

Chapter 6

Equilibrium Chemistry

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

Your ability to “think as a chemist” is a product of your experience in the classroom and in the laboratory. The material in this text assumes your familiarity with topics from earlier courses. Because of its importance to analytical chemistry, this chapter provides a review of equilibrium chemistry. Much of the material in this chapter should be familiar to you, although some topics—ladder diagrams and activity, for example—afford you with new ways to look at equilibrium chemistry.

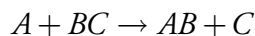
Napoleon's expedition to Egypt was the first to include a significant scientific presence. The Commission of Sciences and Arts, which included Claude Berthollet, began with 151 members, and operated in Egypt for three years. In addition to Berthollet's work, other results included a publication on mirages, and detailed catalogs of plant and animal life, mineralogy, and archeology. For a review of the Commission's contributions, see Gillispie, C. G. "Scientific Aspects of the French Egyptian Expedition, 1798-1801," *Proc. Am. Phil. Soc.* **1989**, *133*, 447-474.

Natron is another name for the mineral sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. In nature, it usually contains impurities of NaHCO_3 , and NaCl . In ancient Egypt, natron was mined and used for a variety of purposes, including as a cleaning agent and in mummification.

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 an example of chemical reasoning and introduces us to the topic of this chapter.

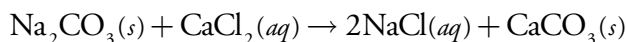
At the end of the 18th century, chemical reactivity was explained in terms of elective affinities.¹ If, for example, substance A reacts with substance BC to form AB



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.

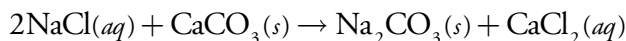


From his experience in the laboratory, Berthollet knew that adding solid Na_2CO_3 to a solution of CaCl_2 produces a precipitate of CaCO_3 .

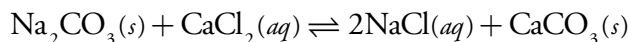


Understanding this, Berthollet was surprised to find solid Na_2CO_3 forming on the edges of the lake, particularly since the deposits formed only when the lake's salt water was in contact with limestone, CaCO_3 . Where the lake was in contact with clay soils, there was little or no Na_2CO_3 .

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.



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 writing the reaction.



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 . If during

¹ Quilez, J. *Chem. Educ. Res. Pract.* **2004**, *5*, 69-87 (<http://www.uoi.gr/cerp>).

the reaction we monitor the mass of Ca^{2+} remaining in solution and the mass of CaCO_3 that precipitates, the result looks something 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 reverse reactions continue to occur. A reaction at equilibrium exists in a **STEADY-STATE**, in which the rate at which a species forms equals the rate at which it is consumed.

6B Thermodynamics and Equilibrium Chemistry

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

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



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

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

$$\Delta G = \Delta H - T\Delta S \quad 6.2$$

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. Reactions releasing heat have a negative ΔH and are called exothermic. Endothermic reactions absorb heat from their surroundings and have a positive ΔH . **ENTROPY** is a measure of energy that is unavailable for useful, chemical work. The entropy of an individual species is always posi-

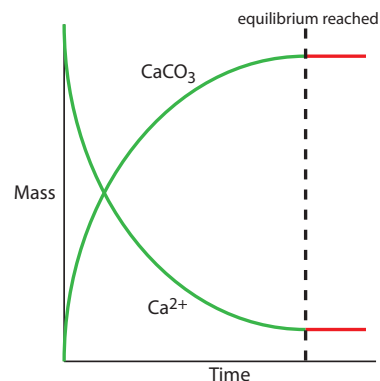


Figure 6.1 Graph showing how the masses of Ca^{2+} and CaCO_3 change as a function of time during the precipitation of CaCO_3 . The dashed line indicates when the reaction reaches equilibrium. Prior to equilibrium the masses of Ca^{2+} and CaCO_3 are **changing**; after reaching equilibrium, their masses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

For obvious reasons, we call the double arrow, \rightleftharpoons , an equilibrium arrow.

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.com/>.

Equation 6.2 shows that the sign of ΔG depends on the signs of ΔH and 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

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

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, the 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 split the Gibb's free energy into two terms.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad 6.3$$

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

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

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

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

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

where K is an **EQUILIBRIUM CONSTANT** that defines the reaction's equilibrium position. The equilibrium constant is just the numerical value of the reaction quotient, Q , when substituting equilibrium concentrations into equation 6.4.

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

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

where $[C]^\circ$ 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.

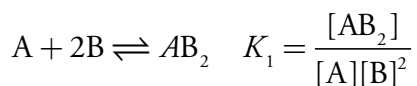
$$K = \frac{[C]_{\text{eq}}^c [D]_{\text{eq}}^d}{[A]_{\text{eq}}^a [B]_{\text{eq}}^b} \quad 6.5$$

Here we include the subscript “eq” to indicate a concentration at equilibrium. Although we usually will omit the “eq” when writing equilibrium constant expressions, it is important to remember that the value of K is determined by equilibrium concentrations.

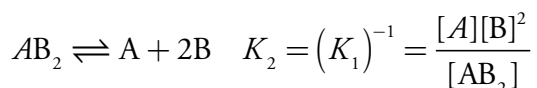
As written, equation 6.5 is a limiting law that applies only to infinitely dilute solutions where the chemical behavior of one species is unaffected by the presence of other species. Strictly speaking, equation 6.5 should be written in terms of activities instead of concentrations. We will return to this point in [Section 6I](#). For now, we will stick with concentrations as this convention is already familiar to you.

6C Manipulating Equilibrium Constants

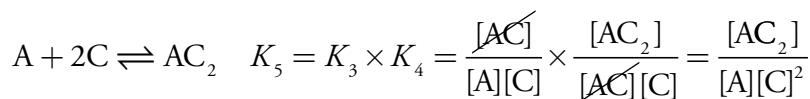
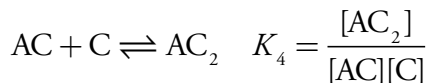
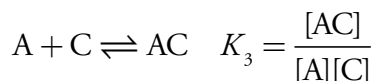
We will take advantage of two useful relationships when working with equilibrium constants. First, if we reverse a reaction's direction, the equilibrium constant for the new reaction is simply the inverse of that for the original reaction. For example, the equilibrium constant for the reaction



is the inverse of that for the reaction

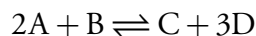


Second, if we add together two reactions to obtain a new reaction, the equilibrium constant for the new reaction is the product of the equilibrium constants for the original reactions.



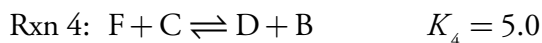
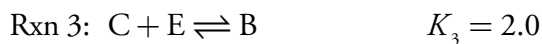
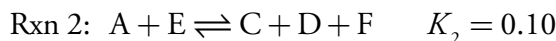
Example 6.1

Calculate the equilibrium constant for the reaction

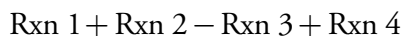


given the following information



**SOLUTION**

The overall reaction is equivalent to

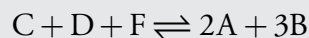


Subtracting a reaction is equivalent to adding the reverse reaction; thus, the overall equilibrium constant is

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

Practice Exercise 6.1

Calculate the equilibrium constant for the reaction



using the equilibrium constants from Example 6.1.

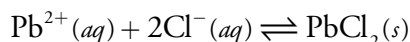
Click [here](#) to review your answer to this exercise.

