Chapter 6

Equilibrium Chemistry

Chapter Overview

Regardless of the problem on which an analytical chemist is working, its solution requires a knowledge of chemistry and the ability to use that knowledge. For example, an analytical chemist who is 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.

The ability to "think as a chemist" is a product of your experience in the classroom and in the laboratory. For the most part, the material in this text assumes you are familiar with topics covered in earlier courses; however, 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—likely afford you with new ways to look at equilibrium chemistry.

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 Na_2CO_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 us with 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.[1] If, for example, substance A reacts with substance BC to form AB

$$A + BC \longrightarrow AB + C$$

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.

$$AB + C \xrightarrow{\quad\times\quad} A + BC$$

From his experience in the laboratory, Berthollet knew that adding solid Na_2CO_3 to a solution of $CaCl_2$ produces a precipitate of $CaCO_3$.

$$Na_2CO_3\,(s) + CaCl_2\,(aq) \longrightarrow 2NaCl\,(aq) + CaCO_3\,(s)$$

Understanding this, Berthollet was surprised to find solid Na_2CO_3 forming on the edges of the lake, particularly since the deposits formed only when the lake's salt water, NaCl(aq), was in contact with limestone, $CaCO_3$. Where the lake was in contact with clay soils, there was little or no Na_2CO_3.

Berthollet's important insight was recognizing that the chemistry leading to the formation of Na_2CO_3 is the reverse of that seen in the laboratory.

$$2NaCl\,(aq) + CaCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CaCl_2\,(aq)$$
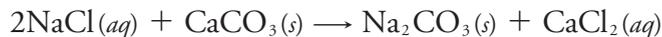
Using this insight Berthollet reasoned that the reaction is reversible, and that the relative amounts of NaCl, $CaCO_3$, Na_2CO_3, and $CaCl_2$ determine the direction in which the reaction occurs and the final composition of the reaction mixture. We recognize a reaction's ability to move in both directions by using a double arrow when we write the reaction.

$$Na_2CO_3\,(s) + CaCl_2\,(aq) \rightleftharpoons 2NaCl\,(aq) + CaCO_3\,(s)$$
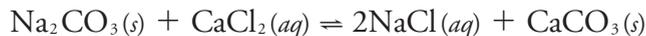
Berthollet's reasoning that reactions are reversible was an important step in understanding chemical reactivity. When we mix together solutions of Na_2CO_3 and $CaCl_2$ they react to produce NaCl and $CaCO_3$. As the reaction takes place, if we monitor the mass of Ca^{2+} that remains in solution and the mass of $CaCO_3$ that precipitates, the result looks something

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1   Quilez, J. *Chem. Educ. Res. Pract.* **2004**, *5*, 69–87.

like Figure 6.1. At the start of the reaction the mass of Ca^{2+} decreases and the mass of $CaCO_3$ 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 the 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 how energy changes during a chemical reaction.

Consider, for example, the general equilibrium reaction shown in equation 6.1, which involves the species A, B, C, and D, with stoichiometric coefficients of a, b, c, and d.

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D} \qquad 6.1$$

By convention, we identify the 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, it may move to the right, or it may exist 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, which is typical of many benchtop chemical reactions, a reaction's free energy is given by the GIBB'S FREE ENERGY function

$$\triangle G = \triangle H - T \triangle S \qquad 6.2$$

where T is the temperature in kelvin, and ΔG, ΔH, and ΔS 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. A reaction that releases heat has a negative ΔH and is called exothermic. An endothermic reaction absorbs heat from its surroundings and has a positive ΔH. ENTROPY is a measure of energy that is unavailable for useful, chemical work. The entropy of an individual species is always positive and generally is larger for gases than for solids, and for more complex molecules than for simpler molecules. Reactions that produce a large number of simple, gaseous products usually have a positive ΔS.
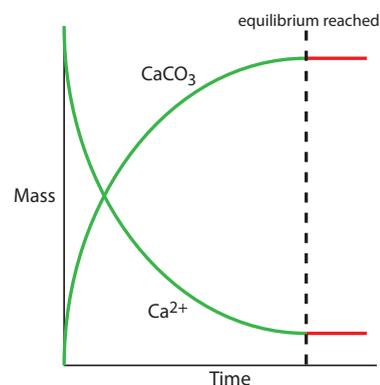

Figure 6.1 Graph showing how the masses of Ca^{2+} and $CaCO_3$ change as a function of time during the precipitation of $CaCO_3$. The dashed line indicates when the reaction reaches equilibrium. Prior to equilibrium the masses of Ca^{2+} and $CaCO_3$ are **changing**; after equilibrium is reached, their masses remain **constant**.

For many students, entropy is the most difficult topic in thermodynamics to understand. For a rich resource on entropy, visit the following web site: http://www.entropysite.oxy.edu.

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

As a reaction moves from its initial, non-equilibrium condition to its equilibrium position, its value of ΔG 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 divide the Gibb's free energy, ΔG, into two terms.

$$\Delta G = \Delta G° + RT \ln Q \qquad 6.3$$

The first term, $\Delta G°$, is the change in the Gibb's free energy when each species in the reaction is in its STANDARD STATE, which we define as follows: gases with unit partial pressures, solutes with unit concentrations, and pure solids and pure liquids. The second term includes the reaction quotient, Q, which accounts for non-standard state pressures and concentrations. For reaction 6.1 the reaction quotient is

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad 6.4$$

where the terms in brackets are the concentrations of the reactants and products. Note that we define the reaction quotient with the products in the numerator and the reactants 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

$$\Delta G° = -RT \ln K$$

where K is an EQUILIBRIUM CONSTANT that defines the reaction's equilibrium position. The equilibrium constant is just the reaction quotient's numerical value when we substitute equilibrium concentrations into equation 6.4.

$$K = \frac{[C]^c_{eq} [D]^d_{eq}}{[A]^a_{eq} [B]^b_{eq}} \qquad 6.5$$

Here we include the subscript "eq" to indicate a concentration at equilibrium. Although we will omit the "eq" when we write an equilibrium constant

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Equation 6.2 shows that the sign of ΔG depends on the signs of ΔH and of ΔS, and the temperature, T. The following table summarizes the possibilities.

ΔH	ΔS	ΔG
−	+	$\Delta G < 0$ at all temperatures
−	−	$\Delta G < 0$ at low temperatures
−	+	$\Delta G < 0$ at high temperatures
+	−	$\Delta G > 0$ at all temperatures

Although not shown here, each concentration term in equation 6.4 is divided by the corresponding standard state concentration; thus, the term $[C]^c$ really means

$$\left\{ \frac{[C]}{[C]°} \right\}^c$$

where $[C]°$ is the standard state concentration for C. There are two important consequences of this: (1) the value of Q is unitless; and (2) the ratio has a value of 1 for a pure solid or a pure liquid. This is the reason that pure solids and pure liquids do not appear in the reaction quotient.

As written, equation 6.5 is a limiting law that applies only to infinitely dilute solutions where the chemical behavior of one species is unaffected by the presence of other species. Strictly speaking, equation 6.5 is written in terms of activities instead of concentrations. We will return to this point in Section 6I. For now, we will stick with concentrations as this convention already is familiar to you.
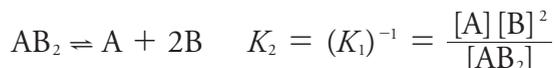
expressions, it is important to remember that the value of K is determined by equilibrium concentrations.

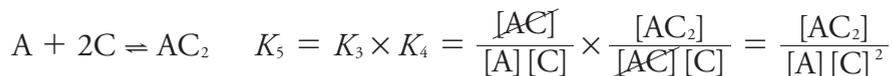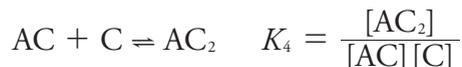## 6C   Manipulating Equilibrium Constants

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

$$A + 2B \rightleftharpoons AB_2 \qquad K_1 = \frac{[AB_2]}{[A][B]^2}$$
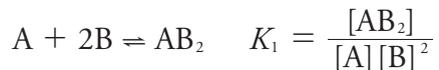
is the inverse of that for the reaction

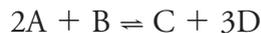$$AB_2 \rightleftharpoons A + 2B \qquad K_2 = (K_1)^{-1} = \frac{[A][B]^2}{[AB_2]}$$

Second, if we add together two reactions to form a new reaction, the equilibrium constant for the new reaction is the product of the equilibrium constants for the original reactions.
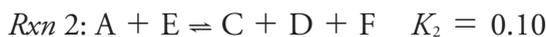
$$A + C \rightleftharpoons AC \qquad K_3 = \frac{[AC]}{[A][C]}$$

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

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

Example 6.1

Calculate the equilibrium constant for the reaction

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

given the following information

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

SOLUTION

The overall reaction is equivalent to
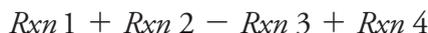
$$Rxn\ 1 + Rxn\ 2 - Rxn\ 3 + Rxn\ 4$$

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

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

## 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

Another common name for an oxidation–reduction reaction is a REDOX REACTION, where "red" is short for reduction and "ox" is short for oxidation.

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, a precipitate of lead chloride, $PbCl_2$, forms. We usually write a precipitation reaction as a net ionic equation, which shows only the precipitate and those ions that form the precipitate; thus, the precipitation reaction for $PbCl_2$ is

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$$

When we write the equilibrium constant for a precipitation reaction, we focus on the precipitate's solubility; thus, for $PbCl_2$, the solubility reaction is

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$
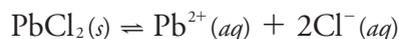
and its equilibrium constant, or SOLUBILITY PRODUCT, K_{sp}, is

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \qquad 6.6$$

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 between these definitions—defining a base as a proton acceptor implies there is an acid available to donate the proton. For example,

in reaction 6.7 acetic acid, CH_3COOH, donates a proton to ammonia, NH_3, which serves as the base.

$$CH_3COOH(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq) \quad 6.7$$

When an acid and a base react, the products are a new acid and a new base. For example, the acetate ion, CH_3COO^-, 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 we call the ammonium ion 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.

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

We use a single arrow ($\longrightarrow$) in place of the equilibrium arrow ($\rightleftharpoons$) because we treat HCl as if it dissociates completely in an aqueous solution. 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_2SO_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.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
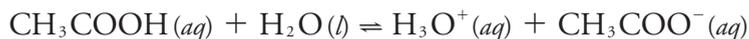
The equilibrium constant for this reaction is an ACID DISSOCIATION CONSTANT, K_a, which we write as

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5}$$

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, NH_4^+, for example, has a K_a of 5.702×10^{-10} and is a weaker acid than acetic acid.

A MONOPROTIC weak acid, such as acetic acid, has only a single acidic proton and a single acid dissociation constant. Other acids, such as phosphoric acid, have multiple acidic protons, each characterized by an acid dissociation constant. We call such acids POLYPROTIC. Phosphoric acid, for example, has three acid dissociation reactions and three acid dissociation constants.
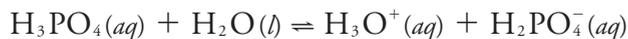
In a different solvent, HCl may not be a strong acid. For example, HCl does not act as a strong acid in methanol. In this case we use the equilibrium arrow when writing the acid–base reaction.
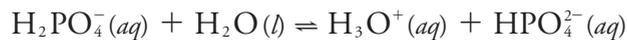
$$HCl + CH_3OH \rightleftharpoons CH_3OH_2^+ + Cl^-$$

Earlier we noted that we omit pure solids and pure liquids from equilibrium constant expressions. Because the solvent, H_2O, is not pure, you might wonder why we have not included it in acetic acid's K_a expression. Recall that we divide each term in an equilibrium constant expression by its standard state value. Because the concentration of H_2O is so large—it is approximately 55.5 mol/L—its concentration as a pure liquid and as a solvent are virtually identical. The ratio

$$\frac{[H_2O]}{[H_2O]^o}$$

is essentially 1.00.

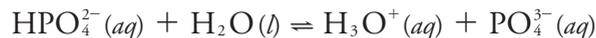$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

$$K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} = 6.32 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

$$K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} = 4.5 \times 10^{-13}$$

The decrease in the acid dissociation constants from K_{a1} to K_{a3} tells us that each successive proton is harder to remove. Consequently, H_3PO_4 is a stronger acid than $H_2PO_4^-$, and $H_2PO_4^-$ is a stronger acid than 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.

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$
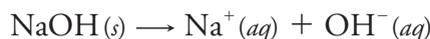
A weak base, such as the acetate ion, CH_3COO^-, only partially accepts a proton from the solvent, and is characterized by a BASE DISSOCIATION CONSTANT, K_b. For example, the base dissociation reaction and the base dissociation constant for the acetate ion are
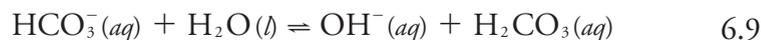
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq)$$
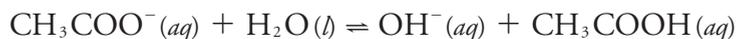
$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.71 \times 10^{-10}$$

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, HCO_3^-, in water.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad 6.8$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2CO_3(aq) \qquad 6.9$$

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

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

is smaller than the base dissociation constant for <u>reaction 6.9</u>.

$$K_{b2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.25 \times 10^{-8}$$

Because bicarbonate is a stronger base than it is an acid, we expect that an aqueous solution of HCO_3^- is 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.

$$2H_2O\,(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad 6.10$$

We identify the equilibrium constant for this reaction as water's dissociation constant, K_w,

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \qquad 6.11$$

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

An important consequence of equation 6.11 is that the concentration of H_3O^+ and the concentration of OH^- are related. If we know $[H_3O^+]$ for a solution, then we can calculate $[OH^-]$ using equation 6.11.

Example 6.2

What is the $[OH^-]$ if the $[H_3O^+]$ is 6.12×10^{-5} M?

SOLUTION

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{6.12 \times 10^{-5}} = 1.63 \times 10^{-10}$$

THE pH SCALE

Equation 6.11 allows us to develop a pH SCALE that indicates a solution's acidity. When the concentrations of H_3O^+ and OH^- are equal a solution is neither acidic nor basic; that is, the solution is neutral. Letting

$$pH = -\log[H_3O^+]$$

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

substituting into equation 6.11

$$K_w = [H_3O^+]^2 = 1.00 \times 10^{-14}$$

and solving for $[H_3O^+]$ gives

pH

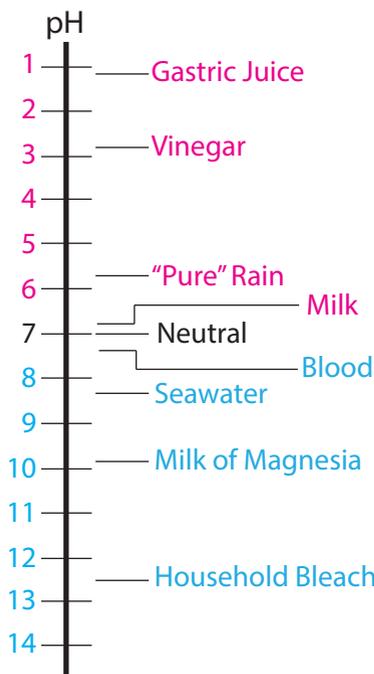**Figure 6.2** Scale showing the pH value for representative solutions. Milk of Magnesia is a saturated solution of $Mg(OH)_2$.

A common mistake when using equation 6.14 is to forget that it applies to a conjugate acid–base pair only.

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}$$

A neutral solution has a hydronium ion concentration of 1.00×10^{-7} M and a pH of 7.00. In an acidic solution the concentration of H_3O^+ is greater than that for OH^-, which means that

$$[H_3O^+] > 1.00 \times 10^{-7} \text{ M}$$

The pH of an acidic solution, therefore, is 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 weak acids and weak bases is that the strength of a weak base is inversely proportional to the strength of its conjugate weak acid. Consider, for example, the dissociation reactions of acetic acid and acetate.

