\) is 1.0 M for basic solutions.
   
   a. \(\text{MnO}_4^- (aq) + H_2SO_4 (aq) \rightleftharpoons \text{Mn}^{2+} (aq) + \text{SO}_4^{2-} (aq)\) \hspace{1cm} \text{acidic solution}
   
   b. \(\text{IO}_3^- (aq) + I^- (aq) \rightleftharpoons I_2 (s)\) \hspace{1cm} \text{acidic solution}
   
   c. \(\text{ClO}^- (aq) + I^- (aq) \rightleftharpoons \text{IO}_3^- (aq) + \text{Cl}^- (aq)\) \hspace{1cm} \text{basic solution}

5. One analytical method for determining the concentration of sulfur is to oxidize it to \(\text{SO}_4^{2-}\) and then precipitate it as \(\text{BaSO}_4\) by adding \(\text{BaCl}_2\). The mass of the resulting precipitate is proportional to the amount of sulfur in the original sample. The accuracy of this method depends on the solubility of \(\text{BaSO}_4\), the reaction for which is shown here.

   \[
   \text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)
   \]

   How do the following affect the solubility of \(\text{BaSO}_4\) and, therefore, the accuracy of the analytical method?
   
   a. decreasing the solution's pH
   b. adding more \(\text{BaCl}_2\)
   c. increasing the volume of the solution by adding \(\text{H}_2\text{O}\)

6. Write a charge balance equation and mass balance equations for the following solutions. Some solutions may have more than one mass balance equation.

   a. 0.10 M NaCl
   b. 0.10 M HCl
   c. 0.10 M HF
   d. 0.10 M NaH\(_2\)PO\(_4\)
   e. MgCO\(_3\) (saturated solution)
   f. 0.10 M Ag(CN)\(_2^-\)
   g. 0.10 M HCl and 0.050 M NaNO\(_2\)

7. Using the systematic approach to equilibrium problems, calculate the pH of the following solutions. Be sure to state and justify any assumptions you make in solving the problems.

   a. 0.050 M HClO\(_4\)
   b. \(1.00 \times 10^{-7}\) M HCl
   c. 0.025 M HClO
   d. 0.010 M HCOOH
   e. 0.050 M Ba(OH)\(_2\)
   f. 0.010 M C\(_5\)H\(_3\)N
8. Construct ladder diagrams for the following diprotic weak acids (H$_2$L) and estimate the pH of 0.10 M solutions of H$_2$L, HL$^-$ and L$^{2-}$:
   a. maleic acid
   b. malonic acid
   c. succinic acid

9. Using the systematic approach to solving equilibrium problems, calculate the pH of the diprotic weak acid in problem 8. Be sure to state and justify any assumptions you make in solving the problems.

10. Ignoring activity effects, calculate the concentration of Hg$_2^{2+}$ in the following solutions. Be sure to state and justify any assumption you make in solving the problems.
   a. a saturated solution of Hg$_2$Br$_2$
   b. 0.025 M Hg$_2$(NO$_3$)$_2$ saturated with Hg$_2$Br$_2$
   c. 0.050 M NaBr saturated with Hg$_2$Br$_2$

11. The solubility of CaF$_2$ is controlled by the following two reactions
   \[ \text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq) \]
   \[ \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \]
   Calculate the solubility of CaF$_2$ in a solution buffered to a pH of 7.00. Use a ladder diagram to help simplify the calculations. How would your approach to this problem change if the pH is buffered to 2.00? What is the solubility of CaF$_2$ at this pH? Be sure to state and justify any assumptions you make in solving the problems.

12. Calculate the solubility of Mg(OH)$_2$ in a solution buffered to a pH of 7.00. How does this compare to its solubility in unbuffered deionized water? Be sure to state and justify any assumptions you make in solving the problem.

13. Calculate the solubility of Ag$_3$PO$_4$ in a solution buffered to a pH of 7.00. Be sure to state and justify any assumptions you make in solving the problem.

14. Determine the equilibrium composition of saturated solution of AgCl. Assume that the solubility of AgCl is influenced by the following reactions.
   \[ \text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \]
   \[ \text{Ag}^+(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{AgCl}(aq) \]
   \[ \text{AgCl}(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{AgCl}_2^-(aq) \]
   Be sure to state and justify any assumptions you make in solving the problem.