6D Equilibrium Constants for Chemical Reactions

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

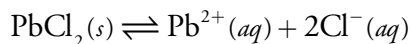
6D.1 Precipitation Reactions

In a precipitation reaction, two or more soluble species combine to form an insoluble **PRECIPITATE**. The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. For example, if we add a solution of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, to a solution of potassium chloride, KCl , the result is a precipitate of lead chloride, PbCl_2 . We usually write a precipitation reaction as a net ionic equation, showing only the precipitate and those ions forming the precipitate. Thus, the precipitation reaction for PbCl_2 is



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

When writing an equilibrium constant for a precipitation reaction, we focus on the precipitate's solubility. Thus, for PbCl_2 , the solubility reaction is



and its equilibrium constant, which we call the **SOLUBILITY PRODUCT**, K_{sp} , is

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

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

6D.2 Acid–Base Reactions

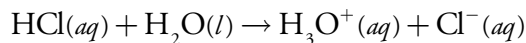
A useful definition of acids and bases is that independently introduced in 1923 by Johannes Brønsted and Thomas Lowry. In the Brønsted–Lowry definition, an **ACID** is a proton donor and a **BASE** is a proton acceptor. Note the connection in these definitions—defining a base as a proton acceptor implies that there is an acid available to donate the proton. For example, in reaction 6.7 acetic acid, CH_3COOH , donates a proton to ammonia, NH_3 , which serves as the base.



When an acid and a base react, the products are a new acid and a new base. For example, the acetate ion, $\text{CH}_3\text{COO}^{-}$, in reaction 6.7 is a base that can accept a proton from the acidic ammonium ion, NH_4^{+} , forming acetic acid and ammonia. We call the acetate ion the conjugate base of acetic acid, and the ammonium ion is the conjugate acid of ammonia.

STRONG AND WEAK ACIDS

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

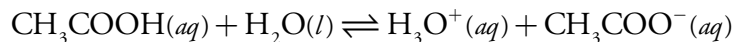


We use a single arrow (\rightarrow) in place of the equilibrium arrow (\rightleftharpoons) because we treat HCl as if it completely dissociates in aqueous solutions. In water, the common strong acids are hydrochloric acid (HCl), hydroiodic acid (HI), hydrobromic acid (HBr), nitric acid (HNO_3), perchloric acid (HClO_4), and the first proton of sulfuric acid (H_2SO_4).

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.



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.

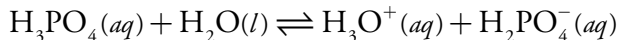


The equilibrium constant for this reaction is an **ACID DISSOCIATION CONSTANT**, K_a , which we write as

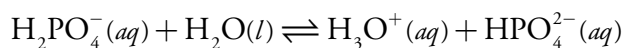
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5}$$

The magnitude of K_a provides information about a weak acid's relative strength, with a smaller K_a corresponding to a weaker acid. The ammonium ion, NH_4^+ , for example, with a K_a of 5.702×10^{-10} , is a weaker acid than acetic acid.

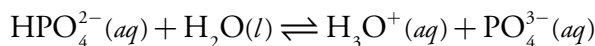
MONOPROTIC weak acids, such as acetic acid, have only a single acidic proton and a single acid dissociation constant. Other acids, such as phosphoric acid, have more than one acidic proton, each characterized by an acid dissociation constant. We call such acids **POLYPROTIC** weak acids. Phosphoric acid,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



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



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



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

The decrease in the acid dissociation constants from K_{a1} to K_{a3} tells us that each successive proton is harder to remove. Consequently, H_3PO_4 is a stronger acid than H_2PO_4^- , and H_2PO_4^- is a stronger acid than HPO_4^{2-} .

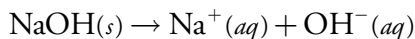
Earlier we noted that we omit pure solids and pure liquids from equilibrium constant expressions. Because the solvent, H_2O , is not pure, you might wonder why we have not included it in acetic acid's K_a expression. Recall that we divide each term in the equilibrium constant expression by its standard 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

$$\frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]^0}$$

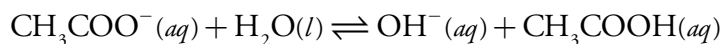
is essentially 1.00.

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.



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

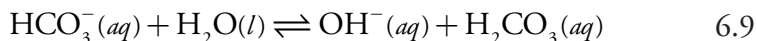
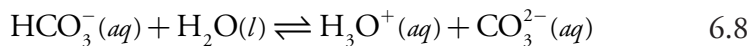


$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.71 \times 10^{-10}$$

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

AMPHIPROTIC SPECIES

Some species can behave as either a weak acid or as a weak base. For example, the following two reactions show the chemical reactivity of the bicarbonate ion, HCO_3^- , in water.



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

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

is smaller than the base dissociation constant for reaction 6.9.

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

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

DISSOCIATION OF WATER

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



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

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad 6.11$$

which has a value of 1.0000×10^{-14} 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 $[\text{H}_3\text{O}^+]$ for a solution, then we can calculate $[\text{OH}^-]$ using equation 6.11.

Example 6.2

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

SOLUTION

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

THE pH SCALE

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

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

substituting into equation 6.11

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

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

$$[\text{H}_3\text{O}^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}$$

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

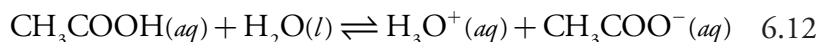
A neutral solution has a hydronium ion concentration of 1.00×10^{-7} M and a pH of 7.00. For a solution to be acidic the concentration of H_3O^+ must be greater than that for OH^- , which means that

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

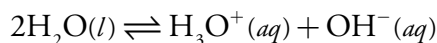
The pH of an acidic solution, therefore, must be less than 7.00. A basic solution, on the other hand, has a pH greater than 7.00. Figure 6.2 shows the pH scale and pH values for some representative solutions.

TABULATING VALUES FOR K_a AND K_b

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



Adding together these two reactions gives the reaction



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^- .

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

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

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

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

Example 6.3

Using [Appendix 11](#), calculate values for the following equilibrium constants.

- K_b for pyridine, $\text{C}_5\text{H}_5\text{N}$
- K_b for dihydrogen phosphate, H_2PO_4^-

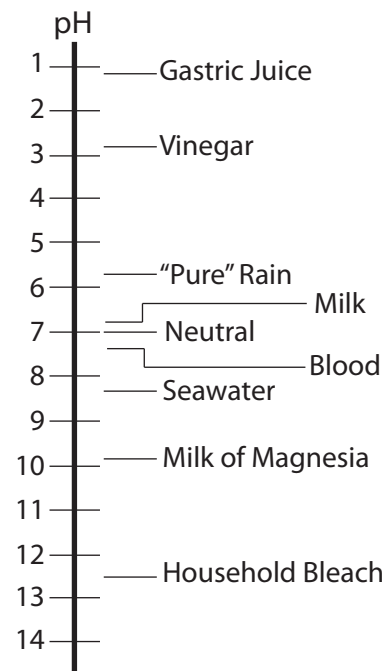


Figure 6.2 Scale showing the pH value for representative solutions. Milk of Magnesia is a saturated solution of $\text{Mg}(\text{OH})_2$.

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

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

SOLUTION

$$(a) K_{b, \text{C}_5\text{H}_5\text{N}} = \frac{K_w}{K_{a, \text{C}_5\text{H}_5\text{NH}^+}} = \frac{1.00 \times 10^{-14}}{5.90 \times 10^{-6}} = 1.69 \times 10^{-9}$$

$$(b) K_{b, \text{H}_2\text{PO}_4^-} = \frac{K_w}{K_{a, \text{H}_3\text{PO}_4}} = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$$

Practice Exercise 6.2

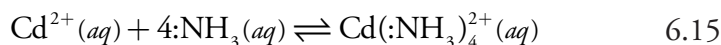
Using [Appendix 11](#), calculate the K_b values for hydrogen oxalate, HC_2O_4^- , and oxalate, $\text{C}_2\text{O}_4^{2-}$.