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq) \quad 6.12$$

$$CH_3COO^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + CH_3COOH\,(aq) \quad 6.13$$

Adding together these two reactions gives the reaction

$$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

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 CH_3COOH and K_b for CH_3COO^-.

$$K_w = K_{a,CH_3COOH} \times K_{b,CH_3COO^-}$$

For any weak acid, HA, and its conjugate weak base, A^-, we can generalize this to the following equation

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

where HA and A^- are a conjugate acid–base pair. 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, C_5H_5N

(b) K_b for dihydrogen phosphate, $H_2PO_4^-$

SOLUTION

(a) $K_{b,C_5H_5N} = \dfrac{K_w}{K_{a,C_5H_5NH^+}} = \dfrac{1.00 \times 10^{-14}}{5.90 \times 10^{-6}} = 1.69 \times 10^{-9}$

(b) $K_{b,H_2PO_4^-} = \dfrac{K_w}{K_{a,H_3PO_4}} = \dfrac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$

When finding the K_b value for a polyprotic weak base, be careful to choose the correct K_a value. Remember that equation 6.14 applies to a conjugate acid–base pair only. The conjugate acid of $H_2PO_4^-$ is H_3PO_4, not HPO_4^{2-}.

Practice Exercise 6.2

Using Appendix 11, calculate K_b values for hydrogen oxalate, $HC_2O_4^-$, and oxalate, $C_2O_4^{2-}$.

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 the forming of covalent bonds to describe acids and bases. 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 Cd^{2+} and the LIGAND NH_3 is typical of a complexation reaction.

$$Cd^{2+}(aq) + 4:NH_3(aq) \rightleftharpoons Cd(:NH_3)_4^{2+}(aq) \qquad 6.15$$

The product of this reaction is a METAL–LIGAND COMPLEX. In writing this reaction we show ammonia as $:NH_3$, using a pair of dots to emphasize the pair of electrons that it donates to Cd^{2+}. In subsequent reactions we will omit this notation.
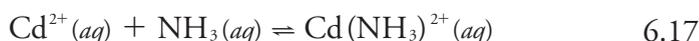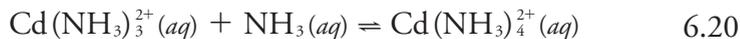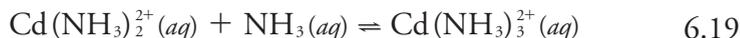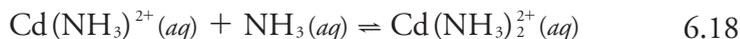
METAL-LIGAND FORMATION CONSTANTS

We characterize the formation of a metal–ligand complex by a FORMATION CONSTANT, K_f. The complexation reaction between Cd^{2+} and NH_3, for example, has the following equilibrium constant.

$$K_f = \dfrac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = 5.5 \times 10^7 \qquad 6.16$$

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 Cd^{2+} and NH_3 involves four successive reactions.

$$Cd^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)^{2+}(aq) \qquad 6.17$$

$$Cd(NH_3)^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_2^{2+}(aq) \qquad 6.18$$

$$Cd(NH_3)_2^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_3^{2+}(aq) \qquad 6.19$$

$$Cd(NH_3)_3^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq) \qquad 6.20$$

To avoid ambiguity, we divide formation constants into two categories. A STEPWISE FORMATION CONSTANT, which we designate as K_i for the ith step, describes 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. An overall, or CUMULATIVE FORMATION CONSTANT, which we designate as β_i, describes the addition of i ligands to the free metal ion. The equilibrium constant in equation 6.16 is correctly identified as β_4, where

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$$

In general

$$\beta_i = K_1 \times K_2 \times \cdots \times K_i = \prod_{i=1}^{n} K_i$$

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

### METAL-LIGAND COMPLEXATION AND SOLUBILITY

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

$$AgCl(s) + Cl^-(aq) \rightleftharpoons Ag(Cl)_2^-(aq) \qquad 6.21$$

We can write this reaction as the sum of three other equilibrium reactions with known equilibrium constants—the solubility of AgCl, which is described by its K_{sp} reaction
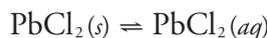
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
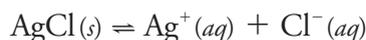
and the stepwise formation of $AgCl_2^-$, which is described by K_1 and K_2 reactions.

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

$$AgCl(aq) + Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)$$
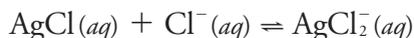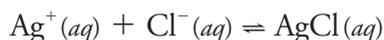
The equilibrium constant for reaction 6.21, therefore, is $K_{sp} \times K_1 \times K_2$.

Example 6.4

Determine the value of the equilibrium constant for the reaction
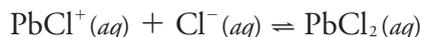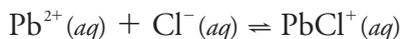
$$PbCl_2(s) \rightleftharpoons PbCl_2(aq)$$

SOLUTION

We can write this reaction as the sum of three other reactions. The first of these reactions is the solubility of $PbCl_2(s)$, which is described by its K_{sp} reaction.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$
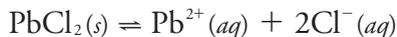
The remaining two reactions are the stepwise formation of $PbCl_2(aq)$, which are described by K_1 and K_2.

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

$$PbCl^+(aq) + Cl^-(aq) \rightleftharpoons PbCl_2(aq)$$
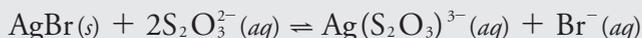
Using values for K_{sp}, K_1, and K_2 from Appendix 10 and Appendix 12, we find that the equilibrium constant is

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


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.

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$$

Click here to review your answer to this exercise.
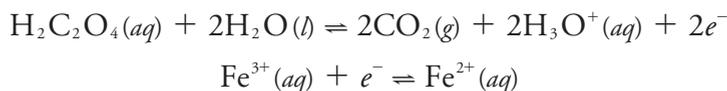
6D.4 Oxidation–Reduction (Redox) Reactions

An oxidation–reduction reaction occurs when electrons move from one reactant to another reactant. As a result of this transfer of electrons, the reactants undergo a change in oxidation state. Those reactant that increases its oxidation state undergoes OXIDATION, and the reactant that decreases its oxidation state undergoes REDUCTION. For example, in the following redox reaction between Fe^{3+} and oxalic acid, $H_2C_2O_4$, iron is reduced because its oxidation state changes from +3 to +2.

$$2Fe^{3+}(aq) + H_2C_2O_4(aq) + 2H_2O(l) \rightleftharpoons$$
$$2Fe^{2+}(aq) + 2CO_2(g) + 2H_3O^+(aq)$$

6.22
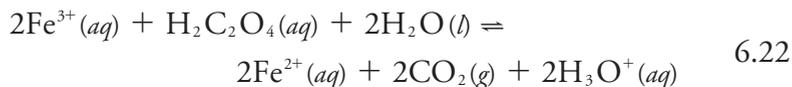
Oxalic acid, on the other hand, is oxidized because the oxidation state for carbon increases from +3 in $H_2C_2O_4$ to +4 in CO_2.

We can divide a redox reaction, such as reaction 6.22, into separate HALF-REACTIONS that show the oxidation and the reduction processes.

$$H_2C_2O_4(aq) + 2H_2O(l) \rightleftharpoons 2CO_2(g) + 2H_3O^+(aq) + 2e^-$$
$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$

It is important to remember, however, that an oxidation reaction and a reduction reaction always occur as a pair. We formalize this relationship

by identifying as a REDUCING AGENT the reactant that is oxidized, because it provides the electrons for the reduction half-reaction. Conversely, the reactant that is reduced is an OXIDIZING AGENT. In reaction 6.22, Fe^{3+} is the oxidizing agent and $H_2C_2O_4$ is the reducing agent.

The products of a redox reaction also have redox properties. For example, the Fe^{2+} in reaction 6.22 is oxidized to Fe^{3+} when CO_2 is reduced to $H_2C_2O_4$. Borrowing some terminology from acid–base chemistry, Fe^{2+} is the conjugate reducing agent of the oxidizing agent Fe^{3+}, and CO_2 is the conjugate oxidizing agent of the reducing agent $H_2C_2O_4$.

THERMODYNAMICS OF REDOX REACTIONS

Unlike precipitation reactions, acid–base reactions, and complexation reactions, we rarely express the equilibrium position of a redox reaction with 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 C/mol). The free energy, ΔG, to move this charge, Q, over a change in POTENTIAL, E, is

$$\Delta G = EQ$$

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

$$\Delta G = -nFE \qquad 6.23$$

where ΔG has units of kJ/mol. The minus sign in equation 6.23 is the result of a different convention for assigning a reaction's favorable direction. In thermodynamics, a reaction is favored when ΔG is negative, but an oxidation-reduction reaction is favored when E is positive. Substituting equation 6.23 into equation 6.3

$$-nFE = -nFE^\circ + RT\ln Q$$

and dividing by $-nF$, leads to the well-known NERNST EQUATION

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

$\ln(x) = 2.303\log(x)$

where E° 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

$$E = E^\circ - \frac{0.05916}{n}\log Q \qquad 6.24$$

STANDARD POTENTIALS

A redox reaction's STANDARD POTENTIAL, E^o, provides an alternative way of expressing its equilibrium constant and, therefore, its equilibrium position. Because a reaction at equilibrium has a ΔG of zero, the potential, E, also is zero at equilibrium. Substituting these values into equation 6.24 and rearranging provides a relationship between E^o and K.

$$E^o = \frac{0.05916}{n}\log K \qquad\qquad 6.25$$

We generally do not tabulate standard potentials for redox reactions. Instead, we calculate E^o 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^o, is

$$E^o = E^o_{red} - E^o_{ox}$$

where E^o_{red} and E^o_{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

$$2H_3O^+(aq) + 2e^- \rightleftharpoons 2H_2O(l) + H_2(g)$$
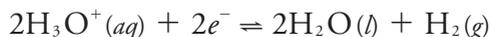
and report all other reduction potentials relative to this reference. Appendix 13 contains a list of selected standard reduction potentials. The more positive the standard reduction potential, the more favorable the reduction reaction is under standard state conditions. For example, under standard state conditions the reduction of Cu^{2+} to Cu ($E^o=+0.3419$ V) is more favorable than the reduction of Zn^{2+} to Zn ($E^o=-0.7618$ V).

A standard potential is the potential when all species are in their standard states. You may recall that we define standard state conditions as follows: all gases have unit partial pressures, all solutes have unit concentrations, and all solids and liquids are pure.

Example 6.5

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

$$Cd(s) + 2Ag^+(aq) \rightleftharpoons 2Ag(s) + Cd^{2+}(aq)$$
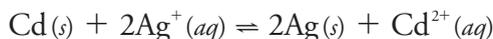
SOLUTION

(a) In this reaction Cd is oxidized and Ag^+ is reduced. 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 $[Cd^{2+}]$ is 0.050 M, we use the appropriate relationship for the reaction quotient, Q, in equation 6.24.
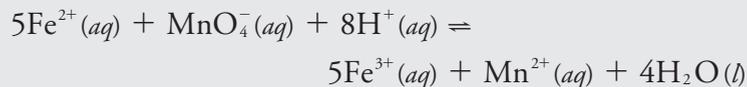
$$E = E^\circ - \frac{0.05916 \text{ V}}{n} \log \frac{[Cd^{2+}]}{[Ag^+]^2}$$

$$E = 1.2026 \text{ V} - \frac{0.05916 \text{ V}}{2} \log \frac{0.050}{(0.020)^2} = 1.14 \text{ V}$$

Practice Exercise 6.4

For the following reaction at 25 °C

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

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

Click here to review your answer to this exercise.

When writing precipitation, acid–base, and metal–ligand complexation reactions, we represent acidity as H_3O^+. Redox reactions more commonly are written using H^+ instead of H_3O^+. For the reaction in Practice Exercise 6.4, we could replace H^+ with H_3O^+ and increase the stoichiometric coefficient for H_2O from 4 to 12.

6E Le Châtelier's Principle

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

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

has an equilibrium constant of
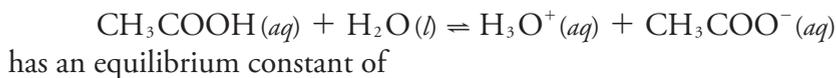
$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5} \qquad 6.26$$

Because equation 6.26 has three variables—$[CH_3COOH]$, $[CH_3COO^-]$, and $[H_3O^+]$—it does not have a unique mathematical solution. Nevertheless, although two solutions of acetic acid may have different values for $[CH_3COOH]$, $[CH_3COO^-]$, and $[H_3O^+]$, each solution has the same value of K_a.

If we add sodium acetate to a solution of acetic acid, the concentration of CH_3COO^- increases, which suggests there is an increase in the value of K_a; however, 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 CH_3COO^- and H_3O^+ decreases their con-
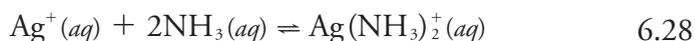
centrations, increases the concentration of CH_3COOH, and reestablishes the equilibrium.

The observation that a system at equilibrium responds to an external action by reequilibrating itself in a manner that diminishes that action, is formalized as LE CHÂTELIER'S PRINCIPLE. One common action is to change the concentration of a reactant or product for a system at equilibrium. As noted above for a solution of acetic acid, 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 directly apply the action to the system. It is also possible to apply a change concentration indirectly. Consider, for example, the solubility of AgCl.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad 6.27$$
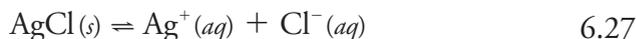
The effect on the solubility of AgCl of adding $AgNO_3$ is obvious, but what is the effect of if we add a ligand that forms a stable, soluble complex with Ag^+? Ammonia, for example, reacts with Ag^+ as shown here

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad 6.28$$

Adding ammonia decreases the concentration of Ag^+ as the $Ag(NH_3)_2^+$ complex forms. In turn, a decrease in 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.

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad 6.29$$

So what is the effect on the solubility of AgCl of adding $AgNO_3$? Adding $AgNO_3$ increases the concentration of Ag^+ in solution. To reestablish equilibrium, some of the Ag^+ and Cl^- react to form additional AgCl; thus, the solubility of AgCl decreases. The solubility product, K_{sp}, of course, remains unchanged.

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

$$HNO_3(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + NO_3^-(aq)$$
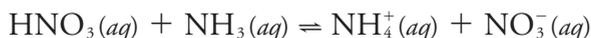
Adding nitric acid lowers the concentration of ammonia. Decreasing ammonia's concentration causes reaction 6.29 to move from products to reactants, decreasing the solubility of AgCl.

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 the solution, then the concen-

We can use the ideal gas law to deduce the relationship between pressure and concentration. Starting with $PV = nRT$, we solve for the molar concentration

$$M = \frac{n}{V} = \frac{P}{RT}$$

Of course, this assumes that the gas is behaving ideally, which usually is a reasonable assumption under normal laboratory conditions.

trations of all reactants and products must increase; conversely, if we allow the solvent to evaporate partially, then the concentration of the solutes must increase. The effect of simultaneously changing the concentrations of all reactants and products is not intuitively as obvious as when we change 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

$$\beta_2 = \frac{[Ag(NH_3)_2^+]_{eq}}{[Ag^+]_{eq}[NH_3]_{eq}^2} \qquad 6.30$$

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

$$Q = \frac{0.5\,[Ag(NH_3)_2^+]_{eq}}{0.5\,[Ag^+]_{eq}(0.5)^2[NH_3]_{eq}^2} = \frac{0.5}{(0.5)^3} \times \frac{[Ag(NH_3)_2^+]_{eq}}{[Ag^+]_{eq}[NH_3]_{eq}^2} = 4\beta_2$$

Because Q is greater than β_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 that has 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 reestablished in the opposite direction. This is a general conclusion that we can apply to any reaction. Increasing volume always favors the direction that produces the greatest number of particles, and decreasing volume always favors the direction that produces 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

One of the primary sources of determinate errors in many analytical methods is failing to account for potential chemical interferences.

When we develop or evaluate an analytical method, we often need to understand how the chemistry that takes 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 does not adversely affect the solubility of AgCl. It is a mistake to use NH_3 to adjust the pH, for example, because it increases the solubility of AgCl (reaction 6.29).

Ladder diagrams are a great tool for helping you to think intuitively about analytical chemistry. We will make frequent use of them in the chapters to follow.