Most of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants:

- Appendix 10: Solubility Products
- Appendix 11: Acid Dissociation Constants
- Appendix 12: Metal-Ligand Formation Constants
- Appendix 13: Standard State Reduction Potentials
15. Calculate the ionic strength of the following solutions
   a. 0.050 M NaCl
   b. 0.025 M CuCl₂
   c. 0.10 M Na₂SO₄

16. Repeat the calculations in problem 10, this time correcting for the effect of ionic strength. Be sure to state and justify any assumptions you make in solving the problems.

17. Over what pH range do you expect Ca₃(PO₄)₂ to have its minimum solubility?

18. Construct ladder diagrams for the following systems, each consisting of two or three equilibria. Using your ladder diagrams, what reactions are likely to occur in each system?
   a. HF and H₃PO₄
   b. Ag(CN)₂⁻, Ni(CN)₄²⁻ and Fe(CN)₆³⁻
   c. Cr₂O₇²⁻/Cr³⁺ and Fe³⁺/Fe²⁺

19. Calculate the pH of the following acid–base buffers. Be sure to state and justify any assumptions you make in solving the problems.
   a. 100 mL of 0.025 M formic acid and 0.015 M sodium formate
   b. 50.00 mL of 0.12 M NH₃ and 5.30 mL of 1.0 M HCl
   c. 5.00 g of Na₂CO₃ and 5.00 g of NaHCO₃ diluted to 100 mL

20. Calculate the pH of the buffers in problem 19 after adding 5.0 mL of 0.10 M HCl. Be sure to state and justify any assumptions you make in solving the problems.

21. Calculate the pH of the buffers in problem 19 after adding 5.0 mL of 0.10 M NaOH. Be sure to state and justify any assumptions you make in solving the problems.

22. Consider the following hypothetical complexation reaction between a metal, M, and a ligand, L
   \[ \text{M}(aq) + \text{L}(aq) \rightleftharpoons \text{ML}(aq) \]
   with a formation constant of \(1.5 \times 10^8\). Derive an equation, similar to the Henderson–Hasselbalch equation, relating pM to the concentrations of L and ML. What is the pM for a solution containing 0.010 mol of M and 0.020 mol of L? What is pM be if you add 0.002 mol of M to this solution? Be sure to state and justify any assumptions you make in solving the problem.

23. A redox buffer contains an oxidizing agent and its conjugate reducing agent. Calculate the potential of a solution containing 0.010 mol of Fe³⁺ and 0.015 mol of Fe²⁺. What is the potential if you add sufficient...
oxidizing agent to convert 0.002 mol of Fe$^{2+}$ to Fe$^{3+}$? Be sure to state and justify any assumptions you make in solving the problem.

24. Use either Excel or R to solve the following problems. For these problems, make no simplifying assumptions.
   a. the solubility of CaF$_2$ in deionized water
   b. the solubility of AgCl in deionized water (see Problem 14 for the relevant equilibria)
   c. the pH of 0.10 M fumaric acid

25. Beginning with the relevant equilibrium reactions, derive equation 6.64 for the rigorous solution to the pH of 0.1 M HF.

60 Solutions to Practice Exercises

Practice Exercise 6.1

The overall reaction is equivalent to

\[ \text{Rxn 4} - 2 \times \text{Rxn 1} \]

Subtracting a reaction is equivalent to adding the reverse reaction; thus, the overall equilibrium constant is

\[ K = \frac{K_4}{(K_1)^2} = \frac{5.0}{(0.40)^2} = 31.25 \approx 31 \]

Click here to return to the chapter.

Practice Exercise 6.2

The $K_b$ for hydrogen oxalate is

\[ K_{b,\text{HC}_2\text{O}_4^-} = \frac{K_w}{K_{a,\text{HC}_2\text{O}_4^-}} = \frac{1.00 \times 10^{-14}}{5.60 \times 10^{-2}} = 1.79 \times 10^{-13} \]

and the $K_b$ for oxalate is

\[ K_{b,\text{C}_2\text{O}_4^2-} = \frac{K_w}{K_{a,\text{C}_2\text{O}_4^2-}} = \frac{1.00 \times 10^{-14}}{5.42 \times 10^{-5}} = 1.85 \times 10^{-10} \]

As we expect, the $K_b$ value for C$_2$O$_4^{2-}$ is larger than that for HC$_2$O$_4^-$.  