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

6D.3 Complexation Reactions

A more general definition of acids and bases was proposed in 1923 by G. N. Lewis. The Brønsted-Lowry definition of acids and bases focuses on an acid's proton-donating ability and a base's proton-accepting ability. Lewis theory, on the other hand, uses the breaking and forming of covalent bonds to describe acid–base characteristics. In this treatment, an acid is an electron pair acceptor and a base is 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.



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

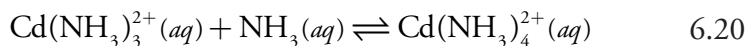
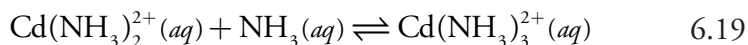
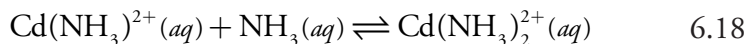
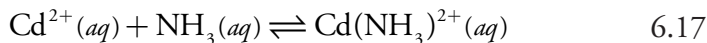
METAL-LIGAND FORMATION CONSTANTS

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.

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

The reverse of reaction 6.15 is a dissociation reaction, which we characterize by a **DISSOCIATION CONSTANT**, K_d , that is the reciprocal of K_f .

Many complexation reactions occur in a stepwise fashion. For example, the reaction between Cd^{2+} and NH_3 involves four successive reactions.



To avoid ambiguity, we divide formation constants into two categories. **STEPWISE FORMATION CONSTANTS**, which we designate as K_i for the i th step, describe the successive addition of one ligand to the metal–ligand complex from the previous step. Thus, the equilibrium constants for reactions 6.17–6.20 are, respectively, K_1 , K_2 , K_3 , and K_4 . Overall, or **CUMULATIVE FORMATION CONSTANTS**, which we designate as β_i , describe 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

$$\beta_i = K_1 \times K_2 \times \cdots \times K_i$$

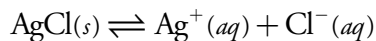
Stepwise and overall formation constants for selected metal–ligand complexes are in [Appendix 12](#).

METAL-LIGAND COMPLEXATION AND SOLUBILITY

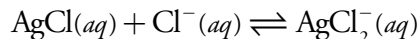
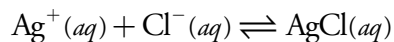
A formation constant characterizes the addition of one or more ligands to a free metal ion. To find the equilibrium constant for a complexation reaction involving a solid, we combine appropriate K_{sp} and K_f expressions. For example, the solubility of AgCl increases in the presence of excess chloride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



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



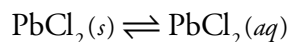
and the stepwise formation of AgCl_2^- , described by K_1 and K_2 .



The equilibrium constant for reaction 6.21, therefore, is $K_{\text{sp}} \times K_1 \times K_2$.

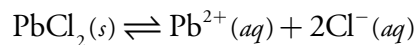
Example 6.4

Determine the value of the equilibrium constant for the reaction

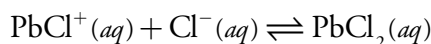
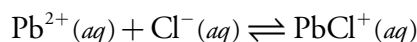


SOLUTION

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



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

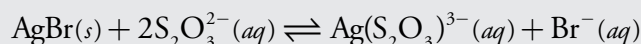


Using values for K_{sp} , K_1 , and K_2 from [Appendix 10](#) and [Appendix 12](#), we find that the equilibrium constant is

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

Practice Exercise 6.3

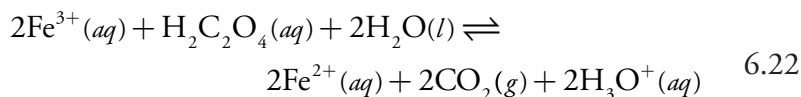
What is the equilibrium constant for the following reaction? You will find appropriate equilibrium constants in [Appendix 10](#) and [Appendix 11](#).



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

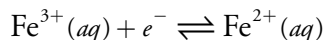
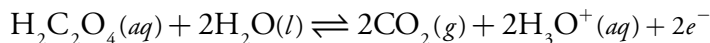
6D.4 Oxidation–Reduction (Redox) Reactions

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



Oxalic acid, on the other hand, undergoes oxidation because the oxidation state for carbon increases from +3 in $\text{H}_2\text{C}_2\text{O}_4$ 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.



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

The products of a redox reaction also have redox properties. For example, the Fe^{2+} in [reaction 6.22](#) can be oxidized to Fe^{3+} , while CO_2 can be reduced to $\text{H}_2\text{C}_2\text{O}_4$. 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 $\text{H}_2\text{C}_2\text{O}_4$.

THERMODYNAMICS OF REDOX REACTIONS

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

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

$$Q = nF$$

where n is the moles of electrons per mole of reactant, and F is Faraday's constant (96,485 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

$$\Delta G = -nFE \tag{6.23}$$

where ΔG has units of kJ/mol. The minus sign in equation 6.23 is the result of a difference in the conventions for assigning a reaction's favorable direction. In thermodynamics, a reaction is favored when ΔG is negative, but a redox 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**

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

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

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

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

STANDARD POTENTIALS

A redox reaction's **STANDARD POTENTIAL**, E° , 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 must be zero at equilibrium. Substituting these values into equation 6.24 and rearranging provides a relationship between E° and K .

A standard potential is the potential when all species are in their standard states. You may recall that we define standard state conditions as: all gases have partial pressures of 1 atm, all solutes have concentrations of 1 mol/L, and all solids and liquids are pure.

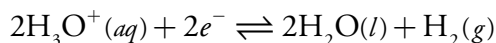
$$E^\circ = \frac{0.05916}{n} \log K \quad 6.25$$

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

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

where E°_{red} and E°_{ox} are the standard reduction potentials for the reduction half-reaction and the oxidation half-reaction.

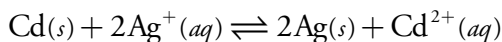
Because we cannot measure the potential for a single half-reaction, we arbitrarily assign a standard reduction potential of zero to a reference half-reaction and report all other reduction potentials relative to this reference. The reference half-reaction is



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

Example 6.5

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

**SOLUTION**

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

$$E^\circ = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cd}^{2+}/\text{Cd}} = 0.7996 - (-0.4030) = 1.2026 \text{ V}$$

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

$$E^\circ = 1.2026 \text{ V} = \frac{0.05916 \text{ V}}{2} \log K$$

Solving for K gives the equilibrium constant as

$$\begin{aligned} \log K &= 40.6558 \\ K &= 4.527 \times 10^{40} \end{aligned}$$

- (c) To calculate the potential when $[\text{Ag}^+]$ is 0.020 M and $[\text{Cd}^{2+}]$ is 0.050 M, we use the appropriate relationship for the reaction quotient, Q , in [equation 6.24](#).

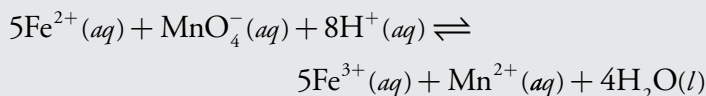
$$E = E^\circ - \frac{0.05916 \text{ V}}{n} \log \frac{[\text{Cd}^{2+}]}{[\text{Ag}^+]^2}$$

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

$$E = 1.14 \text{ V}$$

Practice Exercise 6.4

For the following reaction at 25 °C



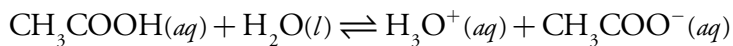
calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential under these conditions: $[\text{Fe}^{2+}] = 0.50 \text{ M}$, $[\text{Fe}^{3+}] = 0.10 \text{ M}$, $[\text{MnO}_4^-] = 0.025 \text{ M}$, $[\text{Mn}^{2+}] = 0.015 \text{ M}$, and a pH of 7.00. See [Appendix 13](#) for standard state reduction potentials.