   In this section we introduce the LADDER DIAGRAM as a simple graphical tool for visualizing equilibrium chemistry.[2] We will use ladder diagrams to determine what reactions occur when we combine several reagents, to esti-

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2   Although not specifically on the topic of ladder diagrams as developed in this section, the following papers provide appropriate background information: (a) Runo, J. R.; Peters, D. G. *J. Chem. Educ.* **1993**, *70*, 708–713; (b) Vale, J.; Fernández-Pereira, C.; Alcalde, M. *J. Chem. Educ.* **1993**, *70*, 790–795; (c) Fernández-Pereira, C.; Vale, J. *Chem. Educator* **1996**, *6*, 1–18; (d) Fernández-Pereira, C.; Vale, J.; Alcalde, M. *Chem. Educator* **2003**, *8*, 15–21; (e) Fernández-Pereira, C.; Alcalde, M.; Villegas, R.; Vale, J. *J. Chem. Educ.* **2007**, *84*, 520–525.

mate the approximate composition of a system at equilibrium, and to 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_3COOH, to illustrate the process we will use to draw and to interpret an acid–base ladder diagram. Before we draw the diagram, however, let's consider the equilibrium reaction in more detail. The equilibrium constant expression for acetic acid's dissociation reaction

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$$
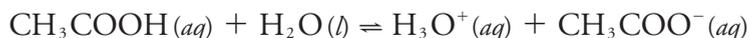
is

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5}$$

First, let's take the logarithm of each term in this equation and multiply through by –1

$$-\log K_a = 4.76 = -\log[H_3O^+] - \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

Now, let's replace $-\log[H_3O^+]$ with pH and rearrange the equation to obtain the result shown here.

$$pH = 4.76 + \log\frac{[CH_3COO^-]}{[CH_3COOH]} \qquad\qquad 6.31$$

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 CH_3COOH and CH_3COO^- are equal, then equation 6.31 reduces to

$$pH = 4.76 + \log(1) = 4.76 + 0 = 4.76$$

If the concentration of CH_3COO^- is greater than that of CH_3COOH, then the log term in equation 6.31 is positive and the pH is greater than 4.76. This is a reasonable result because we expect the concentration of the conjugate base, CH_3COO^-, to increase as the pH increases. Similar reasoning will convince you that the pH is less than 4.76 when the concentration of CH_3COOH exceeds that of CH_3COO^-.

Now we are ready to construct acetic acid's ladder diagram (Figure 6.3). First, we draw a vertical arrow that represents 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 pK_a value. This line, or step on the ladder, divides the pH axis into regions where either CH_3COOH or CH_3COO^- 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 CH_3COOH. If we add sufficient base to the solution such that the pH increases to 6.5, the predominate form of acetic acid is CH_3COO^-.
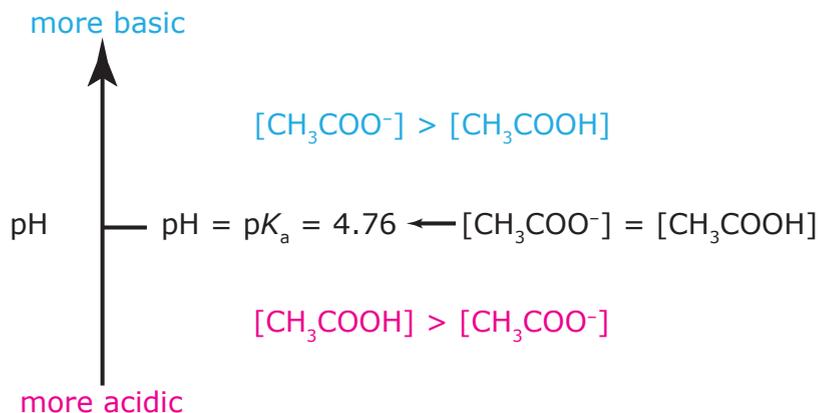
more basic

$[CH_3COO^-] > [CH_3COOH]$

pH ——— pH = pK_a = 4.76 ◄—— $[CH_3COO^-] = [CH_3COOH]$

$[CH_3COOH] > [CH_3COO^-]$

more acidic

Figure 6.3 Acid–base ladder diagram for acetic acid showing the relative concentrations of CH_3COOH and CH_3COO^-. A simpler version of this ladder diagram dispenses with the equalities and shows only the predominate species in each region.
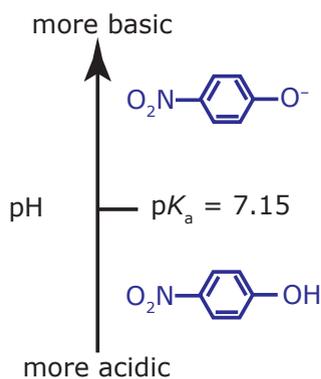
more basic

O_2N—⬡—O^-

pH ——— pK_a = 7.15

O_2N—⬡—OH

more acidic

Figure 6.4 Acid–base ladder diagram for *p*-nitrophenolate.

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.

A ladder diagram is particularly useful for evaluating the reactivity between a weak acid and a weak base. Figure 6.5, for example, shows a single ladder diagram for acetic acid/acetate and for *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

$$C_6H_4NO_2^- (aq) + CH_3COOH (aq) \rightleftharpoons$$
$$CH_3COO^- (aq) + C_6H_4NO_2H (aq) \qquad 6.32$$
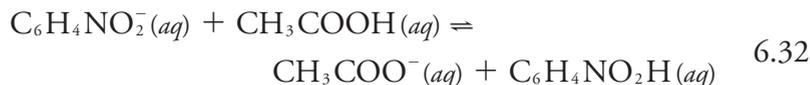
occurs because the areas of predominance for acetic acid and *p*-nitrophenolate do not overlap. The solution's final composition depends on which spe-
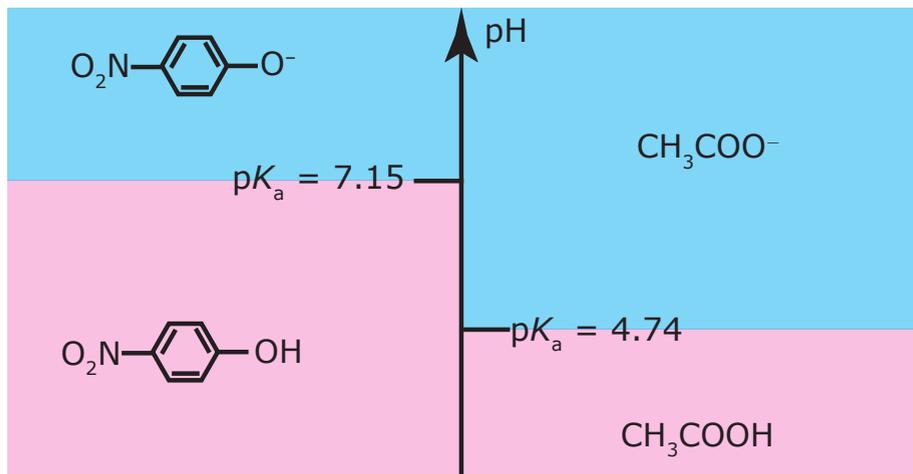
Figure 6.5 Acid–base ladder diagram showing the areas of predominance for acetic acid/acetate and for *p*-nitrophenol/*p*-nitrophenolate. The areas shaded in **blue** shows the pH range where the weak bases are the predominate species; the weak acid forms are the predominate species in the areas shaded in **pink**.

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 after 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 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 the solution formed by mixing together 0.090 moles of *p*-nitrophenolate and 0.040 moles of acetic acid.
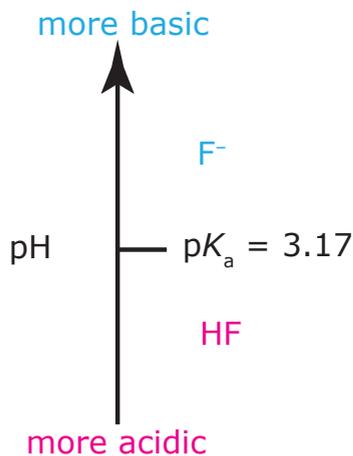
Click here to review your answer to this exercise.

more basic

↑

F⁻

pH   ⎯ $pK_a = 3.17$

HF

more acidic

Figure 6.6 Acid–base ladder diagram for HF. To minimize the solubility of CaF_2, we need to keep the pH above 3.17, with more basic pH levels leading to smaller solubility losses. See Chapter 8 for a more detailed discussion.
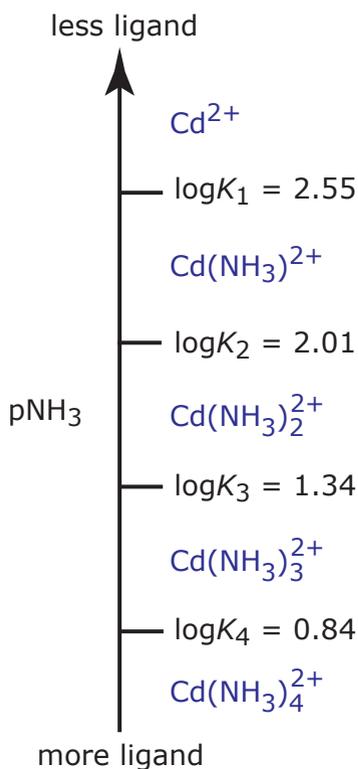
less ligand

↑

Cd^{2+}

⎯ $\log K_1 = 2.55$

$Cd(NH_3)^{2+}$

⎯ $\log K_2 = 2.01$

pNH₃ $Cd(NH_3)_2^{2+}$

⎯ $\log K_3 = 1.34$

$Cd(NH_3)_3^{2+}$

⎯ $\log K_4 = 0.84$

$Cd(NH_3)_4^{2+}$

more ligand

Figure 6.7 Metal–ligand ladder diagram for Cd^{2+}–NH_3 complexation reactions. Note that higher-order complexes form when pNH₃ is smaller (which corresponds to larger concentrations of NH_3).

If the areas of predominance for an acid and a base overlap, then we do not expect that much of a reaction will occur. For example, if we mix together solutions of CH_3COO^- and *p*-nitrophenol, we do not expect a 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

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
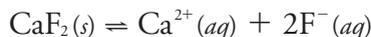
is affected by pH because F^- is a weak base. From Le Châtelier's principle, we know that converting F^- to HF will increase the solubility of CaF_2. To minimize the solubility of CaF_2 we need to maintain the solution's pH so that F^- is the predominate species. The ladder diagram for HF (Figure 6.6) shows us that maintaining a pH of more than 3.17 will minimize solubility losses.

6F.2   Ladder Diagrams for Complexation Equilibria

We can apply the same principles for constructing and interpreting an acid–base ladder diagram to equilibria that involve 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 $Cd(NH_3)^{2+}$ as an example

$$Cd^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)^{2+}(aq)$$
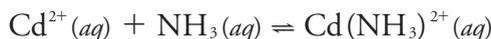
we can show that $\log K_1$ is the dividing line between the areas of predominance for Cd^{2+} and for $Cd(NH_3)^{2+}$.

$$K_1 = 3.55 \times 10^2 = \frac{[Cd(NH_3)^{2+}]}{[Cd^{2+}][NH_3]}$$

$$\log K_1 = \log(3.55 \times 10^2) = \log\frac{[Cd(NH_3)^{2+}]}{[Cd^{2+}]} - \log[NH_3]$$

$$\log K_1 = 2.55 = \log\frac{[Cd(NH_3)^{2+}]}{[Cd^{2+}]} + pNH_3$$

$$pNH_3 = \log K_1 + \log\frac{[Cd^{2+}]}{[Cd(NH_3)^{2+}]} = 2.55 + \log\frac{[Cd^{2+}]}{[Cd(NH_3)^{2+}]}$$

Thus, Cd^{2+} is the predominate species when pNH₃ is greater than 2.55 (a concentration of NH_3 smaller than 2.82×10^{-3} M) and for a pNH₃ value less than 2.55, $Cd(NH_3)^{2+}$ is the predominate species. Figure 6.7 shows a complete metal–ligand ladder diagram for Cd^{2+} and NH_3 that includes additional Cd–NH_3 complexes.

Example 6.9

Draw a single ladder diagram for the $Ca(EDTA)^{2-}$ and the $Mg(EDTA)^{2-}$ metal–ligand complexes. Use your ladder diagram to 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

$$Ca^{2+}(aq) + Mg(EDTA)^{2-}(aq) \rightleftharpoons Ca(EDTA)^{2-}(aq) + Mg^{2+}(aq)$$
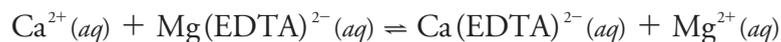
proceeds essentially to completion. Because Ca^{2+} is the excess reagent, the composition of the final solution is approximately

$$\text{moles } Ca^{2+} = 0.080 - 0.060 = 0.020 \text{ mol}$$
$$\text{moles } Ca(EDTA)^{2-} = 0.060 \text{ mol}$$
$$\text{moles } Mg^{2+} = 0.060 \text{ mol}$$
$$\text{moles } Mg(EDTA)^{2-} = 0 \text{ mol}$$
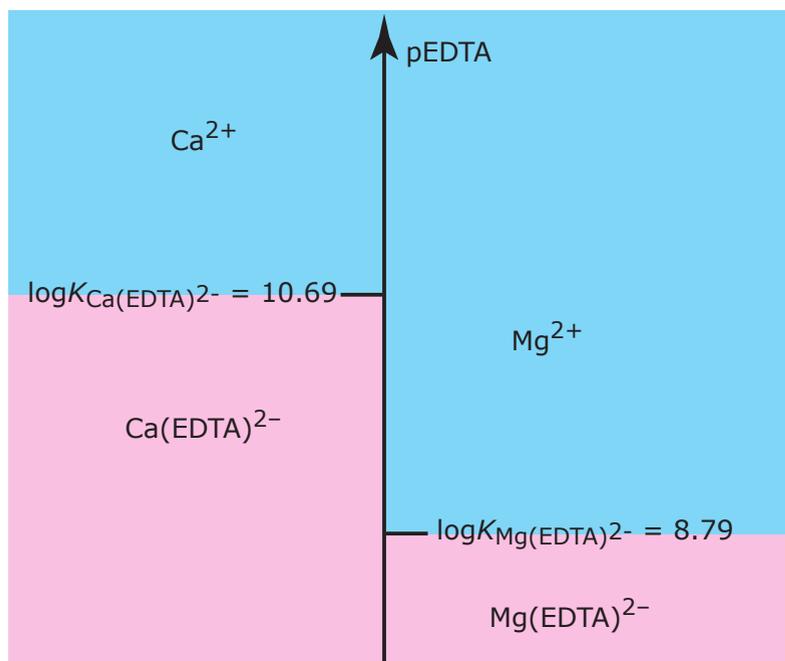
Figure 6.8 Metal–ligand ladder diagram for $Ca(EDTA)^{2-}$ and for $Mg(EDTA)^{2-}$. The areas shaded in **blue** show the pEDTA range where the free metal ions are the predominate species; the metal–ligand complexes are the predominate species in the areas shaded in **pink**.

The metal–ligand ladder diagram in Figure 6.7 uses stepwise formation constants. We also can construct a ladder diagram using cumulative formation constants. For example, the first three stepwise formation constants for the reaction of Zn^{2+} with NH_3

$$Zn^{2+}(aq) + NH_3(aq) \rightleftharpoons Zn(NH_3)^{2+}(aq) \quad K_1 = 1.6 \times 10^2$$

$$Zn(NH_3)^{2+}(aq) + NH_3(aq) \rightleftharpoons Zn(NH_3)_2^{2+}(aq) \quad K_2 = 1.95 \times 10^2$$

$$Zn(NH_3)_2^{2+}(aq) + NH_3(aq) \rightleftharpoons Zn(NH_3)_3^{2+}(aq) \quad K_3 = 2.3 \times 10^2$$
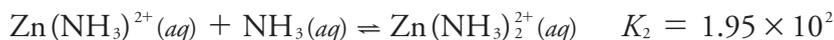
suggests that the formation of $Zn(NH_3)_3^{2+}$ is more favorable than the formation of $Zn(NH_3)^{2+}$ or $Zn(NH_3)_2^{2+}$. For this reason, the equilibrium is best represented by the cumulative formation reaction shown here.

$$Zn^{2+}(aq) + 3NH_3(aq) \rightleftharpoons Zn(NH_3)_3^{2+}(aq) \quad \beta_3 = 7.2 \times 10^6$$
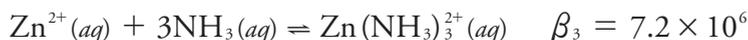
To see how we incorporate this cumulative formation constant into a ladder diagram, we begin with the reaction's equilibrium constant expression.

$$\beta_3 = \frac{[Zn(NH_3)_3^{2+}]}{[Zn^{2+}][NH_3]^3}$$

Taking the log of each side

$$\log \beta_3 = \log \frac{[Zn(NH_3)_3^{2+}]}{[Zn^{2+}]} - 3\log[NH_3]$$

and rearranging gives

$$pNH_3 = \frac{1}{3}\log \beta_3 + \frac{1}{3}\log\frac{[Zn^{2+}]}{[Zn(NH_3)_3^{2+}]}$$

When the concentrations of Zn^{2+} and $Zn(NH_3)_3^{2+}$ are equal, then

$$pNH_3 = \frac{1}{3}\log \beta_3 = 2.29$$

In general, for the metal–ligand complex 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 Zn^{2+}–NH_3 system.