Click here to return to the chapter.

Practice Exercise 6.3

We can write the reaction as a sum of three other reactions. The first reaction is the solubility of AgCl(s), which we characterize by its $K_{sp}$.  

Most of the problems that follow require one or more equilibrium constants or standard state potentials. For your convenience, here are hyperlinks to the appendices containing these constants:
AgBr(s) ⇌ Ag⁺(aq) + Br⁻(aq)

The remaining two reactions are the stepwise formation of Ag(S₂O₃)₂³⁻, which we characterize by $K_1$ and $K_2$.

\[
\begin{align*}
\text{Ag}^+(aq) + S_2O_3^{2-}(aq) & \rightleftharpoons \text{Ag}(S_2O_3)^-(aq) \\
\text{Ag}(S_2O_3)^-(aq) + S_2O_3^{2-}(aq) & \rightleftharpoons \text{Ag}(S_2O_3)_2^{3-}(aq)
\end{align*}
\]

Using values for $K_{sp}$, $K_1$, and $K_2$ from Appendix 10 and Appendix 11, we find that the equilibrium constant for our reaction is

\[
K = K_{sp} \times K_1 \times K_2 = (5.0 \times 10^{-13})(6.6 \times 10^8)(7.1 \times 10^4) = 23
\]

Practice Exercise 6.4

The two half-reactions are the oxidation of Fe²⁺ and the reduction of MnO₄⁻.

\[
\begin{align*}
\text{Fe}^{2+}(aq) & \rightleftharpoons \text{Fe}^{3+}(aq) + e^- \\
\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- & \rightleftharpoons \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)
\end{align*}
\]

From Appendix 13, the standard state reduction potentials for these half-reactions are

\[
E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \text{ V} \quad E^{\circ}_{\text{MnO}_4^{-}/\text{Mn}^{2+}} = 1.51 \text{ V}
\]

(a) The standard state potential for the reaction is

\[
E^{\circ} = E^{\circ}_{\text{MnO}_4^{-}/\text{Mn}^{2+}} - E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 1.51 \text{ V} - 0.771 \text{ V} = 0.74 \text{ V}
\]

(b) To calculate the equilibrium constant we substitute appropriate values into equation 6.25.

\[
E^{\circ} = 0.74 \text{ V} = \frac{0.05916}{5} \log K
\]

Solving for $K$ gives its value as

\[
\log K = 62.5 \quad K = 3.2 \times 10^{62}
\]

(c) To calculate the potential under these non-standard state conditions, we make appropriate substitutions into the Nernst equation.

\[
E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[H^+]^8}
\]
Chapter 6 Equilibrium Chemistry

\[ E = 0.74 - \frac{0.05916}{5} \log \left( \frac{(0.015)(0.10)^{5}}{(0.025)(0.50)^{5}(1 \times 10^{-7})^{8}} \right) \]

\[ E = 0.74 - \frac{0.05916}{5} \log \left( \frac{(0.015)(0.10)^{5}}{(0.025)(0.50)^{5}(1 \times 10^{-7})^{8}} \right) = 0.12 \text{ V} \]

Click here to return to the chapter.

**Practice Exercise 6.5**

From Appendix 11, the \( pK_a \) values for \( \text{H}_2\text{CO}_3 \) are 6.352 and 10.329. The ladder diagram for \( \text{H}_2\text{CO}_3 \) is shown to the side. The predominante form at a pH of 7.00 is \( \text{HCO}_3^- \).

Click here to return to the chapter.

**Practice Exercise 6.6**

The ladder diagram in Figure 6.5 indicates that the reaction between acetic acid and \( p \)-nitrophenolate is favorable. Because \( p \)-nitrophenolate is in excess, we assume that the reaction of acetic acid to acetate is complete. At equilibrium essentially no acetic acid remains and there are 0.040 moles of acetate. Converting acetic acid to acetate consumes 0.040 moles of \( p \)-nitrophenolate; thus

\[
\text{moles } p\text{-nitrophenolate} = 0.090 - 0.040 = 0.050 \text{ mol}
\]

\[
\text{moles } p\text{-nitrophenol} = 0.040 \text{ mol}
\]

According to the ladder diagram for this system, the pH is 7.15 when there are equal concentrations of \( p \)-nitrophenol and \( p \)-nitrophenolate. Because we have slightly more \( p \)-nitrophenolate than we have \( p \)-nitrophenol, the pH is slightly greater than 7.15.