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

When writing precipitation, acid–base, and metal–ligand complexation reactions, we represent acidity as H_3O^+ . Redox reactions are more commonly 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



has an equilibrium constant of

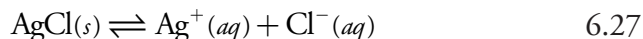
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5} \quad 6.26$$

Because equation 6.26 has three variables— $[\text{CH}_3\text{COOH}]$, $[\text{CH}_3\text{COO}^-]$, and $[\text{H}_3\text{O}^+]$ —it does not have a unique mathematical solution. Nevertheless, although two solutions of acetic acid may have different values for $[\text{CH}_3\text{COOH}]$, $[\text{CH}_3\text{COO}^-]$, and $[\text{H}_3\text{O}^+]$, each solution must have the same value of K_a .

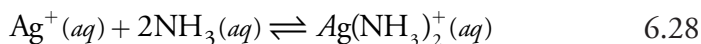
If we add sodium acetate to a solution of acetic acid, the concentration of CH_3COO^- increases, suggesting an apparent increase in the value of K_a . Because K_a must remain constant, the concentration of all three species in equation 6.26 must change to restore K_a to its original value. In this case, a partial reaction of CH_3COO^- and H_3O^+ decreases their concentrations, producing additional CH_3COOH and reestablishing the equilibrium.

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

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



The effect on the solubility of AgCl of adding AgNO_3 is obvious, but what is the effect of adding a ligand that forms a stable, soluble complex with Ag^+ ? Ammonia, for example, reacts with Ag^+ as shown here



Adding ammonia decreases the concentration of Ag^+ as the $\text{Ag}(\text{NH}_3)_2^+$ complex forms. In turn, decreasing the concentration of Ag^+ increases the solubility of AgCl as reaction 6.27 reestablishes its equilibrium position. Adding together reaction 6.27 and reaction 6.28 clarifies the effect of ammonia on the solubility of AgCl , by showing ammonia as a reactant.



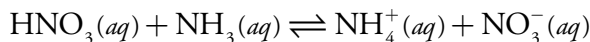
So what is the effect on the solubility of AgCl of adding AgNO_3 ? Adding AgNO_3 increases the concentration of Ag^+ in solution. To reestablish equilibrium, some of the Ag^+ and Cl^- react to form additional AgCl ; thus, the solubility of AgCl decreases. The solubility product, K_{sp} , of course, remains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

Example 6.6

What happens to the solubility of AgCl if we add HNO₃ to the equilibrium solution defined by [reaction 6.29](#)?

SOLUTION

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



Adding nitric acid lowers the concentration of ammonia. Decreasing ammonia's concentration causes [reaction 6.29](#) to move from products to reactants, decreasing the solubility of AgCl.

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

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

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]_{\text{eq}}}{[\text{Ag}^+]_{\text{eq}}[\text{NH}_3]_{\text{eq}}^2} \quad 6.30$$

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

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

Because Q is greater than β_2 , equilibrium is reestablished by shifting the reaction to the left, decreasing the concentration of $\text{Ag}(\text{NH}_3)_2^+$. Note that the new equilibrium position lies toward the side of the equilibrium reaction having the greatest number of solute particles (one Ag^+ ion and two molecules of NH_3 versus a single metal-ligand complex). If we concentrate the solution of $\text{Ag}(\text{NH}_3)_2^+$ 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 direc-

The relationship between pressure and concentration can be deduced using the ideal gas law. Starting with $PV = nRT$, we solve for the molar concentration

$$\text{molar concentration} = \frac{n}{V} = \frac{P}{RT}$$

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

tion producing the greatest number of particles, and decreasing volume always favors the direction producing the fewest particles. If the number of particles is the same on both sides of the reaction, then the equilibrium position is unaffected by a change in volume.

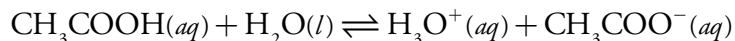
6F Ladder Diagrams

When developing or evaluating an analytical method, we often need to understand how the chemistry taking place affects our results. Suppose we wish to isolate Ag^+ by precipitating it as AgCl . If we also need to control pH, then we must use a reagent that will not adversely affect the solubility of AgCl . It is a mistake to add NH_3 to the reaction mixture, for example, because it increases the solubility of AgCl ([reaction 6.29](#)).

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

6F.1 Ladder Diagrams for Acid–Base Equilibria

Let's use acetic acid, CH_3COOH , to illustrate the process of drawing and interpreting an acid–base ladder diagram. Before drawing the diagram, however, let's consider the equilibrium reaction in more detail. The equilibrium constant expression for acetic acid's dissociation reaction



is

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

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

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

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

² Although not specifically on the topic of ladder diagrams as developed in this section, the following sources 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.

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

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.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.76 \quad 6.31$$

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

$$\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a = 4.76$$

If the concentration of CH_3COO^- is greater than that of CH_3COOH , then the log term in equation 6.31 is positive and

$$\text{pH} > \text{p}K_a \quad \text{or} \quad \text{pH} > 4.76$$

This is a reasonable result because we expect the concentration of the conjugate base, CH_3COO^- , to increase as the pH increases. Similar reasoning shows that the concentration of CH_3COOH exceeds that of CH_3COO^- when

$$\text{pH} < \text{p}K_a \quad \text{or} \quad \text{pH} < 4.76$$

Now we are ready to construct acetic acid's ladder diagram (Figure 6.3). First, we draw a vertical arrow representing the solution's pH, with smaller (more acidic) pH levels at the bottom and larger (more basic) pH levels at the top. Second, we draw a horizontal line at a pH equal to acetic acid's $\text{p}K_a$ 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^- .

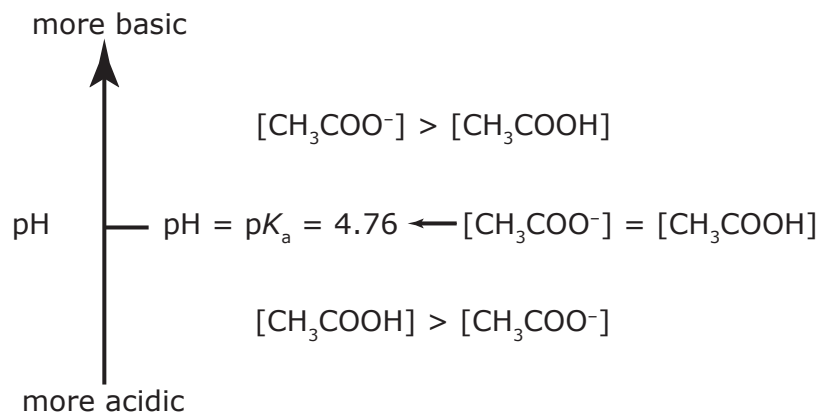


Figure 6.3 Acid–base ladder diagram for acetic acid showing the relative concentrations of CH_3COOH and CH_3COO^- . A simpler version of this ladder diagram dispenses with the equalities and shows only the predominate species in each region.