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 $Zn(NH_3)^{2+}$. The value of β_3 is
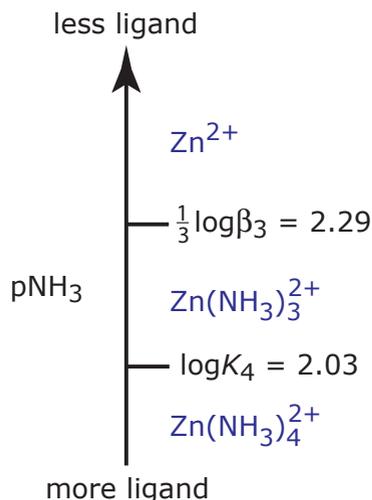
$$\beta_3 = K_1 \times K_2 \times K_3$$

Figure 6.9 Ladder diagram for Zn^{2+}–NH_3 metal–ligand complexation reactions showing both a step based on a cumulative formation constant and a step based on a stepwise formation constant.
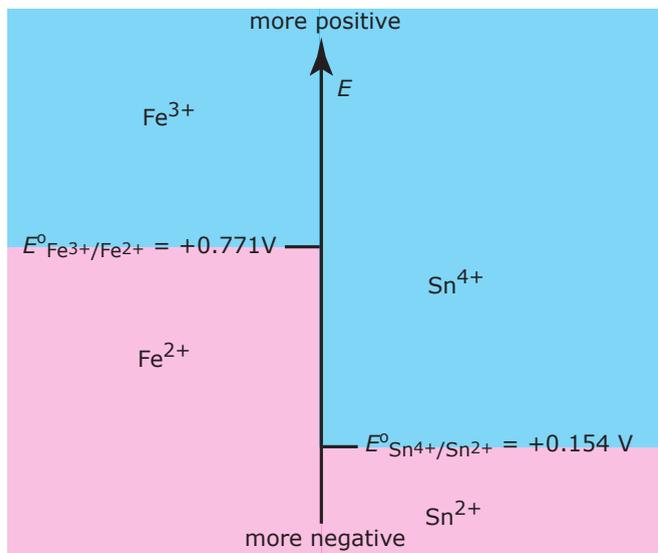
6F.3 Ladder Diagram for Oxidation/Reduction Equilibria

We also can construct ladder diagrams to help us 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 Fe^{3+}/Fe^{2+} half-reaction as an example, we write

$$E = E^\circ - \frac{RT}{nF}\ln\frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.771 - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

At a potential more positive than the standard state potential, the predominate species is Fe^{3+}, whereas Fe^{2+} predominates at potentials more negative

Figure 6.10 Redox ladder diagram for Fe^{3+}/Fe^{2+} and for Sn^{4+}/Sn^{2+}. The areas shaded in **blue** show the potential range where the oxidized forms are the predominate species; the reduced forms are the predominate species in the areas shaded in **pink**. Note that a more positive potential favors the oxidized form.

than E°. When coupled with the step for the Sn^{4+}/Sn^{2+} half-reaction we see that Sn^{2+} is a useful reducing agent for Fe^{3+}. If Sn^{2+} is in excess, the potential of the resulting solution is near $+0.154$ V.

Because the steps on a redox ladder diagram are standard state potentials, a complication arises 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

$$UO_2^{2+}(aq) + 4H_3O^+(aq) + 2e^- \rightleftharpoons U^{4+}(aq) + 6H_2O(l)$$
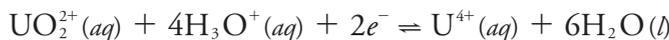
depends on the solution's pH. To define areas of predominance in this case we begin with the Nernst equation

$$E = +0.327 - \frac{0.05916}{2}\log\frac{[U^{4+}]}{[UO_2^{2+}][H_3O^+]^4}$$

and factor out the concentration of H_3O^+.

$$E = +0.327 + \frac{0.05916}{2}\log[H_3O^+]^4 - \frac{0.05916}{2}\log\frac{[U^{4+}]}{[UO_2^{2+}]}$$

From this equation we see that the area of predominance for UO_2^{2+} and U^{4+} is defined by a step at a potential where $[U^{4+}] = [UO_2^{2+}]$.

$$E = +0.327 + \frac{0.05916}{2}\log[H_3O^+]^4 = +0.327 - 0.1183\text{pH}$$

Figure 6.11 shows how pH affects the step for the UO_2^{2+}/U^{4+} half-reaction.

Figure 6.11 Redox ladder diagram for the UO_2^{2+}/U^{4+} half-reaction showing the effect of pH on the step defined by the standard state's potential.

6G   Solving Equilibrium Problems

Ladder diagrams are a useful tool for evaluating chemical reactivity and for providing a reasonable estimate 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; instead, we need to find an algebraic solution. In this section we will learn how to set-up and
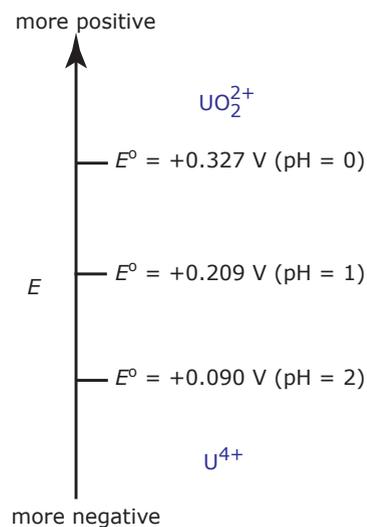
solve equilibrium problems. We will start with a simple problem and work toward more complex problems.

6G.1   A Simple Problem—Solubility of Pb(IO₃)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 means simply 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 $Pb(IO_3)_2$.

$$Pb(IO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2IO_3^-(aq)$$
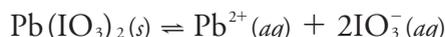
$$K_{sp} = [Pb^{2+}][IO_3^-]^2 = 2.5 \times 10^{-13} \qquad 6.33$$

As $Pb(IO_3)_2$ dissolves, two IO_3^- ions form 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^-.

Concentrations	$Pb(IO_3)_2$ (s)	$\rightleftharpoons$	Pb^{2+} (aq)	+	$2IIO_3^-$ (aq)
Initial	solid		0		0
Change	solid		+x		+2x
Equilibrium	solid		x		2x

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

$$[Pb^{2+}] = x = 4.0 \times 10^{-5}\ M \quad \text{and} \quad [IO_3^-] = 2x = 7.9 \times 10^{-5}$$

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 4.0×10^{-5} M.

Practice Exercise 6.7

Calculate the molar solubility and the mass solubility for Hg_2Cl_2, given the following solubility reaction and K_{sp} value.

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 1.2 \times 10^{-8}$$

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 because 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 $Pb(NO_3)_2$? 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.

Concentrations	$Pb(IO_3)_2$ (s)	$\rightleftharpoons$	Pb^{2+} (aq)	+	$2 IO_3^-$ (aq)
Initial	solid		0.10		0
Change	solid		$+x$		$+2x$
Equilibrium	solid		$0.10 + x$		$2x$

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

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

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 computational 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+} will decrease significantly the solubility of $Pb(IO_3)_2$. One reasonable assumption is that the initial concentration of Pb^{2+} is very close to its equilibrium concentration. If this assumption is correct, then the following approximation is reasonable

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

Substituting this approximation into equation 6.33 and solving for x gives

$$(0.10)(2x)^2 = 0.4x^2 = 2.5 \times 10^{-13}$$

$$x = 7.91 \times 10^{-7}$$

Before we accept this answer, we must verify that our approximation is reasonable. The difference between the actual concentration of Pb^{2+}, which is $0.10 + x$ M, and our assumption that the concentration of Pb^{2+} is 0.10 M is 7.9×10^{-7}, or 7.9×10^{-4}% of the assumed concentration. This is a negligible error. If we accept the result of our calculation, we find that the equilibrium concentrations of Pb^{2+} and IO_3^- are

$$[Pb^{2+}] = 0.10 + x \approx 0.10 \text{ M} \quad \text{and} \quad [IO_3^-] = 2x = 1.6 \times 10^{-6} \text{ M}$$

Beginning a problem by thinking about the likely answer is a good habit to develop. Knowing what answers are reasonable will help you spot errors in your calculations and give you more confidence that your solution to a problem is correct.

Because the solution already contains a source of Pb^{2+}, we can use Le Châtelier's principle to predict that the solubility of $Pb(IO_3)_2$ is smaller than that in our previous problem.

There are several approaches to solving cubic equations, but none are computationally easy using paper and pencil.

$$\%error = \frac{actual - assumed}{assumed} \times 100$$

$$= \frac{(0.10 + x) - 0.10}{0.10} \times 100$$

$$= \frac{7.91 \times 10^{-7}}{0.10} \times 100$$

$$= 7.91 \times 10^{-4}\%$$

The molar solubility of $Pb(IO_3)_2$ is equal to the additional concentration of Pb^{2+} in solution, or 7.9×10^{-4} mol/L. As expected, we find that $Pb(IO_3)_2$ 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 error that is unacceptably large, then we can extend the process of making and evaluating approximations.

Example 6.10

Calculate the solubility of $Pb(IO_3)_2$ in 1.0×10^{-4} M $Pb(NO_3)_2$.

SOLUTION

If we let x equal the change in the concentration of Pb^{2+}, then the equilibrium concentrations of Pb^{2+} and IO_3^- are

$$[Pb^{2+}] = 1.0 \times 10^{-4} + x \quad \text{and} \quad [IO_3^-] = 2x$$

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, let's make the following assumption

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

Solving for x gives its value as 2.50×10^{-5}; however, when we substitute this value for x back, we find that the calculated concentration of Pb^{2+} at equilibrium

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

is 25% greater than our assumption of 1.0×10^{-4} M. This error is unreasonably large.

Rather than shouting in frustration, let's make a new assumption. Our first assumption—that the concentration of Pb^{2+} is 1.0×10^{-4} M—was too small. The calculated concentration of 1.25×10^{-4} M, therefore, probably is a too large, but closer to the correct concentration than was our first assumption. For our second approximation, let's assume that

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

Substituting into equation 6.33 and solving for x gives its value as 2.24×10^{-5}. The resulting concentration of Pb^{2+} is

$$[Pb^{2+}] = 1.0 \times 10^{-4} + 2.24 \times 10^{-5} = 1.22 \times 10^{-4} \text{ M}$$

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

$$[Pb^{2+}] = 1.2 \times 10^{-4} \text{ M} \quad \text{and} \quad [IO_3^-] = 4.5 \times 10^{-5} \text{ M}$$

and the molar solubility of $Pb(IO_3)_2$ is 2.2×10^{-5} mol/L. This iterative approach to solving the problems is known as the METHOD OF SUCCESSIVE APPROXIMATIONS.

Practice Exercise 6.8

Calculate the molar solubility for Hg_2Cl_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 $Pb(IO_3)_2$ in a solution of $Pb(NO_3)_2$ is more complicated than calculating its solubility in deionized water. The calculation, however, is still relatively easy to organize and the simplifying assumption are 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.

In addition to equilibrium constant expressions, two other equations are important to this systematic approach to solving an equilibrium problem. The first of these equations is a MASS BALANCE EQUATION, which simply is a statement that matter is conserved during a chemical reaction. In a solution of acetic acid, for example, the combined concentrations of the conjugate weak acid, CH_3COOH, and the conjugate weak base, CH_3COO^-, must equal acetic acid's initial concentration, C_{CH_3COOH}.

Table 6.1 Systematic Approach to Solving Equilibrium Problems

Step 1:	Write all relevant equilibrium reactions and equilibrium constant expressions.
Step 2:	Count the unique species that appear 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.
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 of 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.

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

$$HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)$$
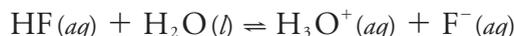
for which the equilibrium constant expression is

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4} \qquad 6.35$$

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

$$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \qquad 6.36$$

Counting unknowns, we find four: $[HF]$, $[F^-]$, $[H_3O^+]$, and $[OH^-]$. To solve this problem we need two additional equations. These equations are a mass balance equation on hydrofluoric acid

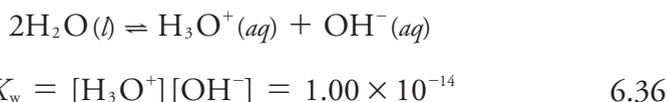$$C_{HF} = [HF] + [F^-] = 1.0 \text{ M} \qquad 6.37$$

and a charge balance equation

$$[H_3O^+] = [OH^-] + [F^-] \qquad 6.38$$

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, we know that the solution is acidic. For an acidic solution it is reasonable to assume that

$$[H_3O^+] >> [OH^-]$$

which simplifies the charge balance equation to

$$[H_3O^+] = [F^-] \qquad 6.39$$

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

$$[HF] >> [F^-]$$

which simplifies the mass balance equation to

$$C_{HF} = [HF] = 1.0 \text{ M} \qquad 6.40$$

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_3O^+ gives us

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{[H_3O^+][H_3O^+]}{C_{HF}} = \frac{[H_3O^+]^2}{C_{HF}} = 6.8 \times 10^{-4}$$

Step 1: Write all relevant equilibrium reactions and equilibrium constant expressions.

Step 2: Count the unique species that appear 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.

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.

$$[H_3O^+] = \sqrt{K_a C_{HF}} = \sqrt{(6.8 \times 10^{-4})(1.0)} = 2.6 \times 10^{-2}$$

Before accepting this answer, we must verify our assumptions. The first assumption is that $[OH^-]$ is significantly smaller than $[H_3O^+]$. Using equation 6.36, we find that

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{2.6 \times 10^{-2}} = 3.8 \times 10^{-13}$$

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

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

Because $[F^-]$ is 2.60% of C_{HF}, this assumption also is acceptable. Given that $[H_3O^+]$ is 2.6×10^{-2} M, the pH of 1.0 M HF is 1.59.

How does the calculation change if we require that the error introduced in our assumptions be less than ±1%? In this case we no longer can assume that $[HF] \gg [F^-]$ and we cannot simplify the mass balance equation. Solving the mass balance equation for $[HF]$

$$[HF] = C_{HF} - [F^-] = C_{HF} - [H_3O^+]$$

and substituting into the K_a expression along with equation 6.39 gives

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

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

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

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

$$x = 2.57 \times 10^{-2} \quad \text{or} \quad -2.64 \times 10^{-2}$$

Only the positive root is chemically significant because the negative root gives a negative concentration for H_3O^+. Thus, $[H_3O^+]$ is 2.57×10^{-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 NH_3. State any assumptions you make in solving the problem, limiting the error for any assumption to $\pm 5\%$. The K_b value for NH_3 is 1.75×10^{-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 that contains 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^-.

pH OF 0.10 M ALANINE HYDROCHLORIDE (H_2L^+)

Alanine hydrochloride is the salt of the diprotic weak acid H_2L^+ and Cl^-. Because H_2L^+ 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 H_2L^+ and L^- are so far apart, we can assume that a solution of H_2L^+ will not contain a significant amount of L^-. As a result, we can treat H_2L^+ 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 H_2L^+ and L^- are so far apart, we can assume that a solution of L^- will not contain a significant amount of H_2L^+. 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 either
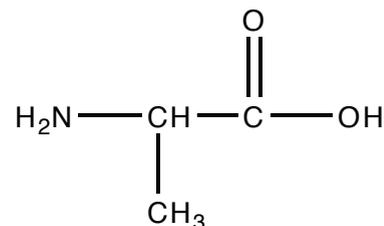

Figure 6.12 Structure of the amino acid alanine, which has pK_a values of 2.348 (–COOH) and 9.867 (–NH$_2$).