Click here to return to the chapter.

**Practice Exercise 6.7**

As \( \text{Hg}_2\text{Cl}_2 \) dissolves, two \( \text{Cl}^- \) are produced for each ion of \( \text{Hg}_2^{2+} \). If we assume that \( x \) is the change in the molar concentration of \( \text{Hg}_2^{2+} \), then the change in the molar concentration of \( \text{Cl}^- \) is 2\( x \). The following table helps us keep track of our solution to this problem.

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>( \text{Hg}_2\text{Cl}_2(s) )</th>
<th>( \text{Hg}_2^{2+} \text{ (aq)} )</th>
<th>2( \text{Cl}^- \text{ (aq)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>solid</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>solid</td>
<td>+( x )</td>
<td>+2( x )</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>solid</td>
<td>( x )</td>
<td>2( x )</td>
</tr>
</tbody>
</table>

Substituting the equilibrium concentrations into the \( K_{sp} \) expression for \( \text{Hg}_2\text{Cl}_2 \) gives
$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (x)(2x)^2 = 4x^3 = 1.2 \times 10^{-18}$$

$$x = 6.69 \times 10^{-7}$$

Substituting $x$ back into the equilibrium expressions for $\text{Hg}_2^{2+}$ and $\text{Cl}^-$ gives their concentrations as

$$[\text{Hg}_2^{2+}] = x = 6.7 \times 10^{-7} \text{ M} \quad [\text{Cl}^-] = 2x = 1.3 \times 10^{-6} \text{ M}$$

The molar solubility is equal to $[\text{Hg}_2^{2+}]$, or $6.7 \times 10^{-7} \text{ mol/L}$.

**Practice Exercise 6.8**

We begin by setting up a table to help us keep track of the concentrations of $\text{Hg}_2^{2+}$ and $\text{Cl}^-$ as this system moves toward and reaches equilibrium.

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>$\text{Hg}_2\text{Cl}_2(s)$</th>
<th>$\Leftrightarrow$</th>
<th>$\text{Hg}_2^{2+}(aq)$</th>
<th>$+2\text{Cl}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>solid</td>
<td>0</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>solid</td>
<td>$+x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>solid</td>
<td>$x$</td>
<td>$0.10 + 2x$</td>
<td></td>
</tr>
</tbody>
</table>

Substituting the equilibrium concentrations into the $K_{sp}$ expression for $\text{Hg}_2\text{Cl}_2$ leaves us with a difficult to solve cubic equation.

$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (x)(0.10)^2 = 4x^3 + 0.40x^2 + 0.10x$$

Let’s make an assumption to simplify this problem. Because we expect the value of $x$ to be small, let’s assume that

$$[\text{Cl}^-] = 0.10 + x \approx 0.10 \text{ M}$$

This simplifies our problems to

$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (x)(0.10)^2 = 0.010x = 1.2 \times 10^{-18}$$

which gives the value of $x$ as

$$x = 1.2 \times 10^{-16} \text{ M}$$

The difference between the actual concentration of $\text{Cl}^-$, which is $(0.10 + x)$ M, and our assumption that it is 0.10 M introduces an error of $1.2 \times 10^{-14}\%$. This is a negligible error. The molar solubility of $\text{Hg}_2\text{Cl}_2$ is the same as the concentration of $\text{Hg}_2^{2+}$, or $1.2 \times 10^{-16} \text{ M}$. As expected, the molar solubility in 0.10 M NaCl is less than $6.7 \times 10^{-7} \text{ mol/L}$, which is its solubility in water (see solution to Practice Exercise 6.7).