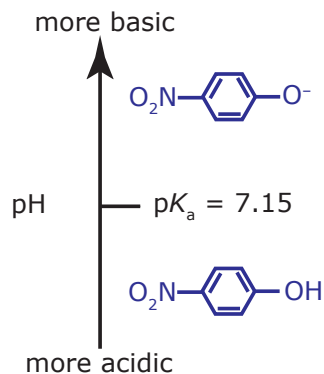


Figure 6.4 Acid–base ladder diagram for *p*-nitrophenolate.

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

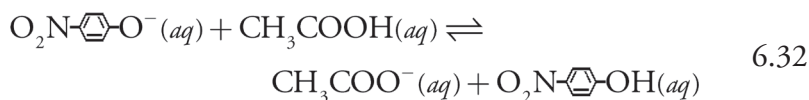
To draw a ladder diagram for a weak base, we simply draw the ladder diagram for its conjugate weak acid. From [Appendix 12](#), the pK_a for *p*-nitrophenol is 7.15. The resulting ladder diagram is shown in [Figure 6.4](#). At a pH of 6.00, *p*-nitrophenolate is present primarily in its weak acid form.

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.

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



occurs because the areas of predominance for acetic acid and *p*-nitrophenolate do not overlap. The solution's final composition depends on which spe-

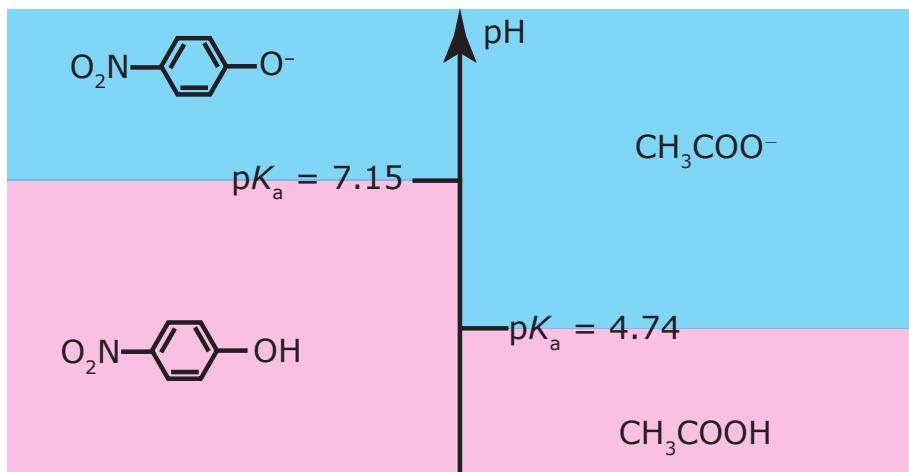


Figure 6.5 Acid–base ladder diagram showing the areas of predominance for acetic acid/acetate and for *p*-nitrophenol/*p*-nitrophenolate. The areas in blue shading show the pH range where the weak bases are the predominate species; the weak acid forms are the predominate species in the areas shown in pink shading.

cies is the limiting reagent. The following example shows how we can use the ladder diagram in [Figure 6.5](#) to evaluate the result of mixing together solutions of acetic acid and *p*-nitrophenolate.

Example 6.8

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

SOLUTION

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

$$\text{moles CH}_3\text{COOH} = 0.090 - 0.040 = 0.050 \text{ mol}$$

$$\text{moles CH}_3\text{COO}^- = 0.040 \text{ mol}$$

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

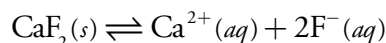
Practice Exercise 6.6

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

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

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

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



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

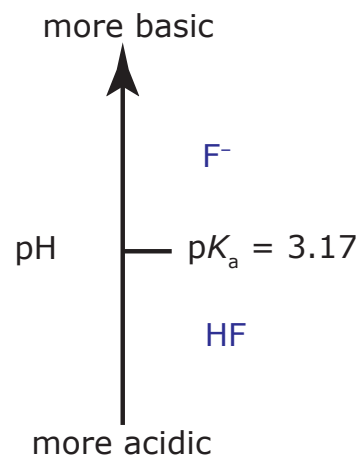


Figure 6.6 Acid–base ladder diagram for HF. To minimize the solubility of CaF_2 , we need to keep the pH above 3.17, with more basic pH levels leading to smaller solubility losses. See [Chapter 8](#) for a more detailed discussion.

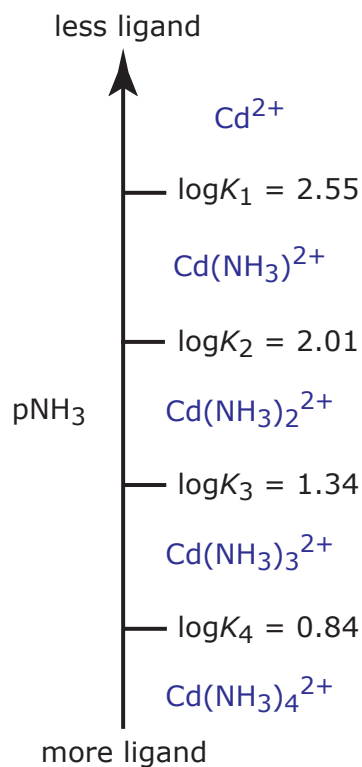
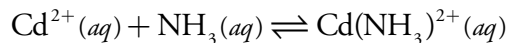


Figure 6.7 Metal–ligand ladder diagram for Cd^{2+} – NH_3 complexation reactions. Note that higher-order complexes form when pNH_3 is smaller (which corresponds to larger concentrations of NH_3).

6F.2 Ladder Diagrams for Complexation Equilibria

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



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

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

$$\log K_1 = \log \frac{[\text{Cd}(\text{NH}_3)^{2+}]}{[\text{Cd}^{2+}]} - \log[\text{NH}_3] = 2.55$$

$$\log K_1 = \log \frac{[\text{Cd}(\text{NH}_3)^{2+}]}{[\text{Cd}^{2+}]} + \text{pNH}_3 = 2.55$$

$$\text{pNH}_3 = \log K_1 + \log \frac{[\text{Cd}^{2+}]}{[\text{Cd}(\text{NH}_3)^{2+}]} = 2.55$$

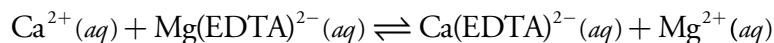
Thus, Cd^{2+} is the predominate species when pNH_3 is greater than 2.55 (a concentration of NH_3 smaller than 2.82×10^{-3} M) and for pNH_3 values less than 2.55, $\text{Cd}(\text{NH}_3)^{2+}$ is the predominate species. Figure 6.7 shows a complete metal–ligand ladder diagram for Cd^{2+} and NH_3 .