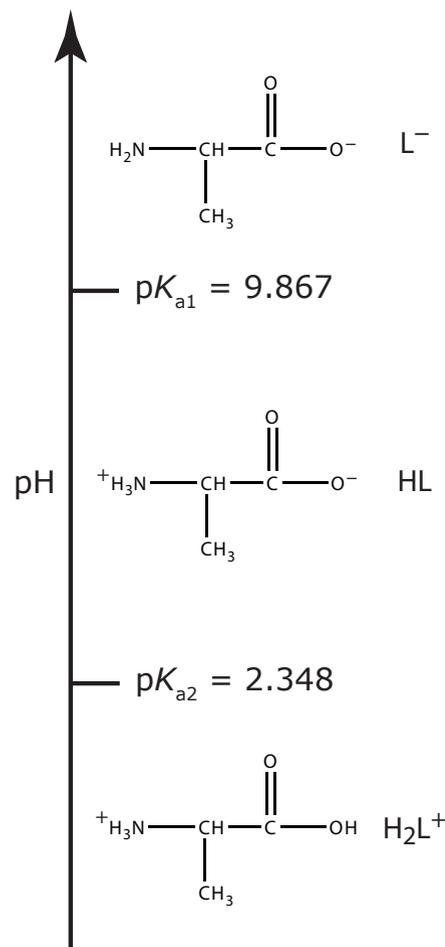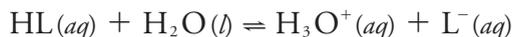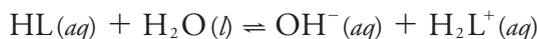**Figure 6.13** Ladder diagram for alanine.

H_2L^+ or L^-. To calculate the solution's pH we must consider alanine's acid dissociation reaction

$$HL\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + L^-\,(aq)$$

and its base dissociation reaction

$$HL\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + H_2L^+\,(aq)$$

and, 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—$[H_2L^+]$, $[HL]$, $[L^-]$, $[H_3O^+]$, and $[OH^-]$—for which we need five equations. These equations are K_{a2} and K_{b2} for alanine

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

$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{[OH^-][H_2L^+]}{[HL]}$$

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 little of it will dissociate and that

$$[HL] \gg [H_2L^+] + [L^-]$$

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 solve 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 $[L^-]$, and 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

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

$$[H_3O^+]^2 = \frac{(K_{a2}C_{HL} + K_w)}{\dfrac{C_{HL}}{K_{a1}} + 1} = \frac{K_{a1}(K_{a2}C_{HL} + K_w)}{C_{HL} + K_{a1}}$$

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

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

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

For a solution of 0.10 M alanine the $[H_3O^+]$ is

$$[H_3O^+] = \sqrt{(4.487 \times 10^{-3})(1.358 \times 10^{-10})} = 7.806 \times 10^{-7} \text{ M}$$

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 $\pm 5\%$ 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_2O, and the metal-ligand complexation chemistry between Ag^+ and NH_3.

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

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

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$
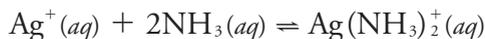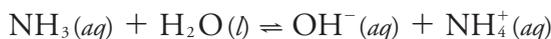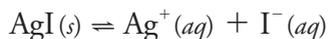
This leaves us with seven unknowns—$[Ag^+]$, $[I^-]$, $[NH_3]$, $[NH_4^+]$, $[OH^-]$, $[H_3O^+]$, and $[Ag(NH_3)_2^+]$—and a need for seven equations. Four of the equations we need to solve this problem are the equilibrium constant expressions

$$K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17} \qquad\qquad 6.41$$

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

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

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

We still need three additional equations. The first of these equations is a mass balance for NH_3.

$$C_{NH_3} = [NH_3] + [NH_4^+] + 2 \times [Ag(NH_3)_2^+] \qquad 6.45$$

In writing this mass balance equation we multiply the concentration of $Ag(NH_3)_2^+$ by two since there are two moles of NH_3 per mole of $Ag(NH_3)_2^+$. The second additional equation is a mass balance between iodide and silver. Because AgI is the only source of I^- and Ag^+, each iodide in solution must have an associated silver ion, which may be Ag^+ or $Ag(NH_3)_2^+$; thus

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

Finally, we include a charge balance equation.

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

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

Assumption One. Because the formation of the $Ag(NH_3)_2^+$ complex is so favorable (β_2 is 1.7×10^7), there is very little free Ag^+ in solution and it is reasonable to assume that

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

Assumption Two. Because NH_3 is a weak base we may reasonably assume that most uncomplexed ammonia remains as NH_3; thus

$$[NH_4^+] << [NH_3]$$

Assumption Three. Because K_{sp} for AgI is significantly smaller than β_2 for $Ag(NH_3)_2^+$, the solubility of AgI probably is small enough that very little ammonia is needed to form the metal–ligand complex; thus

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

As we use these assumptions to simplify the algebra, let's set $\pm 5\%$ as the limit for error.

Assumption two and assumption three suggest that the concentration of NH_3 is much larger than the concentrations of either NH_4^+ or $Ag(NH_3)_2^+$, which allows us to simplify the mass balance equation for NH_3 to

$$C_{NH_3} = [NH_3] \qquad 6.48$$

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

$$[I^-] = [Ag(NH_3)_2^+] \qquad\qquad 6.49$$

Now we are ready to combine equations and to solve the problem. We begin by solving equation 6.41 for $[Ag^+]$ and substitute it into β_2 (equation 6.44), which leaves us with

$$\beta_2 = \frac{[Ag(NH_3)_2^+][I^-]}{K_{sp}[NH_3]^2} \qquad\qquad 6.50$$

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

$$\beta_2 = \frac{[I^-]^2}{K_{sp}(C_{NH_3})^2} \qquad\qquad 6.51$$

Solving equation 6.51 for $[I^-]$ gives

$$[I^-] = C_{NH_3}\sqrt{\beta_2 K_{sp}} =$$
$$(0.10)\sqrt{(1.7\times10^7)(8.3\times10^{-17})} = 3.76\times10^{-6}\ M$$

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

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

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3\times10^{-17}}{3.76\times10^{-6}} = 2.2\times10^{-11}\ M$$

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

$$[Ag(NH_3)_2^+] = [I^-] - [Ag^+] =$$
$$3.76\times10^{-6} - 2.2\times10^{-11} = 3.76\times10^{-11}\,M$$

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

$$[NH_3] = \sqrt{\frac{[Ag(NH_3)_2^+]}{[Ag^+]\beta_2}} = \sqrt{\frac{3.76\times10^{-6}}{(2.2\times10^{-11})(1.7\times10^7)}} = 0.10\ M$$

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 significantly smaller than $[NH_3]$. Our third assumption that $[Ag(NH_3)_2^+]$ is significantly smaller than $[NH_3]$ also is reasonable.

6H   Buffer Solutions

Adding as little as 0.1 mL of concentrated HCl to a liter of H_2O shifts the pH from 7.0 to 3.0. Adding the same amount of HCl to a liter of a solution that 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?

Did you notice that our solution to this problem did not make use of equation 6.47, the charge balance equation? The reason for this is that we did not try to solve for the concentration of all seven species. If we need to know the reaction mixture's complete composition at equilibrium, then we will need to incorporate the charge balance equation into our solution.

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

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$$
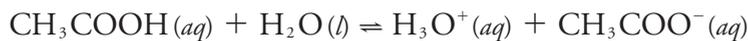
and its corresponding acid dissociation constant

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5} \qquad 6.52$$

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

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} \qquad 6.53$$

$$pH = 4.76 + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

Buffering occurs because of the logarithmic relationship between pH and the concentration ratio 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 $[CH_3COO^-]/[CH_3COOH]$ 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.

The ratio $[CH_3COO^-]/[CH_3COOH]$ becomes 0.9/1.1 = 0.818 and the pH becomes

$$pH = 4.76 + \log(0.818) = 4.67$$

6H.1 Systematic Solution to Buffer Problems

Equation 6.53 is written in terms of the equilibrium concentrations of CH_3COOH and of CH_3COO^-. 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 soluble salt of its conjugate weak base, NaA.

$$NaA\,(s) \longrightarrow Na^+\,(aq) + A^-\,(aq)$$

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

$$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$
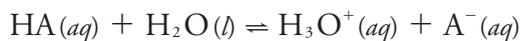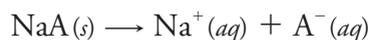
Because the concentrations of Na^+, A^-, HA, H_3O^+, and OH^- are unknown, we need five equations to define the solution's composition. Two of these equations are the equilibrium constant expressions for HA and H_2O.

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

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

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

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

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

and a charge balance equation

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

Substituting equation 6.56 into equation 6.57 and solving for $[A^-]$ gives

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

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

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

Finally, we substitute equations 6.58 and 6.59 into equation 6.54 and solve for pH to arrive at a general equation for a buffer's pH.

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

If the initial concentrations of the weak acid, C_{HA}, and the weak base, C_{NaA}, are significantly greater than $[H_3O^+]$ and $[OH^-]$, then we can simplify the general equation to the HENDERSON–HASSELBALCH EQUATION.

$$pH = pK_a + \log\frac{C_{NaA}}{C_{HA}} \qquad 6.60$$

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 NH_3 and 0.030 M in NH_4Cl. What is the pH after we add 1.0 mL of 0.10 M NaOH to 0.10 L of this buffer?

SOLUTION

The acid dissociation constant for NH_4^+ is 5.70×10^{-10}, which is a pK_a of 9.24. Substituting the initial concentrations of NH_3 and NH_4Cl into equation 6.60 and solving, we find that the buffer's pH is

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

Adding NaOH converts a portion of the NH_4^+ to NH_3 as a result of the following reaction

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + NH_3(aq)$$
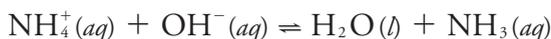
Because this reaction's equilibrium constant is so large (it is 5.7×10^4), we may treat the reaction as if it goes to completion. The new concentrations of NH_4^+ and NH_3 are

$$C_{NH_4^+} = \frac{mol\ NH_4^+ - mol\ OH^-}{V_{total}}$$

$$C_{NH_4^+} = \frac{(0.030\ M)(0.10\ L) - (0.10\ M)(1.0 \times 10^{-3}\ L)}{0.10\ L + 1.0 \times 10^{-3}\ L} = 0.029\ M$$

Lawrence Henderson (1878-1942) first developed a relationship between $[H_3O^+]$, $[HA]$, and $[A^-]$ while studying the buffering of blood. Kurt Hasselbalch (1874-1962) modified Henderson's equation by transforming it to the logarithmic form shown in equation 6.60.

The assumptions that lead to equation 6.60 result in a minimal error in pH ($<\pm 5\%$) for larger concentrations of HA and A^-, for concentrations of HA and A^- that are similar in magnitude, and for weak acid's with pK_a values closer to 7. For most problems in this textbook, equation 6.60 provides acceptable results. Be sure, however, to test your assumptions.

For a discussion of the Henderson–Hasselbalch equation, including the error inherent in equation 6.60, see Po, H. N.; Senozan, N. M. "The Henderson–Hasselbalch Equation: Its History and Limitations," *J. Chem. Educ.* **2001**, *78*, 1499–1503.

With a pH of 9.06, the concentration of H_3O^+ is 8.71×10^{-10} and the concentration of OH^- is 1.15×10^{-5}. Because both of these concentrations are much smaller than either C_{NH_3} or C_{NH_4Cl}, the approximations used to derive equation 6.60 are reasonable.

The equilibrium constant for this reaction is $(K_b)^{-1}$.

$$C_{NH_3} = \frac{\text{mol } NH_3 + \text{mol } OH^-}{V_{total}}$$

$$C_{NH_3} = \frac{(0.020 \text{ M})(0.10 \text{ L}) + (0.10 \text{ M})(1.0 \times 10^{-3} \text{ L})}{0.10 \text{ L} + 1.0 \times 10^{-3} \text{ L}} = 0.021 \text{ M}$$

Substituting these concentrations into the equation 6.60 gives a pH of

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

Practice Exercise 6.12

Calculate the pH of a buffer that is 0.10 M in KH_2PO_4 and 0.050 M in Na_2HPO_4. What is the pH after we add 5.0 mL of 0.20 M HCl to 0.10 L of this buffer. Use Appendix 11 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, for malonic acid ($pK_{a1}=2.85$ and $pK_{a1}=5.70$) we can prepare buffers with pH values of

$$pH = 2.85 + \log\frac{C_{HM^-}}{C_{H_2M}}$$

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

where H_2M, HM^- and M^{2-} are malonic acid's different acid–base forms.

Although our treatment of buffers is based on acid–base chemistry, we can extend buffers to equilibria that involve complexation or redox reactions. For example, the Nernst equation for a solution that contains Fe^{2+} and Fe^{3+} is similar in form to the Henderson-Hasselbalch equation.

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

A solution that contains similar concentrations of Fe^{2+} and Fe^{3+} is buffered to a potential near the standard state reduction potential for 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 way to visualize 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

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

Substituting these ratios into the Henderson–Hasselbalch equation

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

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

shows that an acid–base buffer works over a pH range of $\text{p}K_a \pm 1$.

Using the same approach, it is easy to show that a metal-ligand complexation buffer for ML_n exists when

$$\text{pL} = \log K_n \pm 1 \quad \text{or} \quad \text{pL} = \log \beta_n \pm \frac{1}{n}$$

pL = –log[L]

where K_n or β_n is the relevant stepwise or overall formation constant. For an oxidizing agent and its conjugate reducing agent, a redox buffer exists when

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

Figure 6.14 shows ladder diagrams with buffer regions for several equilibrium systems.

6H.3 Preparing a Buffer

BUFFER CAPACITY is the ability of a buffer to resist a change in pH when we add to it 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 a significant change in its pH.

Although a higher concentration of buffering agents provides greater buffer capacity, there are reasons for using smaller concentrations, including the formation of unwanted precipitates and the tolerance of biological systems for high concentrations of dissolved salts.
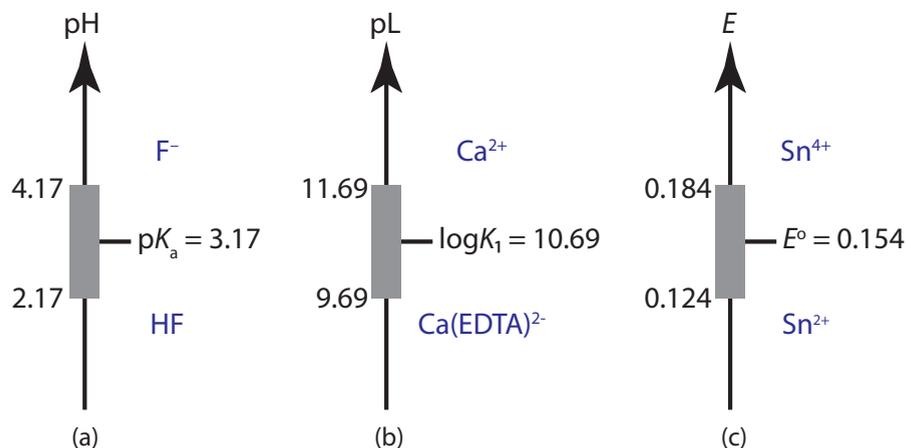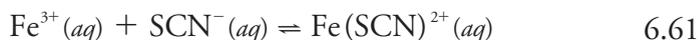

Figure 6.14 Ladder diagrams showing buffer regions shaded in grey for (a) an acid–base buffer of HF and F^-; (b) a metal–ligand complexation buffer of Ca^{2+} and Ca(EDTA)^{2-}; and (c) an oxidation–reduction (redox) buffer of Sn^{4+} and Sn^{2+}.

The relative proportions of a weak acid and a weak base also affects how much the pH changes when we add a strong acid or a strong base. A buffer that is equimolar in weak acid and weak base requires 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.

Buffer solutions are often prepared using standard "recipes" found in the chemical literature.[3] In addition, there are computer programs and on-line calculators to aid in preparing buffers.[4] Perhaps the simplest way to make a buffer, however, is to prepare a solution that contains an appropriate conjugate weak acid and weak base, measure its pH, and then adjust the pH to the desired value by adding small portions of either a strong acid or a strong base.

> 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.

6I   Activity Effects

Careful measurements on the metal–ligand complex $Fe(SCN)^{2+}$ suggest its stability decreases in the presence of inert ions.[5] 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 $Fe(SCN)^{2+}$.

> The 1mM $FeCl_3$ also contains a few drops of concentrated HNO_3 to prevent the precipitation of $Fe(OH)_3$.

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

3   See, for example, (a) Bower, V. E.; Bates, R. G. *J. Res. Natl. Bur. Stand. (U. S.)* **1955**, *55*, 197–200; (b) Bates, R. G. *Ann. N. Y. Acad. Sci.* **1961**, *92*, 341–356; (c) Bates, R. G. *Determination of pH*, 2nd ed.; Wiley-Interscience: New York, 1973.
4   (a) Lambert, W. J. J. Chem. Educ. 1990, 67, 150–153; (b) http://www.bioinformatics.org/JaMBW/5/4/index.html.
5   Lister, M. W.; Rivington, D. E. *Can. J. Chem.* **1995**, *33*, 1572–1590.