Click here to return to the chapter.
Practice Exercise 6.9

To help us in determining what ions are in solution, let’s write down all the reaction leading to the preparation of the solutions and the equilibria within the solutions. These reactions are the dissolution of two soluble salts

\[ \text{KH}_2\text{PO}_4(s) \rightarrow K^+(aq) + \text{H}_2\text{PO}_4^-(aq) \]

\[ \text{Na}_2\text{HPO}_4(s) \rightarrow 2\text{Na}^+(aq) + \text{HPO}_4^{2-}(aq) \]

and the acid–base dissociation reactions for \( \text{H}_2\text{PO}_4^- \), \( \text{HPO}_4^{2-} \), and \( \text{H}_2\text{O} \).

\[ \text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq) \]

\[ \text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_3\text{PO}_4(aq) \]

\[ \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{PO}_4^{3-}(aq) \]

\[ 2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

Note that we did not include the base dissociation reaction for \( \text{HPO}_4^{2-} \) because we already have accounted for its product, \( \text{H}_2\text{PO}_4^- \), in another reaction. The mass balance equations for \( K^+ \) and \( \text{Na}^+ \) are straightforward

\[ [K^+] = 0.10 \text{ M} \quad [\text{Na}^+] = 0.10 \text{ M} \]

but the mass balance equation for the phosphate takes a little bit of thought. Both \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) produce the same ions in solution. We can, therefore, imagine that the solution initially contains 0.15 M \( \text{KH}_2\text{PO}_4 \), which gives the following mass balance equation.

\[ 0.15 \text{ M} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \]

The charge balance equation is

\[ [\text{H}_3\text{O}^+] + [K^+] + [\text{Na}^+] = [H_2PO_4^-] + 2 \times [HPO_4^{2-}] + 3 \times [PO_4^{3-}] + [OH^-] \]

Click here to return to the chapter.

Practice Exercise 6.10

In determining the pH of 0.050 M \( \text{NH}_3 \), we need to consider two equilibrium reactions—the base dissociation reaction for \( \text{NH}_3 \)

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{NH}_4^+(aq) \]

and water’s dissociation reaction.

\[ 2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]
These two reactions contain four species whose concentrations we need to consider: \( \text{NH}_3 \), \( \text{NH}_4^+ \), \( \text{H}_3\text{O}^+ \), and \( \text{OH}^- \). We need four equations to solve the problem—these equations are the \( K_b \) equation for \( \text{NH}_3 \)

\[
K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = 1.75 \times 10^{-5}
\]

the \( K_w \) equation for \( \text{H}_2\text{O} \)

\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}
\]
a mass balance on ammonia

\[
C_{\text{NH}_3} = 0.050 \ \text{M} = [\text{NH}_3] + [\text{NH}_4^+]
\]

and a charge balance equation

\[
[\text{H}_3\text{O}^+] + [\text{NH}_4^+] = [\text{OH}^-]
\]

To solve this problem, we will make two assumptions. Because \( \text{NH}_3 \) is a base, our first assumption is

\[
[\text{OH}^-] >> [\text{H}_3\text{O}^+]
\]

which simplifies the charge balance equation to

\[
[\text{NH}_4^+] = [\text{OH}^-]
\]

Because \( \text{NH}_3 \) is a weak base, our second assumption is

\[
[\text{NH}_3] >> [\text{NH}_4^+]
\]

which simplifies the mass balance equation to

\[
C_{\text{NH}_3} = 0.050 \ \text{M} = [\text{NH}_3]
\]

Substituting the simplified charge balance equation and mass balance equation into the \( K_b \) equation leave us with

\[
K_b = \frac{[\text{OH}^-][\text{OH}^-]}{C_{\text{NH}_3}} = \frac{[\text{OH}^-]^2}{C_{\text{NH}_3}} = 1.75 \times 10^{-5}
\]

\[
[\text{OH}^-] = \sqrt{K_b C_{\text{NH}_3}} = \sqrt{(1.75 \times 10^{-5})(0.050)} = 9.35 \times 10^{-4}
\]

Before accepting this answer, we must verify our two assumptions. The first assumption is that the concentration of \( \text{OH}^- \) is significantly greater than the concentration of \( \text{H}_3\text{O}^+ \). Using \( K_w \), we find that

\[
\frac{[\text{H}_3\text{O}^+]}{[\text{OH}^-]} = \frac{K_w}{9.35 \times 10^{-4}} = 1.07 \times 10^{-11}
\]
Clearly this assumption is acceptable. Our second assumption is that the concentration of NH$_3$ is scientifically greater than the concentration of NH$_4^+$. Using our simplified charge balance equation, we find that

$$[\text{NH}_4^+] = [\text{OH}^-] = 9.35 \times 10^{-4}$$

Because the concentration of NH$_4^+$ is 1.9% of $C_{\text{NH}_3}$, our second assumption also is reasonable. Given that $[\text{H}_3\text{O}^+]$ is $1.07 \times 10^{-11}$, the pH is 10.97.