Example 6.9

Draw a single ladder diagram for the $\text{Ca}(\text{EDTA})^{2-}$ and $\text{Mg}(\text{EDTA})^{2-}$ metal–ligand complexes. Using your ladder diagram, predict the result of adding 0.080 moles of Ca^{2+} to 0.060 moles of $\text{Mg}(\text{EDTA})^{2-}$. 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 $\text{Mg}(\text{EDTA})^{2-}$ do not overlap, the reaction



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

$$\text{moles Ca}^{2+} = 0.080 - 0.060 = 0.020 \text{ mol}$$

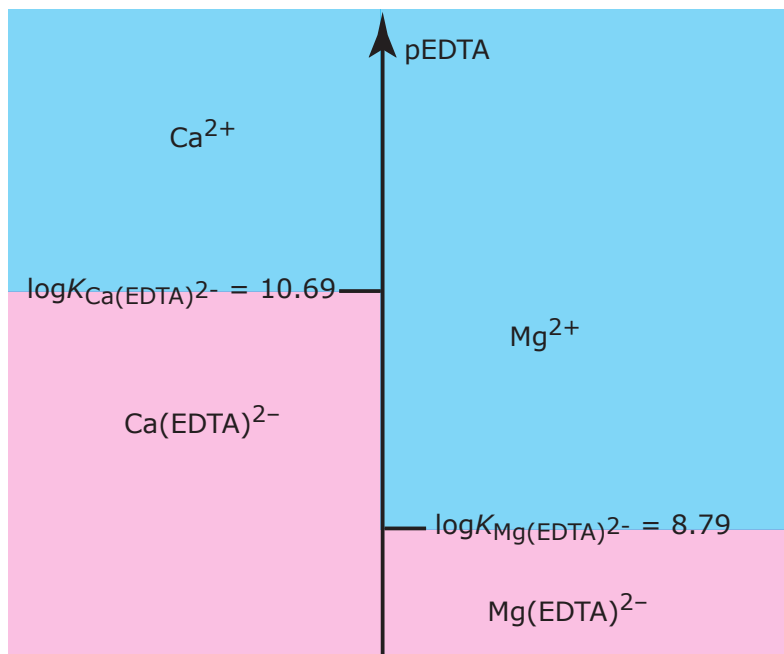
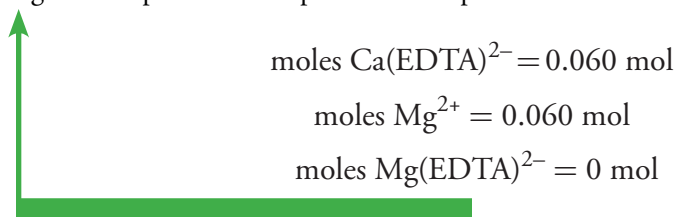
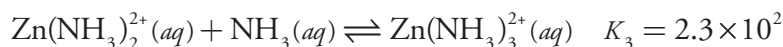
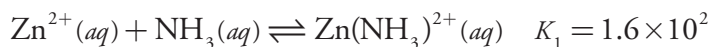


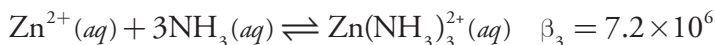
Figure 6.8 Metal–ligand ladder diagram for $\text{Ca}(\text{EDTA})^{2-}$ and for $\text{Mg}(\text{EDTA})^{2-}$. The areas with blue shading shows the pEDTA range where the free metal ions are the predominate species; the metal–ligand complexes are the predominate species in the areas shown with pink shading.



The metal–ligand ladder diagram in [Figure 6.7](#) uses stepwise formation constants. We can also construct ladder diagrams using cumulative formation constants. The first three stepwise formation constants for the reaction of Zn^{2+} with NH_3



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



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

Because K_3 is greater than K_2 , which is greater than K_1 , the formation of the metal–ligand complex $\text{Zn}(\text{NH}_3)_3^{2+}$ is more favorable than the formation of the other metal ligand complexes. For this reason, at lower values of pNH_3 the concentration of $\text{Zn}(\text{NH}_3)_3^{2+}$ is larger than that for $\text{Zn}(\text{NH}_3)_2^{2+}$ and $\text{Zn}(\text{NH}_3)^{2+}$. The value of β_3 is

$$\beta_3 = K_1 \times K_2 \times K_3$$

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

Taking the log of each side gives

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

or

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

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

$$\text{pNH}_3 = \frac{1}{3} \log \beta_3 = 2.29$$

In general, for the metal–ligand complex ML_n , the step for a cumulative formation constant is

$$\text{pL} = \frac{1}{n} \log \beta_n$$

Figure 6.9 shows the complete ladder diagram for the Zn^{2+} – NH_3 system.

6F.3 Ladder Diagram for Oxidation/Reduction Equilibria

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

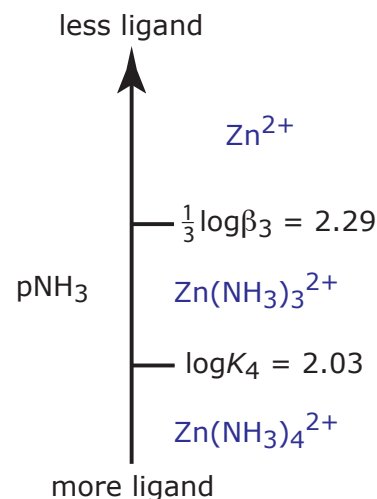
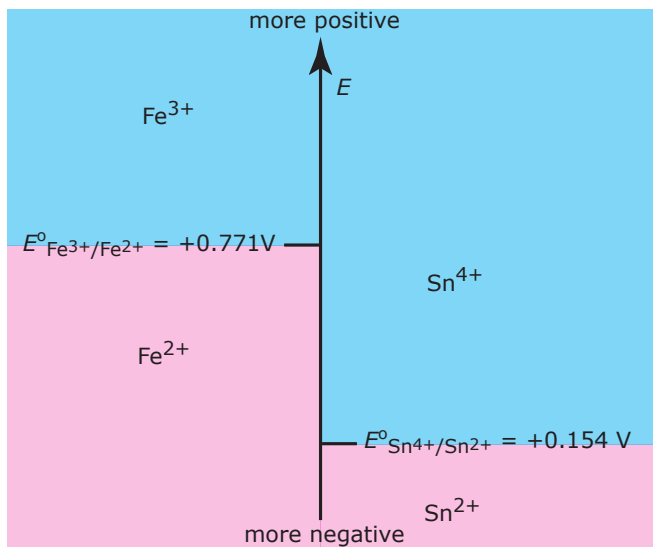


Figure 6.9 Ladder diagram for Zn^{2+} – NH_3 metal–ligand complexation reactions showing both a step based on a cumulative formation constant, and a step based on a stepwise formation constant.

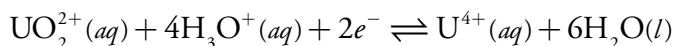
Figure 6.10 Redox ladder diagram for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and for $\text{Sn}^{4+}/\text{Sn}^{2+}$. The areas with blue shading show the potential range where the oxidized forms are the predominate species; the reduced forms are the predominate species in the areas shown with pink shading.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



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

At potentials more positive than the standard state potential, the predominate species is Fe^{3+} , whereas Fe^{2+} predominates at potentials more negative than E° . When coupled with the step for the $\text{Sn}^{4+}/\text{Sn}^{2+}$ 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 +0.151 V.

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



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

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

and factor out the concentration of H_3O^+ .

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

From this equation we see that the area of predominance for UO_2^{2+} and U^{4+} is defined by a step whose potential is

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

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

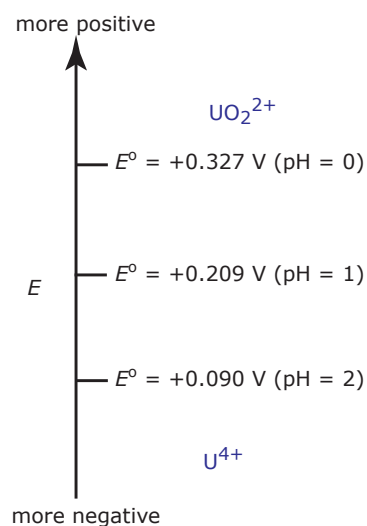


Figure 6.11 Redox ladder diagram for the $\text{UO}_2^{2+}/\text{U}^{4+}$ half-reaction showing the effect of pH on the step.

6G Solving Equilibrium Problems

Ladder diagrams are a useful tool for evaluating chemical reactivity, usually providing a reasonable approximation of a chemical system's composition at equilibrium. If we need a more exact quantitative description of the equilibrium condition, then a ladder diagram is insufficient. In this case we need to find an algebraic solution. In this section we will learn how to set-up and solve equilibrium problems. We will start with a simple problem and work toward more complex problems.