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.

(a)   (b)
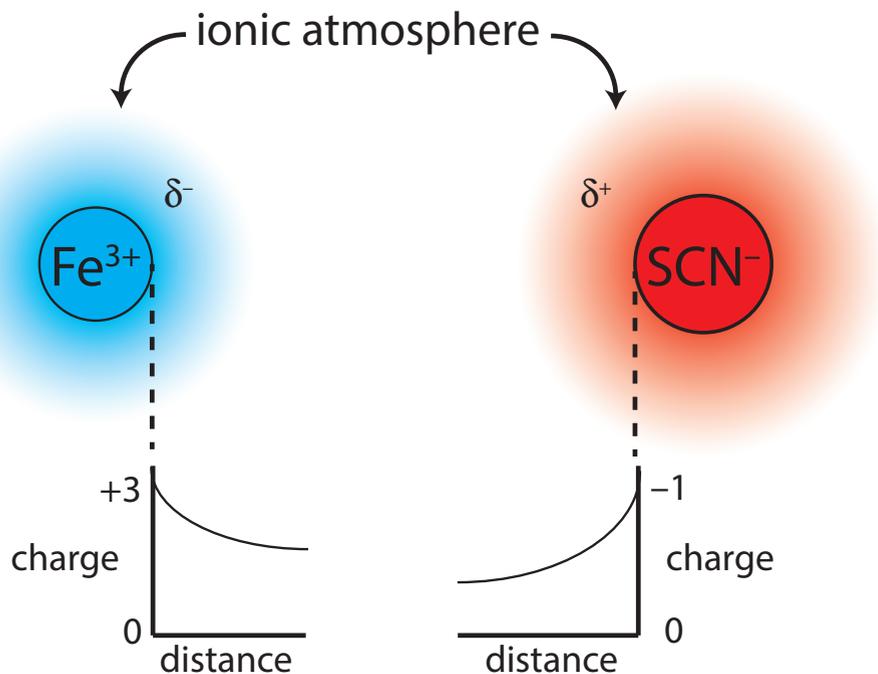
Figure 6.16 Ions of Fe^{3+} and SCN^- are surrounded by ionic atmospheres with net charges of δ^- and δ^+. Because of these ionic atmospheres, each ion's apparent charge at the edge of its ionic atmosphere is less than the ion's actual charge.

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.

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

Why should adding an inert electrolyte affect a reaction's equilibrium position? We can explain the effect of KNO_3 on the formation of $Fe(SCN)^{2+}$ if we consider 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_3O^+, and OH^-. Although the solution is homogeneous, on average, there are slightly more anions in regions near the Fe^{3+} ions, and slightly more cations in regions near the SCN^- ions. As shown in Figure 6.16, each Fe^{3+} ion and each SCN^- ion is surrounded by an ionic atmosphere of opposite charge (δ^- and δ^+) 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 $Fe(SCN)^{2+}$ is slightly less favorable and the formation constant in equation 6.62 is slightly smaller. Higher concentrations of KNO_3 increase δ^- and δ^+, 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, μ as

$$\mu = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$$

where c_i and z_i are the concentration and charge of the ith ion.

<div style="border: 2px solid green;">

Example 6.13

Calculate the ionic strength of a solution of 0.10 M NaCl. Repeat the calculation for a solution of 0.10 M Na_2SO_4.

SOLUTION

The ionic strength for 0.10 M NaCl is

$$\mu = \frac{1}{2}\{[Na^+] \times (+1)^2 + [Cl^-] \times (-1)^2\}$$

$$\mu = \frac{1}{2}\{(0.10) \times (+1)^2 + (0.10) \times (-1)^2\} = 0.10 \text{ M}$$

For 0.10 M Na_2SO_4 the ionic strength is

$$\mu = \frac{1}{2}\{[Na^+] \times (+1)^2 + [SO_4^{2-}] \times (-2)^2\}$$

$$\mu = \frac{1}{2}\{(0.20) \times (+1)^2 + (0.10) \times (-2)^2\} = 0.30 \text{ M}$$

</div>

In calculating the ionic strengths of these solutions we are ignoring the presence of H_3O^+ and OH^-, and, in the case of Na_2SO_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_3O^+ and OH^- are 1.0×10^{-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_3O^+, OH^-, and HSO_4^- are negligible.

Although we can ignore the presence of H_3O^+, OH^-, and HSO_4^- when we calculate the ionic strength of these two solutions, be aware that an equilibrium reaction can generate ions that might affect the solution's ionic strength.

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_2SO_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, $\Delta G°$, and its equilibrium constant, K.

$$\Delta G° = -RT\ln K$$

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, γ_A.

$$a_A = [A]\gamma_A$$

The true thermodynamic formation constant for $Fe(SCN)^{2+}$, therefore, is

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

Unless otherwise specified, the equilibrium constants in the appendices are thermodynamic equilibrium constants.

A species' ACTIVITY COEFFICIENT 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 a reaction that involves 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 estimate activity coefficients using the EXTENDED DEBYE-HÜCKEL EQUATION

For a gas the proper terms are fugacity and fugacity coefficient, instead of activity and activity coefficient.

$$\log\gamma_A = \frac{-0.51 \times z_A^2 \times \sqrt{\mu}}{1 + 3.3 \times \alpha_A \times \sqrt{\mu}} \qquad 6.63$$

where z_A is the ion's charge, α_A is the hydrated ion's effective diameter in nanometers (Table 6.2), μ is the solution's ionic strength, and 0.51 and 3.3 are constants appropriate for an aqueous solution at 25 °C. A hydrated ion's

Table 6.2 Effective Diameters (α) for Selected Ions

Ion	Effective Diameter (nm)
H_3O^+	0.9
Li^+	0.6
Na^+, IO_3^-, HSO_3^-, HCO_3^-, $H_2PO_4^-$	0.45
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, MnO_4^-	0.35
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	0.3
Cs^+, Tl^+, Ag^+, NH_4^+	0.25
Mg^{2+}, Be^{2+}	0.8
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}	0.6
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5
Pb^{2+}, SO_4^{2-}, SO_3^{2-}	0.45
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}	0.40
Al^{3+}, Fe^{3+}, Cr^{3+}	0.9
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4
Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1
$Fe(CN)_6^{4-}$	0.5

Source: Kielland, J. *J. Am. Chem. Soc.* **1937**, *59*, 1675–1678.

effective 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.

Several features of equation 6.63 deserve our attention. 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 estimate of 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 $Pb(IO_3)_2$ in deionized water, obtaining a result of 4.0×10^{-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 Pb^{2+} and IO_3^-. In calculating the solubility of $Pb(IO_3)_2$ in deionized water, we do not need to account for ionic strength.

But what if we need to know the solubility of $Pb(IO_3)_2$ in a solution that contains other, inert ions? In this case we need to include activity coefficients in our calculation.

Example 6.14

Calculate the solubility of $Pb(IO_3)_2$ in a matrix of 0.020 M $Mg(NO_3)_2$.

SOLUTION

We begin by calculating the solution's ionic strength. Since $Pb(IO_3)_2$ is only sparingly soluble, we will assume we can ignore its contribution to the ionic strength; thus

$$\mu = \frac{1}{2}\{(0.020)(+2)^2 + (0.040)(-1)^2\} = 0.060 \text{ M}$$

Next, we use equation 6.63 to calculate the activity coefficients for Pb^{2+} and IO_3^-.

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

$$\gamma_{Pb^{2+}} = 0.431$$

$$\log\gamma_{IO_3^-} = \frac{-0.51 \times (-1)^2 \times \sqrt{0.060}}{1 + 3.3 \times 0.45 \times \sqrt{0.060}} = -0.0916$$

As is true for any assumption, we need to verify that it does not introduce too much error into our calculation.

6   Davies, C. W. *Ion Association*, Butterworth: London, 1962.

$$\gamma_{IO_3^-} = 0.810$$

Defining the equilibrium concentrations of Pb^{2+} and IO_3^- in terms of the variable x

Concentrations	$Pb(IO_3)_2$ (s)	$\rightleftharpoons$	Pb^{2+} (aq)	+	$2\,IO_3^-$ (aq)
Initial	solid		0		0
Change	solid		$+x$		$+2x$
Equilibrium	solid		x		$2x$

and substituting into the thermodynamic solubility product for $Pb(IO_3)_2$ leaves us with

$$K_{sp} = a_{Pb^{2+}} \times a_{IO_3^-}^2 = \gamma_{Pb^{2+}}[Pb^{2+}] \times \gamma_{IO_3^-}^2[IO_3^-]^2 = 2.5 \times 10^{-13}$$

$$K_{sp} = (0.431)(x)(0.810)^2(2x)^2 = 2.5 \times 10^{-13}$$

$$K_{sp} = 1.131x^3 = 2.5 \times 10^{-13}$$

Solving for x gives 6.0×10^{-5} and a molar solubility of 6.0×10^{-5} mol/L for $Pb(IO_3)_2$. If we ignore activity, as we did in our underlined earlier calculation, we report the molar solubility as 4.0×10^{-5} mol/L. Failing to account for activity in this case underestimates the molar solubility of $Pb(IO_3)_2$ by 33%.

Practice Exercise 6.13

Calculate the molar solubility of Hg_2Cl_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.

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 we develop an analytical method; however, it only is when we complete an analysis and evaluate the results that can we judge whether our theory matches reality. In the end, work in the laboratory is the most critical step in developing a reliable analytical method.

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

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The solution's equilibrium composition is

$$[Pb^{2+}] = 6.0 \times 10^{-5}\ M$$
$$[IO_3^-] = 1.2 \times 10^{-4}\ M$$
$$[Mg^{2+}] = 0.020\ M$$
$$[NO_3^-] = 0.040\ M$$

Because the concentrations of both Pb^{2+} and IO_3^- are much smaller than the concentrations of Mg^{2+} and NO_3^- our decision to ignore the contribution of Pb^{2+} and IO_3^- to the ionic strength is reasonable.

How do we handle the calculation if we can not ignore the concentrations of Pb^{2+} and IO_3^- when calculating the ionic strength. One approach is to use the method of successive approximations. First, we recalculate the ionic strength using the concentrations of all ions, including Pb^{2+} and IO_3^-. Next, we recalculate the activity coefficients for Pb^{2+} and IO_3^- using this new ionic strength 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

$$pH = -\log[H_3O^+]$$

Now we see that the correct definition is

$$pH = -\log a_{H_3O^+}$$

$$pH = -\log \gamma_{H_3O^+}[H_3O^+]$$

Failing to account for the effect of ionic strength can lead to a significant error in the reported concentration of H_3O^+. For example, if the pH of a solution is 7.00 and the activity coefficient for H_3O^+ is 0.90, then the concentration of H_3O^+ is 1.11×10^{-7} M, not 1.00×10^{-7} M, an error of +11%. Fortunately, when we develop and carry out an analytical method, we are more interested in controlling pH than in calculating $[H_3O^+]$. As a result, the difference between the two definitions of pH rarely is of significant concern.

Although we focus here on the use of Excel and R to solve equilibrium problems, you also can use WolframAlpha; for details, see Cleary, D. A. "Use of WolframAlpha in Equilibrium Calculations," *Chem. Educator*, **2014**, *19*, 182–186.

cubic equation (or a higher-order equation) that is more challenging 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 the chemically significant root of a polynomial equation. 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 $PB(IO_3)_2$ IN 0.10 M $PB(NO_3)_2$

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 Pb^{2+}. Although there are several approaches for solving cubic equations with paper and pencil, none are computationally easy. One approach is to iterate in on the answer by finding two values of x, one that leads to a result larger than 2.5×10^{-13} and one that gives a result smaller than 2.5×10^{-13}. With boundaries established for the value of x, we 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 cell B1. Because $Pb(IO_3)_2$ is not very soluble, we expect that x is small and set our initial guess to 0. 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

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.

(a)

	A	B
1	x =	0
2	function	=4*b1^3+0.4*b1^2−2.5e−13

(b)

	A	B
1	x =	7.90565E−07
2	function	−5.71156E−19

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 requires a bit more thought. The Solver function uses the precision to decide when to stop its search, doing so when

$$|expected\ value - calculated\ value| \times 100 = precision\ (\%)$$

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 2.5×10^{-13}, accepting the Solver's default precision of 1×10^{-6} will stop the search after one cycle. To be safe, let's set the precision to 1×10^{-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 7.91×10^{-7} M for the solubility of $Pb(IO_3)_2$.

Be sure to evaluate the reasonableness of Solver's answer. If necessary, repeat the process using a smaller value for the precision.

EXAMPLE 2: pH OF 1.0 M HF

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

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4}$$

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

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

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

Next, we made two assumptions that allowed us to simplify the problem to an equation that is easy to solve.

$$[H_3O^+] = \sqrt{K_a C_{HF}} = \sqrt{(6.8 \times 10^{-4})(1.0)} = 2.6 \times 10^{-2}$$

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

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - (K_a C_{HF} + K_w)[H_3O^+] - K_a K_w = 0 \qquad 6.64$$

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 four equations simultane-ously by iterating in on values for [HF], [F⁻], [H₃O⁺], and [OH⁻]. Fig-ure 6.18a shows a spreadsheet for this purpose. The cells in the first row contain initial guesses for the equilibrium pH. Using the ladder diagram in Figure 6.14, 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 $[H_3O^+]$, 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

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

and entering it in the last row; the values in these cells gives the calculation's error for each pH.

(a)

	A	B	C	D
1	pH =	3.00	2.00	1.00
2	[H3O+] =	=10^–b1	=10^–c1	=10^–d1
3	[OH-] =	=1e–14/b2	=1e–14/c2	=1e–14/d2
4	[F-] =	=b2 – b3	=c2 – c3	=d2 – d3
5	[HF] =	=(b2 * b4)/6.8e–4	=(c2 * c4)/6.8e–4	=(d2 * d4)/6.8e–4
6	error	=b5 + b4 – 1	=c5 + c4 – 1	=d5 + d4 – 1

(b)

	A	B	C	D
1	pH =	3.00	2.00	1.00
2	[H3O+] =	1.00E-03	1.00E-02	1.00E-1
3	[OH-] =	1.00E–11	1.00E–12	1.00E–13
4	[F-] =	1.00E–03	1.00E–02	1.00E–01
5	[HF] =	0.001470588	0.147058824	14.70588235
6	error	-9.98E-01	-8.43E-01	1.38E+01

(c)

	A	B	C	D
1	pH =	1.59	1.58	1.57
2	[H3O+] =	2.57E-02	2.63E-02	2.69E-02
3	[OH-] =	3.89E-13	3.80E-13	3.72E-13
4	[F-] =	2.57E-02	2.63E-02	2.69E-02
5	[HF] =	0.971608012	1.017398487	1.065347
6	error	-2.69E-03	4.37E-02	9.23E-02

Figure 6.18 Spreadsheet demonstrating the use of Excel to solve a set of simultaneous equations. The spreadsheet in (a) shows the initial guess for $[H_3O^+]$ in the first row, and the formulas that we enter in rows 2–6. Enter the formulas in cells B2–B6 and then copy and paste them into the appropriate cells in the remaining columns. As shown in (b), Excel replaces the formulas with their equivalent values. The spreadsheet in (c) shows the results after our final iteration. See the text for further details.

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 their combined concentrations are too large. The actual pH, therefore, is between 1.00 and 2.00. 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 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 $Pb(IO_3)_2$ IN 0.10 M $Pb(NO_3)_2$

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 Pb^{2+}. Although there are several approaches for solving cubic equations with paper and pencil, none are computationally easy. One approach to solving the problem is to iterate in on the answer by finding two values of x, one that leads to a result larger than 2.5×10^{-13} and one that gives a result smaller than 2.5×10^{-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 **uniroot** command works.

The general form of the **uniroot** command is

$$\mathbf{uniroot}(function, lower, upper, tol)$$

where *function* is an object that contains the equation whose root we seek, *lower* and *upper* are boundaries for the root, and *tol* is the desired precision for the root. To create an object that contains the equation, we rewrite it so that its right-side equals zero.

$$4x^3 + 0.40x^2 - 2.5 \times 10^{-13}$$

You also can solve this set of simultaneous equations using Excel's Solver function. To do so, create the spreadsheet in Figure 6.18a, but omit all columns other than A and B. Select **Solver...** from the **Tools** menu and define the problem by using B6 for *Set Target Cell*, setting its desired value to 0, and selecting B1 for *By Changing Cells:*. You may need to play with the Solver's options to find a suitable solution to the problem, and it is wise to try several different initial guesses.