Click here to return to the chapter.

**Practice Exercise 6.11**

In solving for the pH of 0.10 M alanine, we made the following three assumptions.

**Assumption One:** $[\text{HL}] >> [\text{H}_2\text{L}^+] + [\text{L}^-]$

**Assumption Two:** $K_{a1}K_w << K_{a1}K_{a2}C_{\text{HL}}$

**Assumption Three:** $K_{a1} << C_{\text{HL}}$

The second and third assumptions are easy to check. The value for $K_{a1}$ ($4.487 \times 10^{-3}$) is 0.45% of $C_{\text{HL}}$ (0.10), and $K_{a1}K_w$ ($4.487 \times 10^{-17}$) is 0.074% of $K_{a1}K_{a2}C_{\text{HL}}$ ($6.093 \times 10^{-14}$). Each assumption introduces an error of less than ±5%.

To test the first assumption, we need to calculate the concentrations of H$_2$L$^+$ and L$, which we accomplish using the equations for $K_{a1}$ and $K_{a2}$.

$$[\text{H}_2\text{L}^+] = \frac{[\text{H}_3\text{O}^+][\text{HL}]}{K_{a1}} = \frac{(7.807 \times 10^{-7})(0.10)}{4.487 \times 10^{-3}} = 1.74 \times 10^{-5}$$

$$[\text{L}^-] = \frac{K_{a2}[\text{HL}]}{[\text{H}_3\text{O}^+]} = \frac{(1.358 \times 10^{-10})(0.10)}{7.807 \times 10^{-7}} = 1.74 \times 10^{-5}$$

Because these concentrations are less than ±5% of CHL, the first assumption also is acceptable.

Click here to return to the chapter.

**Practice Exercise 6.12**

The acid dissociation constant for H$_2$PO$_4^-$ is $6.32 \times 10^{-8}$, or a pH of 7.199. Substituting the initial concentrations of H$_2$PO$_4^-$ and HPO$_4^{2-}$ into equation 6.60 and solving gives the buffer’s pH as

$$\text{pH} = 7.199 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7.199 + \log \frac{0.050}{0.10} = 6.898 \approx 6.90$$
Adding HCl converts a portion of HPO$_4^{2-}$ to H$_2$PO$_4^-$ as a result of the following reaction

$$\text{HPO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{H}_2\text{PO}_4^-(aq)$$

Because this reaction’s equilibrium constant is so large (it is $1.59 \times 10^7$), we may treat the reaction as if it goes to completion. The new concentrations of H$_2$PO$_4^-$ and HPO$_4^{2-}$ are

$$C_{\text{H}_2\text{PO}_4^-} = \frac{\text{mol H}_2\text{PO}_4^- + \text{mol HCl}}{V_{\text{total}}} = \frac{(0.10 \text{ M})(0.10 \text{ L}) + (0.20 \text{ M})(5.0 \times 10^{-3} \text{ L})}{0.10 \text{ L} + 5.0 \times 10^{-3} \text{ L}} = 0.105 \text{ M}$$

$$C_{\text{HPO}_4^{2-}} = \frac{\text{mol HPO}_4^{2-} - \text{mol HCl}}{V_{\text{total}}} = \frac{(0.05 \text{ M})(0.10 \text{ L}) - (0.20 \text{ M})(5.0 \times 10^{-3} \text{ L})}{0.10 \text{ L} + 5.0 \times 10^{-3} \text{ L}} = 0.0381 \text{ M}$$

Substituting these concentrations into equation 6.60 gives a pH of

$$\text{pH} = 7.199 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7.199 + \log \frac{0.0381}{0.105} = 6.759 \approx 6.76$$

As we expect, adding HCl decreases the buffer’s pH by a small amount, dropping from 6.90 to 6.76.

Click here to return to the chapter.