When we first add solid $\text{Pb}(\text{IO}_3)_2$ to water, the concentrations of Pb^{2+} and IO_3^- are zero and the reaction quotient, Q , is

$$Q = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = 0$$

As the solid dissolves, the concentrations of these ions increase, but Q remains smaller than K_{sp} . We reach equilibrium and “satisfy the solubility product” when

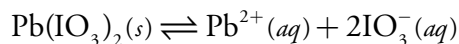
$$Q = K_{\text{sp}}$$

Because a solid, such as $\text{Pb}(\text{IO}_3)_2$, does not appear in the solubility product expression, we do not need to keep track of its concentration. Remember, however, that the K_{sp} value applies only if there is some $\text{Pb}(\text{IO}_3)_2$ present at equilibrium.

6G.1 A Simple Problem—Solubility of $\text{Pb}(\text{IO}_3)_2$

If we place an insoluble compound such as $\text{Pb}(\text{IO}_3)_2$ in deionized water, the solid dissolves until the concentrations of Pb^{2+} and IO_3^- satisfy the solubility product for $\text{Pb}(\text{IO}_3)_2$. At equilibrium the solution is saturated with $\text{Pb}(\text{IO}_3)_2$, which simply means that no more solid can dissolve. How do we determine the equilibrium concentrations of Pb^{2+} and IO_3^- , and what is the molar solubility of $\text{Pb}(\text{IO}_3)_2$ in this saturated solution?

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



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

As $\text{Pb}(\text{IO}_3)_2$ dissolves, two IO_3^- ions are produced for each ion of Pb^{2+} . If we assume that the change in the molar concentration of Pb^{2+} at equilibrium is x , then the change in the molar concentration of IO_3^- is $2x$. The following table helps us keep track of the initial concentrations, the change in concentrations, and the equilibrium concentrations of Pb^{2+} and IO_3^- .

Concentrations	$\text{Pb}(\text{IO}_3)_2(s)$	\rightleftharpoons	$\text{Pb}^{2+}(aq)$	+	$2\text{IO}_3^-(aq)$
Initial	solid		0		0
Change	solid		+ x		+ $2x$
Equilibrium	solid		x		$2x$

Substituting the equilibrium concentrations into equation 6.33 and solving gives

$$\begin{aligned} (x)(2x)^2 &= 4x^3 = 2.5 \times 10^{-13} \\ x &= 3.97 \times 10^{-5} \end{aligned}$$

Substituting this value of x back into the equilibrium concentration expressions for Pb^{2+} and IO_3^- gives their concentrations as

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

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

We can express a compound's solubility in two ways: molar solubility (mol/L) or mass solubility (g/L). Be sure to express your answer clearly.

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

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.



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

6G.2 A More Complex Problem—The Common Ion Effect

Calculating the solubility of $\text{Pb}(\text{IO}_3)_2$ in deionized water is a straightforward problem since the solid's dissolution is the only source of Pb^{2+} and IO_3^- . But what if we add $\text{Pb}(\text{IO}_3)_2$ to a solution of 0.10 M $\text{Pb}(\text{NO}_3)_2$, which provides a second source of Pb^{2+} ? Before we set-up and solve this problem algebraically, think about the system's chemistry and decide whether the solubility of $\text{Pb}(\text{IO}_3)_2$ 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	$\text{Pb}(\text{IO}_3)_2(s)$	\rightleftharpoons	$\text{Pb}^{2+}(aq)$	+	$2\text{IO}_3^-(aq)$
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

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

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

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

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

Substituting our approximation into [equation 6.33](#) and solving for x gives

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

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

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

Before accepting this answer, we must verify that our approximation is reasonable. The difference between the calculated concentration of Pb^{2+} , $0.10 + x$ M, and our assumption that it is 0.10 M is 7.9×10^{-7} , or $7.9 \times 10^{-4}\%$ of

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 $\text{Pb}(\text{IO}_3)_2$ is smaller than that in our previous problem.

There are several approaches to solving cubic equations, but none are computationally easy.

$$\begin{aligned} \% \text{error} &= \frac{(0.10 + x) - 0.10}{0.10} \times 100 \\ &= \frac{7.91 \times 10^{-7}}{0.10} \times 100 \\ &= 7.91 \times 10^{-4} \% \end{aligned}$$

the assumed concentration. This is a negligible error. Accepting the result of our calculation, we find that the equilibrium concentrations of Pb^{2+} and IO_3^- are

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

$$[\text{IO}_3^-] = 2x = 1.6 \times 10^{-6} \text{ M}$$

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

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

Example 6.10

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

SOLUTION

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

$$[\text{Pb}^{2+}] = 1.0 \times 10^{-4} + x \quad [\text{IO}_3^-] = 2x$$

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 , we make the following assumption

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

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

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

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

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

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



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

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

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

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

Practice Exercise 6.8

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

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

Table 6.1 Systematic Approach to Solving Equilibrium Problems

- Step 1: Write all relevant equilibrium reactions and equilibrium constant expressions.
- Step 2: Count the unique species appearing in the equilibrium constant expressions; these are your unknowns. You have enough information to solve the problem if the number of unknowns equals the number of equilibrium constant expressions. If not, add a mass balance equation and/or a charge balance equation. Continue adding equations until the number of equations equals the number of unknowns.
- 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.

In addition to equilibrium constant expressions, two other equations are important to the systematic approach for solving equilibrium problems. The first of these is a **MASS BALANCE EQUATION**, which is simply a statement that matter is conserved during a chemical reaction. In a solution of a acetic acid, for example, the combined concentrations of the conjugate weak acid, CH_3COOH , and the conjugate weak base, CH_3COO^- , must equal acetic acid's initial concentration, $C_{\text{CH}_3\text{COOH}}$.

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

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

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

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

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

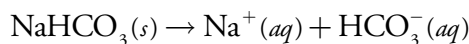
Note that we multiply the concentration of Ca^{2+} by two, and that we include the concentrations of H_3O^+ and OH^- .

Example 6.11

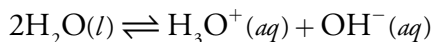
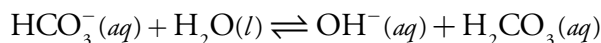
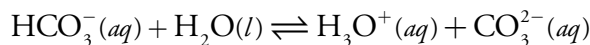
Write mass balance equations and a charge balance equation for a 0.10 M solution of NaHCO_3 .

SOLUTION

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



and the acid–base dissociation reactions of HCO_3^- and H_2O



You may recall from [Chapter 2](#) that this is the difference between a formal concentration and a molar concentration. The variable C represents a formal concentration.

We use absolute values because we are balancing the concentration of charge and concentrations cannot be negative.

There are situations where it is impossible to write a charge balance equation because we do not have enough information about the solution's composition. For example, suppose we fix a solution's pH using a buffer. If the buffer's composition is not specified, then a charge balance equation can not be written.

The mass balance equations are

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

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

and the charge balance equation is

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

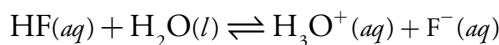
Practice Exercise 6.9

Write appropriate mass balance and charge balance equations for a solution containing 0.10 M KH_2PO_4 and 0.050 M Na_2HPO_4 .

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

6G.4 pH of a Monoprotic Weak Acid

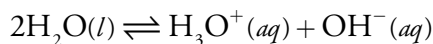
To illustrate the systematic approach to solving equilibrium problems, let's calculate the pH of 1.0 M HF. Two equilibrium reactions affect the pH. The first, and most obvious, is the acid dissociation reaction for HF



for which the equilibrium constant expression is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4} \quad 6.35$$

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



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad 6.36$$

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

$$C_{\text{HF}} = [\text{HF}] + [\text{F}^-] \quad 6.37$$

and a charge balance equation

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{F}^-] \quad 6.38$$

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.