The Solver function works well for relatively simple problems, such as finding the pH of 1.0 M HF. As problems become more complex and include more unknowns, the Solver function becomes a less reliable tool for solving equilibrium problems.

$root
[1] 7.905663e-07

$f.root
[1] 0

$iter
[1] 46

$estim.prec
[1] 1.827271e-12

Figure 6.19 The summary of R's output from the **uniroot** command. See the text for a discussion of how to interpret the results.

For example, entering

> eqn(2)

passes the value x = 2 to the function and returns an answer of 33.6.

Next, we enter the following code, which defines our cubic equation as a function with the name *eqn*.

> eqn = function(x) {4*x^3 + 0.4*x^2 − 2.5e–13}

Because our equation is a function, the **uniroot** command can send a value of *x* to *eqn* and receive back the equation's corresponding value. Finally, we use the **uniroot** command to find the root.

> **uniroot**(eqn, lower = 0, upper = 0.1, tol = 1e–18)

Because $Pb(IO_3)_2$ is not very soluble, we expect that *x* is small and set the lower limit to 0. The choice for the upper limit is less critical. To ensure that the solution has sufficient precision, we set the tolerance to a value that is smaller than the expected root. Figure 6.19 shows the resulting output. The value *$root* is the equation's root, which is in good agreement with our earlier result of 7.91×10^{-7} for the molar solubility of $Pb(IO_3)_2$. 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 earlier solution to this problem we began by identifying four unknowns and writing out the following four equations.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4}$$

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

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

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

Next, we made two assumptions that allowed us to simplify the problem to an equation that is easy to solve.

$$[H_3O^+] = \sqrt{K_a C_{HF}} = \sqrt{(6.8 \times 10^{-4})(1.0)} = 2.6 \times 10^{-2}$$

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

$$[H_3O^+]^3 + K_a[H_3O^+]^2 -$$
$$(K_a C_{HF} + K_w)[H_3O^+] - K_a K_w = 0$$

that we can solve using the **uniroot** command. Of course, this assumes that we successfully complete the derivation!

Another option is to write a function to solve the four equations simultaneously. Here is the code for this function, which we will call *eval*.

```
> eval = function(pH){
+ h3o = 10^–pH
+ oh = 1e–14/h3o
+ hf = (h3o*f)/6.8e–4
+ error = hf+f–1
+ output = data.frame(pH, error)
+ print(output)
+ }
```

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 $[H_3O^+]$, K_w to calculate $[OH^-]$, the charge balance equation to calculate $[F^-]$, and K_a to calculate $[HF]$. The function then evaluates the solution using the mass balance expression for HF, rewriting it as

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

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, *pH*, can contain many values, which makes it easy to search for a solution. Because HF is an acid, we know that the solution is acidic. This sets an upper limit of 7 for the pH. We also know that the pH of 1.0 M HF is no smaller than 1 as this is the pH if HF was a strong acid. For our first pass, let's enter the following code

```
> pH = c(7, 6, 5, 4, 3, 2, 1)
> eval(pH)
```

which varies the pH within these limits. The result, which is shown in Figure 6.20a, indicates that the pH is less than 2 and greater than 1 because it is in this interval that the error changes sign.

For our second pass, let's 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)
> eval(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.

The open { tells R that we intend to enter our function over several lines. When we press enter at the end of a line, R changes its prompt from > to +, indicating that we are continuing to enter the same command. The close } on the last line indicates that we have completed the function.

The command **data.frame** combines two or more objects into a table.

You can adapt this function to other problems by changing the variable you pass to the function and the equations you include within the function.

A simpler, more compact way to do this is

```
> pH = seq(1,7,1)
> eval(pH)
```

or

```
> eval(seq(1,7,1))
```

where the sequence command has a format of

```
seq(lower limit, upper limit, step size)
```

(a) pH	error	(b) pH	error	(c) pH	error
1 7	-1.0000000	1 2.0	-0.84294118	1 1.60	-0.047002688
2 6	-0.9999990	2 1.9	-0.75433822	2 1.59	-0.002688030
3 5	-0.9999899	3 1.8	-0.61475600	3 1.58	0.043701167
4 4	-0.9998853	4 1.7	-0.39459566	4 1.57	0.092262348
5 3	-0.9975294	5 1.6	-0.04700269	5 1.56	0.143097544
6 2	-0.8429412	6 1.5	0.50221101	6 1.55	0.196313586
7 1	13.8058824	7 1.4	1.37053600	7 1.54	0.252022331
8 0	1470.5882353	8 1.3	2.74406936	8 1.53	0.310340901
		9 1.2	4.91761295	9 1.52	0.371391928
		10 1.1	8.35821730	10 1.51	0.435303816
		11 1.0	13.80588235	11 1.50	0.502211012

Figure 6.20 The output of three iterations to find the pH for a solution of 1.0 M HF. The results are for pH values between (a) 7 and 0, (b) 2.0 and 1.0, and (c) 1.60 M and 1.50. The columns labeled "error" show an evaluation of the mass balance equation for HF, with positive values indicating that the pH is too low and negative values indicating that the pH is too high.

> ### Practice Exercise 6.15
>
> Using R, 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.

6K   Some Final Thoughts on Equilibrium Calculations

In this chapter we developed several tools to evaluate the composition of a system at equilibrium. These tools differ in how precisely they allow us to answer questions involving equilibrium chemistry. They also differ in how easy they are to use. An important part of having several tools to choose from is knowing when to each is most useful. If you need to know whether a reaction if favorable or you need to estimate a solution's pH, then a ladder diagram usually will meet your needs. On the other hand, if you require a more accurate or more precise 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 to know what equilibrium reactions to include. The need to include 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, which makes it easy to overlook an important equilibrium reaction. Commercial and freeware computational programs with extensive databases are available for equilibrium modeling, two examples of which are Visual Minteq (Windows only) and CurTiPot (for Excel); Visual Minteq can model acid–base, solubility, complexation,

and redox equilibria; CurTiPot is limited to acid–base equilibria. Both programs account for the effect of activity.

Finally, a consideration of equilibrium chemistry can only help us decide if a reaction is favorable; however, it does not guarantee that the reaction occurs. How fast a reaction approaches its equilibrium position does not depend on the reaction's equilibrium constant because 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	acid dissociation constant	activity
activity coefficient	amphiprotic	base
base dissociation constant	buffer	buffer capacity
charge balance equation	common ion effect	cumulative formation constant
dissociation constant	enthalpy	entropy
equilibrium	equilibrium constant	extended Debye-Hückel equation
formation constant	Gibb's free energy	half-reaction
Henderson–Hasselbalch equation	ionic strength	ladder diagram
Le Châtelier's principle	ligand	mass balance equation
metal–ligand complex	method of successive approximations	monoprotic
Nernst equation	oxidation	oxidizing agent
pH scale	polyprotic	potential
precipitate	redox reaction	reducing agent
reduction	standard-state	standard potential
steady state	stepwise formation constant	solubility product

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 a sample, separate analytes from interferents, transform an analyte into 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 oxidation–reduction reactions. In a precipitation reaction two or more soluble species

combine to produce an insoluble 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 of which describes 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, β_2, for the metal–ligand complex ML_2, in which both ligands are added to M.

In an oxidation–reduction reaction, one of the reactants is oxidized and another reactant is reduced. Instead of using an equilibrium constants to characterize an oxidation–reduction 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 a reactant or product, or by changing the volume—the system will respond 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 rigorous answer is acceptable, then a ladder diagram may help you estimate the equilibrium system's composition.
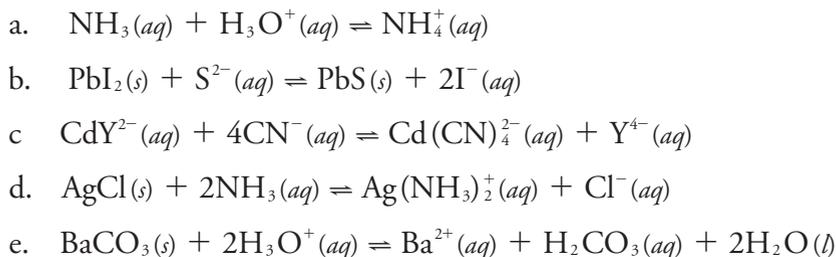
Solutions that contain relatively similar amounts of a weak acid and its conjugate base experience only a small change in pH upon the addition of a small amount of strong acid or of strong base. We call these solutions buffers. A buffer can also be formed using a metal and its metal–ligand complex, or 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, γ. Activity coefficients
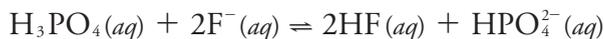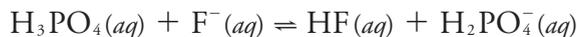
are estimated using the extended Debye-Hückel equation, making possible a more rigorous treatment of equilibria.

6N   Problems

1. Write equilibrium constant expressions for the following reactions. What is the value for each reaction's equilibrium constant?

   a. $NH_3(aq) + H_3O^+(aq) \rightleftharpoons NH_4^+(aq)$

   b. $PbI_2(s) + S^{2-}(aq) \rightleftharpoons PbS(s) + 2I^-(aq)$

   c $CdY^{2-}(aq) + 4CN^-(aq) \rightleftharpoons Cd(CN)_4^{2-}(aq) + Y^{4-}(aq)$

   d. $AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$

   e. $BaCO_3(s) + 2H_3O^+(aq) \rightleftharpoons Ba^{2+}(aq) + H_2CO_3(aq) + 2H_2O(l)$

2. Use a ladder diagram to explain why the first reaction is favorable and why the second reaction is unfavorable.

$$H_3PO_4(aq) + F^-(aq) \rightleftharpoons HF(aq) + H_2PO_4^-(aq)$$

$$H_3PO_4(aq) + 2F^-(aq) \rightleftharpoons 2HF(aq) + HPO_4^{2-}(aq)$$

   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 $[Fe^{3+}] = 0.050$ M, $[Fe^{2+}] = 0.030$ M, $[Sn^{2+}] = 0.015$ M and $[Sn^{4+}] = 0.020$ M.

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$$
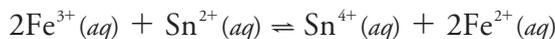
4. Calculate the standard state potential and the equilibrium constant for each of the following redox reactions. Assume that $[H_3O^+]$ is 1.0 M for an acidic solution and that $[OH^-]$ is 1.0 M for a basic solution. Note that these reactions are not balanced. Reactions (a) and (b) are in acidic solution; reaction (c) is in a basic solution.

   a. $MnO_4^-(aq) + H_2SO_3(aq) \rightleftharpoons Mn^{2+}(aq) + SO_4^{2-}(aq)$

   b. $IO_3^-(aq) + I^-(aq) \rightleftharpoons I_2(aq)$

   c. $ClO^-(aq) + I^-(aq) \rightleftharpoons IO_3^-(aq) + Cl^-(aq)$
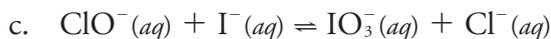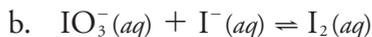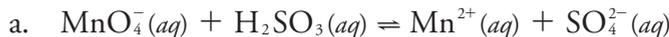
5. One analytical method for determining the concentration of sulfur is to oxidize it to SO_4^{2-} and then precipitate it as $BaSO_4$ by adding $BaCl_2$. The mass of the resulting precipitate is proportional to the amount of sulfur in the original sample. The accuracy of this method depends on the solubility of $BaSO_4$, the reaction for which is shown here.
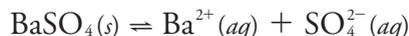
$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Y is the shorthand symbol for EDTA.

For each of the following, predict the affect on the solubility of $BaSO_4$: (a) decreasing the solution's pH; (b) adding more $BaCl_2$; and (c) increasing the solution's volume by adding H_2O.

6. Write a charge balance equation and one or more mass balance equations for the following solutions.

   a. 0.10 M NaCl
   b. 0.10 M HCl
   c. 0.10 M HF
   d. 0.10 M NaH_2PO_4
   e. $MgCO_3$ (saturated solution)
   f. 0.10 M $Ag(CN)_2^-$ (prepared using $AgNO_3$ and KCN)
   g. 0.10 M HCl and 0.050 M $NaNO_2$

7. Use the systematic approach to equilibrium problems to 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. 1.00×10^{-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_5H_5N

8. Construct ladder diagrams for the following diprotic weak acids (H_2A) and estimate the pH of 0.10 M solutions of H_2A, NaHA, and Na_2A.

   a. maleic acid
   b. malonic acid
   c. succinic acid

9. Use the systematic approach to solving equilibrium problems to calculate the pH of (a) malonic acid, H_2A; (b) sodium hydrogenmalonate, NaHA; and (c) sodium malonate, Na_2A. Be sure to state and justify any assumptions you make in solving the problems.

10. Ignoring activity effects, calculate the molar solubility of Hg_2Br_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_2Br_2
   b. 0.025 M $Hg_2(NO_3)_2$ saturated with Hg_2Br_2
   c. 0.050 M NaBr saturated with Hg_2Br_2

11. The solubility of CaF_2 is controlled by the following two reactions

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^-\,(aq)$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$
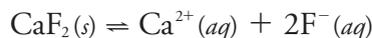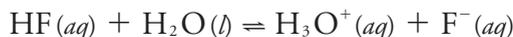
Calculate the molar solubility of CaF_2 in a solution that is buffered to a pH of 7.00. Use a ladder diagram to help simplify the calculations. How would your approach to this problem change if the pH is buffered to 2.00? What is the solubility of CaF_2 at this pH? Be sure to state and justify any assumptions you make in solving the problems.

12. Calculate the molar 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 with an initial pH of 7.00? Be sure to state and justify any assumptions you make in solving the problem.

13. Calculate the solubility of Ag_3PO_4 in a solution buffered to a pH of 9.00. 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.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(aq)$$
$$AgCl(aq) + Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)$$
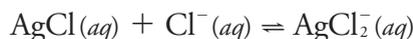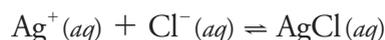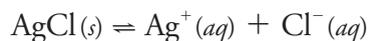
Be sure to state and justify any assumptions you make in solving the problem.

15. Calculate the ionic strength of the following solutions

    a. 0.050 M NaCl
    b. 0.025 M $CuCl_2$
    c. 0.10 M Na_2SO_4

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 $Ca_3(PO_4)_2$ to have its minimum solubility?

18. Construct ladder diagrams for the following systems, each of which consists of two or three equilibrium reactions. Using your ladder diagrams, identify all reactions that are likely to occur in each system?

    a. HF and H_3PO_4
    b. $Ag(CN)_2^-$, $Ni(CN)_4^{2-}$, and $Fe(CN)_6^{3-}$
    c. $Cr_2O_7^{2-}/Cr^{3+}$ and Fe^{3+}/Fe^{2+}

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.   100.0 mL of 0.025 M formic acid and 0.015 M sodium formate
b.   50.00 mL of 0.12 M NH_3 and 3.50 mL of 1.0 M HCl
c.   5.00 g of Na_2CO_3 and 5.00 g of $NaHCO_3$ diluted to 0.100 L

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

$$M\,(aq) + L\,(aq) \rightleftharpoons ML\,(aq)$$
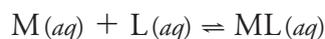
for which the formation constant is 1.5×10^8. (a) Derive an equation similar to the Henderson–Hasselbalch equation that relates pM to the concentrations of L and ML. (b) What is the pM for a solution that contains 0.010 mol of M and 0.020 mol of L? (c) What is pM if you add 0.002 mol of M to this solution? 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 that contains 0.010 mol of Fe^{3+} and 0.015 mol of Fe^{2+}. 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

c.   the pH of 0.10 M fumaric acid

25. Derive equation 6.64 for the rigorous solution to the pH of 0.1 M HF.

6O   Solutions to Practice Exercises

Practice Exercise 6.1

The overall reaction is equivalent to
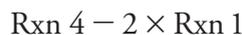
$$\text{Rxn } 4 - 2 \times \text{Rxn } 1$$

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

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

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Practice Exercise 6.2

The K_b for hydrogen oxalate is

$$K_{b,HC_2O_4^-} = \frac{K_w}{K_{a,H_2C_2O_4}} = \frac{1.00 \times 10^{-14}}{5.60 \times 10^{-2}} = 1.79 \times 10^{-13}$$

and the K_b for oxalate is

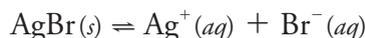$$K_{b,C_2O_4^{2-}} = \frac{K_w}{K_{a,HC_2O_4^-}} = \frac{1.00 \times 10^{-14}}{5.42 \times 10^{-5}} = 1.85 \times 10^{-10}$$

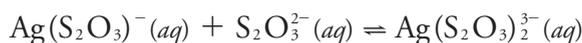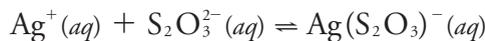As we expect, the K_b value for $C_2O_4^{2-}$ is larger than that for $HC_2O_4^-$.