**Practice Exercise 6.13**

We begin by calculating the solution’s ionic strength. Because NaCl is a 1:1 ionic salt, the ionic strength is the same as the concentration of NaCl; thus $\mu = 0.10 \text{ M}$. This assumes, of course, that we can ignore the contributions of Hg$_2^{2+}$ and Cl$^-$ from the solubility of Hg$_2$Cl$_2$.

Next we use equation 6.63 to calculate the activity coefficients for Hg$_2^{2+}$ and Cl$^-$. 

$$\log \gamma_{\text{Hg}_2^{2+}} = -0.51 \times (+2)^2 \times \sqrt{0.10} \over 1 + 3.3 \times 0.40 \times \sqrt{0.10} = -0.455$$

$$\gamma_{\text{Hg}_2^{2+}} = 0.351$$

$$\log \gamma_{\text{Cl}^-} = -0.51 \times (-1)^2 \times \sqrt{0.10} \over 1 + 3.3 \times 0.3 \times \sqrt{0.10} = -0.12$$

$$\gamma_{\text{Cl}^-} = 0.75$$

Defining the equilibrium concentrations of Hg$_2^{2+}$ and Cl$^-$ in terms of the variable $x$
and substituting into the thermodynamic solubility product for Hg$_2$Cl$_2$, leave us with

$$K_v = a_{Hg}^2 \cdot a_{Cl}^2 = \gamma_{Hg}^2 [Hg^{2+}] \gamma_{Cl}^2 [Cl^-]^2 = 1.2 \times 10^{-18}$$

$$1.2 \times 10^{-18} = (0.351)(x)(0.75)^2(0.10 + x)^2$$

Because the value of $x$ is likely to be small, let’s simplify this equation to

$$1.2 \times 10^{-18} = (0.351)(x)(0.75)^2(0.10)^2$$

Solving for $x$ gives its value as $6.1 \times 10^{-16}$. Because $x$ is the concentration of Hg$_2^{2+}$ and $2x$ is the concentration of Cl$^-$, our decision to ignore their contributions to the ionic strength is reasonable. The molar solubility of Hg$_2$Cl$_2$ in 0.10 M NaCl is $6.1 \times 10^{-16}$ mol/L. In Practice Exercise 6.8, where we ignored ionic strength, we determined that the molar solubility of Hg$_2$Cl$_2$ is $1.2 \times 10^{-16}$ mol/L, a result that is $5 \times$ smaller than the its actual value.

Click here to return to the chapter.

**Practice Exercise 6.14**

To solve this problem, let’s set up the following spreadsheet

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pl =</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>[I$^-$] =</td>
<td>= 10$^{-b1}$</td>
</tr>
<tr>
<td>3</td>
<td>[Ag$^+$] =</td>
<td>= 8.3e$-17$/$b2$</td>
</tr>
<tr>
<td>4</td>
<td>[Ag(NH$_3$)$_2$]$^+$ =</td>
<td>= $b2 - b3$</td>
</tr>
<tr>
<td>5</td>
<td>[NH$_3$] =</td>
<td>= ($b4/(b3*1.7e7))^0.5$</td>
</tr>
<tr>
<td>6</td>
<td>[NH$_4^+$] =</td>
<td>= $0.10 - b5<em>2</em>b4$</td>
</tr>
<tr>
<td>7</td>
<td>[OH$^-$] =</td>
<td>= $1.75e-5*b5$/$b6$</td>
</tr>
<tr>
<td>8</td>
<td>[H$_3$O$^+$] =</td>
<td>= $1.00e-14$/$b7$</td>
</tr>
<tr>
<td>9</td>
<td>error =</td>
<td>= $b3 + b4 + b6 + b8 - b2 - b7$</td>
</tr>
</tbody>
</table>

copying the contents of cells B1-B9 into several additional columns. See our earlier treatment of this problem for the relevant equilibrium reactions and equilibrium constants. The initial guess for pl in cell B1 gives the concentration of I$^-$ in cell B2. Cells B3–B8 calculate the remaining concentrations, using the $K_{sp}$ to obtain [Ag$^+$], using the mass balance on iodide and silver to obtain [Ag(NH$_3$)$_2$]$^+$, using $B_2$ to calculate [NH$_3$], using the mass balance on ammonia to find [NH$_4^+$], using $K_b$ to calculate
[OH\textsuperscript{−}], and using $K_w$ to calculate $[H_3O^+]$. The system’s charge balance equation provides a means for determining the calculation’s error.

$$[Ag^+] + [Ag(NH_3)_2^+] + [NH_4^+] + [H_3O^+] - [I^-] - [OH^-] = 0$$

The largest possible value for pl—corresponding to the smallest concentration of $I^-$ and the lowest possible solubility—occurs for a simple, saturated solution of AgI. When $[Ag^+] = [I^-]$, the concentration of iodide is

$$[I^-] = \sqrt{K_{sp}} = \sqrt{8.3 \times 10^{-17}} = 9.1 \times 10^{-9} \text{ M}$$

corresponding to a pl of 8.04. Entering initial guesses for pl of 4, 5, 6, 7, and 8 shows that the error changes sign between a pl of 5 and 6. Continuing in this way to narrow down the range for pl, we find that the error function is closest to zero at a pl of 5.42. The concentration of $I^-$ at equilibrium, and the molar solubility of AgI, is $3.8 \times 10^{-6}$ mol/L, which agrees with our earlier solution to this problem.

Click here to return to the chapter

**Practice Exercise 6.15**

To solve this problem, let’s use the following function

```
> eval = function(pl){
+ I = 10^-pl
+ Ag = 8.3e-17/I
+ AgNH3 = Ag - I
+ NH3 = (AgNH3/(1.7e7*Ag))^0.5
+ NH4 = 0.10-NH3 - 2*AgNH3
+ OH = 1.75e-5*NH3/NH4
+ H3O = 1e-14/OH
+ error = Ag + AgNH3 + NH4 + H3O - OH - I
+ output = data.frame(pl, error)
+ print(output)
+ }
```

The function accepts an initial guess for pl and calculates the concentrations of species in solution using the definition of pl to calculate $[I^-]$, using the $K_{sp}$ to obtain $[Ag^+]$, using the mass balance on iodide and silver to obtain $[Ag(NH_3)_2^+]$, using $\beta_2$ to calculate $[NH_3]$, using the mass balance on ammonia to find $[NH_4^+]$, using $K_b$ to calculate $[OH^-]$, and using $K_w$ to calculate $[H_3O^+]$. The system’s charge balance equation provides a means for determining the calculation’s error.

$$[Ag^+] + [Ag(NH_3)_2^+] + [NH_4^+] + [H_3O^+] - [I^-] - [OH^-] = 0$$

The largest possible value for pl—corresponding to the smallest concentration of $I^-$ and the lowest possible solubility—occurs for a simple, saturated solution of AgI. When $[Ag^+] = [I^-]$, the concentration of iodide is
\[ [\Gamma^{-}] = \sqrt{K_w} = \sqrt{8.3 \times 10^{-17}} = 9.1 \times 10^{-9} \text{ M} \]

corresponding to a pI of 8.04. The following session shows the function in action.

```r
> pl = c(4, 5, 6, 7, 8)
> eval(pl)
  pl  error
1  4  -2.56235615
2  5  -0.16620930
3  6   0.07337101
4  7   0.09734824
5  8   0.09989073

> pl = c(5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 6.0)
> eval(pl)
  pl  error
1  5.1  -0.11144658
2  5.2  -0.06794105
3  5.3  -0.03336475
4  5.4  -0.00568116
5  5.5   0.01571549
6  5.6   0.03308929
7  5.7   0.04685937
8  5.8   0.05779214
9  5.9   0.06647475
10 6.0   0.07337101

> pl = c(5.40, 5.41, 5.42, 5.43, 5.44, 5.45, 5.46, 5.47, 5.48, 5.49, 5.50)
> eval(pl)
  pl  error
1 5.40  -0.0056811605
2 5.41  -0.0030715484
3 5.42   0.0002310369
4 5.43  -0.0005134898
5 5.44   0.0028281878
6 5.45   0.0052370980
7 5.46   0.0074758181
8 5.47   0.0096260370
9 5.48   0.0117105498
10 5.49   0.0137387291
11 5.50   0.0157154889
```

The error function is closest to zero at a pI of 5.42. The concentration of \( \Gamma^{-} \) at equilibrium, and the molar solubility of AgI, is \( 3.8 \times 10^{-6} \text{ mol/L} \), which agrees with our earlier solution to this problem.

Click [here](#) to return to the chapter