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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}.

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

The remaining two reactions are the stepwise formation of $Ag(S_2O_3)_2^{3-}$, which we characterize by K_1 and K_2.

$$Ag^+(aq) + S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)^-(aq)$$

$$Ag(S_2O_3)^-(aq) + S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$$

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

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

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Practice Exercise 6.4

The two half-reactions are the oxidation of Fe^{2+} and the reduction of MnO_4^-.

$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$
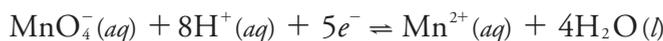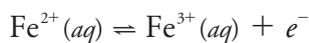
From Appendix 13, the standard state reduction potentials for these half-reactions are

$$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771\,V \quad \text{and} \quad E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\,V$$

(a) The standard state potential for the reaction is

$$E^\circ = E^\circ_{MnO_4^-/Mn^{2+}} - E^\circ_{Fe^{3+}/Fe^{2+}} = 1.51\,V - 0.771\,V = 0.74\,V$$

(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 3.5×10^{62}.

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

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$$

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

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Practice Exercise 6.5

pH

Figure 6.21 Ladder diagram for Practice Exercise 6.5

From Appendix 11, the pK_a values for H_2CO_3 are 6.352 and 10.329. The ladder diagram for H_2CO_3 is shown in Figure 6.21. The predominate form at a pH of 7.00 is HCO_3^-.

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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 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

moles p-nitrophenolate = 0.090 – 0.040 = 0.050 mol

moles p-nitrophenol = 0.040 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.

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Practice Exercise 6.7

When Hg_2Cl_2 dissolves, two Cl^- are produced for each ion of Hg_2^{2+}. If we assume x is the change in the molar concentration of Hg_2^{2+}, then the change in the molar concentration of Cl^- is $2x$. The following table helps us keep track of our solution to this problem.
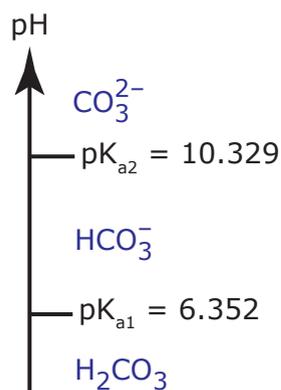
Concentrations	$Hg_2Cl_2\,(s)$	$\rightleftharpoons$	$Hg_2^{2+}\,(aq)$	$+$	$2Cl^-\,(aq)$
Initial	solid		0		0
Change	solid		$+x$		$+2x$
Equilibrium	solid		x		$2x$

Substituting the equilibrium concentrations into the K_{sp} expression for Hg_2Cl_2 gives

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (x)(2x)^2 = 4x^3 = 1.2 \times 10^{-18}$$

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

Substituting x back into the equilibrium expressions for Hg_2^{2+} and Cl^- gives their concentrations as

$$[Hg_2^{2+}] = x = 6.7 \times 10^{-7}\ M \qquad [Cl^-] = 2x = 1.3 \times 10^{-6}\ M$$

The molar solubility is equal to $[Hg_2^{2+}]$, or 6.7×10^{-7} mol/L.

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Practice Exercise 6.8

We begin by setting up a table to help us keep track of the concentrations of Hg_2^{2+} and Cl^- as this system moves toward and reaches equilibrium.

Concentrations	$Hg_2Cl_2\,(s)$	$\rightleftharpoons$	$Hg_2^{2+}\,(aq)$	$+$	$2Cl^-\,(aq)$
Initial	solid		0		0.10
Change	solid		$+x$		$+2x$
Equilibrium	solid		x		$0.10+2x$

Substituting the equilibrium concentrations into the K_{sp} expression for Hg_2Cl_2 leaves us with a difficult to solve cubic equation.

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (x)(0.10 + 2x)^2 = 4x^3 + 0.40x^2 + 0.010x$$

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

$$[Cl^-] = 0.10 + 2x \approx 0.10$$

This simplifies our problem to

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (x)(0.10)^2 = 0.010x = 1.2 \times 10^{-18}$$

which gives the value of x as 1.2×10^{-16} M. The difference between the actual concentration of Cl^-, which is $(0.10+2x)$ M, and our assumption that it is 0.10 M introduces an error of 2.4×10^{-13}%. This is a negligible error. The molar solubility of Hg_2Cl_2 is the same as the concentration of Hg_2^{2+}, or 1.2×10^{-16} M. As expected, the molar solubility in 0.10 M NaCl is less than 6.7×10^{-7} mol/L, which is its solubility in water (see <u>solution</u> to <u>Practice Exercise 6.7</u>).

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Practice Exercise 6.9

To help us determine what ions are in solution, let's write down all the reaction needed to prepare the solutions and the equilibrium reactions that take place within these solutions. These reactions are the dissolution of two soluble salts
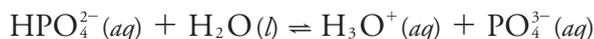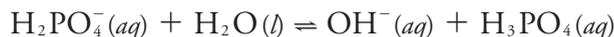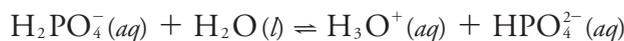
$$KH_2PO_4(s) \longrightarrow K^+(aq) + H_2PO_4^-(aq)$$

$$NaHPO_4(s) \longrightarrow Na^+(aq) + HPO_4^{2-}(aq)$$
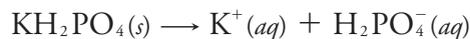
and the acid–base dissociation reactions for $H_2PO_4^-$, HPO_4^{2-}, and H_2O.

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3PO_4(aq)$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

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

Note that we did not include the base dissociation reaction for HPO_4^{2-} because we already accounted for its product, $H_2PO_4^-$, in another reaction. The mass balance equations for K^+ and Na^+ are straightforward

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

but the mass balance equation for phosphate takes a bit more thought. Both $H_2PO_4^-$ and HPO_4^{2-} produce the same ions in solution. We can, therefore, imagine that the solution initially contains 0.15 M KH_2PO_4, which gives the following mass balance equation.

$$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = 0.15\,M$$

The charge balance equation is

$$[H_3O^+] + [K^+] + [Na^+] =$$
$$[H_2PO_4^-] + 2 \times [HPO_4^{2-}] + 3 \times [PO_4^{3-}] + [OH^-]$$

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Practice Exercise 6.10

To determine the pH of 0.050 M NH_3, we need to consider two equilibrium reactions: the base dissociation reaction for NH_3

$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$
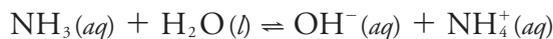
and water's dissociation reaction.

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

These two reactions contain four species whose concentrations we need to consider: NH_3, NH_4^+, H_3O^+, and OH^-. We need four equations to solve the problem—these equations are the K_b equation for NH_3

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

the K_w equation for H_2O

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

a mass balance equation on ammonia

$$C_{NH_3} = 0.050 \text{ M} = [NH_3] + [NH_4^+]$$

and a charge balance equation

$$[H_3O^+] + [NH_4^+] = [OH^-]$$

To solve this problem, we will make two assumptions. Because NH_3 is a base, our first assumption is

$$[OH^-] \gg [H_3O^+]$$

which simplifies the charge balance equation to

$$[NH_4^+] = [OH^-]$$

Because NH_3 is a weak base, our second assumption is

$$[NH_3] \gg [NH_4^+]$$

which simplifies the mass balance equation to

$$C_{NH_3} = 0.050 \text{ M} = [NH_3]$$

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[OH^-][OH^-]}{C_{NH_3}} = \frac{[OH^-]^2}{C_{NH_3}} = 1.75 \times 10^{-5}$$

$$[OH^-] = \sqrt{K_b C_{NH_3}} = \sqrt{(1.75 \times 10^{-5})(0.050)} = 9.35 \times 10^{-4}$$

Before we accept this answer, we must verify our two assumptions. The first assumption is that the concentration of OH^- is significantly greater than the concentration of H_3O^+. Using K_w, we find that

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{9.35 \times 10^{-4}} = 1.07 \times 10^{-11}$$

Clearly this assumption is acceptable. Our second assumption is that the concentration of NH_3 is significantly greater than the concentration of NH_4^+. Using our simplified charge balance equation, we find that

$$[NH_4^+] = [OH^-] = 9.35 \times 10^{-4}$$

Because the concentration of NH_4^+ is 1.9% of C_{NH_3}, our second assumption also is reasonable. Given that $[H_3O^+]$ is 1.07×10^{-11}, the pH is 10.97.

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Practice Exercise 6.11

In solving for the pH of 0.10 M alanine, we made the following three assumptions: (a) $[HL] \gg [H_2L^+] + [L^-]$; (b) $K_{a1}K_w \ll K_{a1}K_{a2}C_{HL}$; and (c) $K_{a1} \ll C_{HL}$. Assumptions (b) and (c) are easy to check. The value of K_{a1} (4.487×10^{-3}) is 4.5% of C_{HL} (0.10), and $K_{a1}K_w$ (4.487×10^{-17}) is

0.074% of $K_{a1}K_{a2}C_{HL}$ (6.093×10^{-14}). Each of these assumptions introduces an error of less than $\pm 5\%$.

To test assumption (a) we need to calculate the concentrations of H_2L^+ and L^-, which we accomplish using the equations for K_{a1} and K_{a2}.

$$[H_2L^+] = \frac{[H_3O^+][HL]}{K_{a1}} = \frac{(7.807 \times 10^{-7})(0.10)}{4.487 \times 10^{-3}} = 1.74 \times 10^{-5}$$

$$[L^-] = \frac{K_{a2}[HL]}{[H_3O^+]} = \frac{(1.358 \times 10^{-10})(0.10)}{7.807 \times 10^{-7}} = 1.74 \times 10^{-5}$$

Because these concentrations are less than $\pm 5\%$ of C_{HL}, the first assumption also is acceptable.

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Practice Exercise 6.12

The acid dissociation constant for $H_2PO_4^-$ is 6.32×10^{-8}, or a pK_a of 7.199. Substituting the initial concentrations of $H_2PO_4^-$ and HPO_4^{2-} into equation 6.60 and solving gives the buffer's pH as

$$pH = 7.199 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.199 + \log\frac{0.050}{0.10} = 6.898 \approx 6.90$$

Adding HCl converts a portion of HPO_4^{2-} to $H_2PO_4^-$ as a result of the following reaction

$$HPO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons H_2O(l) + H_2PO_4^-(aq)$$
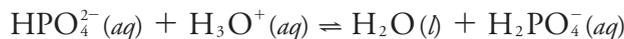
Because this reaction's equilibrium constant is so large (it is 1.59×10^7), we may treat the reaction as if it goes to completion. The new concentrations of $H_2PO_4^-$ and HPO_4^{2-} are

$$C_{H_2PO_4^-} = \frac{\text{mol } H_2PO_4^- + \text{mol HCl}}{V_{total}}$$

$$= \frac{(0.10 \text{ M})(0.10 \text{ L}) + (0.20 \text{ M})(5.0 \times 10^{-3} \text{ L})}{0.10 \text{ L} + 5.0 \times 10^{-3}\text{L}} = 0.105 \text{ M}$$

$$C_{HPO_4^{2-}} = \frac{\text{mol } HPO_4^{2-} - \text{mol HCl}}{V_{total}}$$

$$= \frac{(0.05 \text{ M})(0.10 \text{ L}) - (0.20 \text{ M})(5.0 \times 10^{-3} \text{ L})}{0.10 \text{ L} + 5.0 \times 10^{-3}\text{L}} = 0.0381 \text{ M}$$

Substituting these concentrations into equation 6.60 gives a pH of

$$pH = 7.199 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.199 + \log\frac{0.0381}{0.105} = 6.759 \approx 6.76$$

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

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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 $\mu = 0.10$ M. This assumes, of course, that we can ignore the contributions of Hg_2^{2+} and Cl^- from the solubility of Hg_2Cl_2.

Next we use equation 6.63 to calculate the activity coefficients for Hg_2^{2+} and Cl^-.

$$\log \gamma_{Hg_2^{2+}} = \frac{-0.51 \times (+2)^2 \times \sqrt{0.10}}{1 + 3.3 \times 0.40 \times \sqrt{0.10}} = -0.455$$

$$\gamma_{Hg_2^{2+}} = 0.351$$

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

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

Defining the equilibrium concentrations of Hg_2^{2+} and Cl^- in terms of the variable x

Concentrations	Hg_2Cl_2 (s)	$\rightleftharpoons$	Hg_2^{2+} (aq)	+	$2Cl^-$ (aq)
Initial	solid		0		0.10
Change	solid		+x		+2x
Equilibrium	solid		x		0.10 + 2x

and substituting into the thermodynamic solubility product for Hg_2Cl_2, leave us with

$$K_{sp} = a_{Hg_2^{2+}}(a_{Cl^-})^2 = \gamma_{Hg_2^{2+}}[Hg_2^{2+}](\gamma_{Cl^-})^2[Cl^-]^2 = 1.2 \times 10^{-18}$$

$$(0.351)(x)(0.75)^2(0.1 + 2x)^2 = 1.2 \times 10^{-18}$$

Because the value of x likely is small, let's simplify this equation to

$$(0.351)(x)(0.75)^2(0.1)^2 = 1.2 \times 10^{-18}$$

Solving for x gives its value as 6.1×10^{-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_2Cl_2 in 0.10 M NaCl is 6.1×10^{-16} mol/L. In Practice Exercise 6.8, where we ignored ionic strength, we determined that the molar solubility of Hg_2Cl_2 is 1.2×10^{-16} mol/L, a result that is 5× smaller than the its actual value.

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Practice Exercise 6.14

For a list of the relevant equilibrium reactions and equilibrium constants, see our earlier treatment of this problem. To solve this problem using Excel, let's set up the following spreadsheet

	A	B
1	pI =	3
2	[I-] =	= 10^–b1
3	[Ag+] =	= 8.3e–17/b2
4	[Ag(NH3)2+] =	= b2 – b3
5	[NH3] =	= (b4/(b3*1.7e7))^0.5
6	[NH4+] =	= 0.10 – b5-2*b4
7	[OH-] =	= 1.75e–5*b5/b6
8	[H3O+] =	= 1.00e–14/b7
9	error	= b3 + b4 + b6 + b8 – b2 – b7

copying the contents of cells B1-B9 into several additional columns. The initial guess for pI 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 β_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 pI which corresponds 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

$$[I^-] = \sqrt{K_{sp}} = \sqrt{8.3 \times 10^{-17}} = 9.1 \times 10^{-9}$$

which corresponds to a pI of 8.04. Entering initial guesses for pI of 4, 5, 6, 7, and 8 shows that the error changes sign between a pI of 5 and 6. Continuing in this way to narrow down the range for pI, we find that the error function is closest to zero at a pI of 5.42. The concentration of I^- at equilibrium, and the molar solubility of AgI, is 3.8×10^{-6} mol/L, which agrees with our earlier solution to this problem.

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Practice Exercise 6.15

To solve this problem, let's use the following function

```
> eval = function(pI){
+ I=10^–pI
+ 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(pI, error)
+ print(output)
+ }
```

The function accepts an initial guess for pI and calculates the concentrations of each species in solution using the definition of pI 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 β_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 pI—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

$$[I^-] = \sqrt{K_{sp}} = \sqrt{8.3 \times 10^{-17}} = 9.1 \times 10^{-9}$$

corresponding to a pI of 8.04. The following session shows the function in action.

```
> pI=c(4, 5, 6, 7, 8)
> eval(pI)
  pI    error
1  4 -2.56235615
2  5 -0.16620930
3  6  0.07337101
4  7  0.09734824
5  8  0.09989073
> pI=c(5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 6.0)
> eval(pI)
   pI     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
>pI=c(5.40, 5.41, 5.42, 5.43, 5.44, 5.45, 5.46, 5.47, 5.48, 5.49, 5.50)
> eval(pI)
   pI      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 I^- at equilibrium, and the molar solubility of AgI, is 3.8×10^{-6} mol/L, which agrees with our earlier solution to this problem.

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