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

Step 2: Count the unique species appearing in the equilibrium constant expressions; these are your unknowns. You have enough information to solve the problem if the number of unknowns equals the number of equilibrium constant expressions. If not, add a mass balance equation and/or a charge balance equation. Continue adding equations until the number of equations equals the number of unknowns.

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.

Assumption One. Because HF is a weak acid, the solution must be acidic. For an acidic solution it is reasonable to assume that

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

which simplifies the charge balance equation to

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

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

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

which simplifies the mass balance equation to

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

For this exercise let's accept an assumption if it introduces an error of less than $\pm 5\%$.

Substituting equation 6.39 and equation 6.40 into [equation 6.35](#), and solving for the concentration of H_3O^+ gives us

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

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

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

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

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

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

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

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

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

and substituting into the K_a expression along with equation 6.39 gives

Step 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.

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

Rearranging this equation leaves us with a quadratic equation

$$[\text{H}_3\text{O}^+]^2 + K_a[\text{H}_3\text{O}^+] - K_a C_{\text{HF}} = 0$$

which we solve using the quadratic formula

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

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

$$ax^2 + bx + c = 0$$

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

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

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

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

Only the positive root is chemically significant because the negative root gives a negative concentration for H_3O^+ . Thus, $[\text{H}_3\text{O}^+]$ is 2.6×10^{-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 $[\text{OH}^-]$ in place of $[\text{H}_3\text{O}^+]$.

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

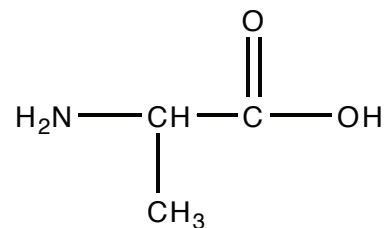


Figure 6.12 Structure of the amino acid alanine, which has pK_a values of 2.348 and 9.867.

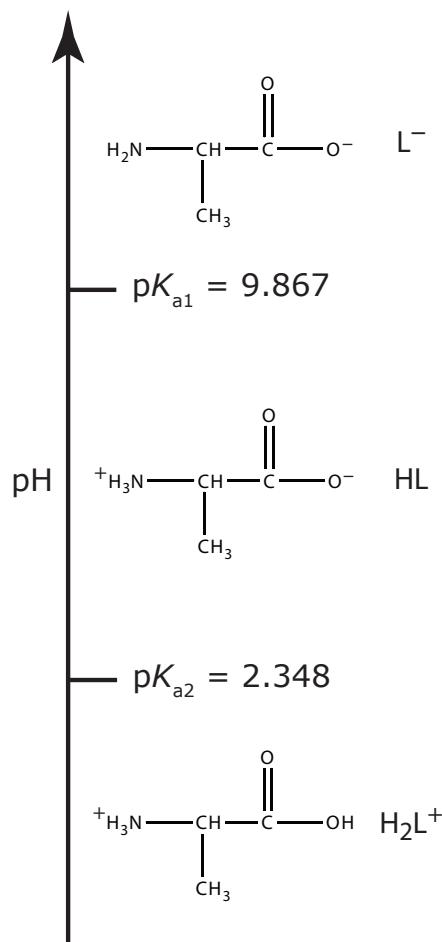


Figure 6.13 Ladder diagram for alanine.

pH OF 0.10 M ALANINE HYDROCHLORIDE (H_2L^+)

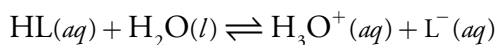
Alanine hydrochloride is a salt of the diprotic weak acid H_2L^+ and Cl^- . Because H_2L^+ has two acid dissociation reactions, a complete systematic solution to this problem is more complicated than that for a monoprotic weak acid. The ladder diagram in Figure 6.13 helps us simplify the problem. Because the areas of predominance for H_2L^+ and L^- are so far apart, we can assume that a solution of H_2L^+ is not likely to contain significant amounts 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^-)

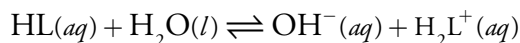
The alaninate ion is a diprotic weak base. Because L^- has two base dissociation reactions, a complete systematic solution to this problem is more complicated than that for a monoprotic weak base. Once again, the ladder diagram in Figure 6.13 helps us simplify the problem. Because the areas of predominance for H_2L^+ and L^- are so far apart, we can assume that a solution of L^- is not likely to contain significant amounts 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)

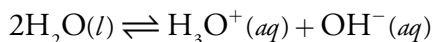
Finding the pH of a solution of alanine is more complicated than our previous two examples because we cannot ignore the presence of both H_2L^+ and L^- . To calculate the solution's pH we must consider alanine's acid dissociation reaction



and its base dissociation reaction



As always, we must also consider the dissociation of water



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

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

$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{[\text{OH}^-][\text{H}_2\text{L}^+]}{[\text{HL}]}$$

the K_w equation

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

a mass balance equation for alanine

$$C_{\text{HL}} = [\text{H}_2\text{L}^+] + [\text{HL}] + [\text{L}^-]$$

and a charge balance equation

$$[\text{H}_2\text{L}^+] + [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{L}^-]$$

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

$$[\text{HL}] \gg [\text{H}_2\text{L}^+] + [\text{L}^-]$$

which allows us to simplify the mass balance equation to

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

Next we solve K_{b2} for $[\text{H}_2\text{L}^+]$

$$[\text{H}_2\text{L}^+] = \frac{K_w[\text{HL}]}{K_{a1}[\text{OH}^-]} = \frac{[\text{H}_3\text{O}^+][\text{HL}]}{K_{a1}} = \frac{C_{\text{HL}}[\text{H}_3\text{O}^+]}{K_{a1}}$$

and K_{a2} for $[\text{L}^-]$

$$[\text{L}^-] = \frac{K_{a2}[\text{HL}]}{[\text{H}_3\text{O}^+]} = \frac{K_{a2}C_{\text{HL}}}{[\text{H}_3\text{O}^+]}$$

Substituting these equations for $[\text{H}_2\text{L}^+]$ and $[\text{L}^-]$, along with the equation for K_w , into the charge balance equation give us

$$\frac{C_{\text{HL}}[\text{H}_3\text{O}^+]}{K_{a1}} + [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{H}_3\text{O}^+]} + \frac{K_{a2}C_{\text{HL}}}{[\text{H}_3\text{O}^+]}$$

which we simplify to

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

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

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{\text{a}1}K_{\text{a}2}C_{\text{HL}} + K_{\text{a}1}K_{\text{w}}}{C_{\text{HL}} + K_{\text{a}1}}}$$

We can further simplify this equation if $K_{\text{a}1}K_{\text{w}} \ll K_{\text{a}1}K_{\text{a}2}C_{\text{HL}}$, and if $K_{\text{a}1} \ll C_{\text{HL}}$, leaving us with

$$[\text{H}_3\text{O}^+] = \sqrt{K_{\text{a}1}K_{\text{a}2}}$$

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

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

or a pH of 6.11.

Practice Exercise 6.11

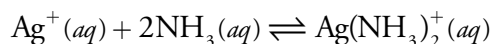
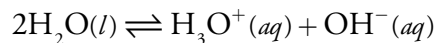
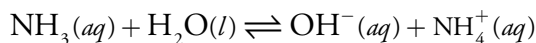
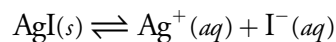
Verify that each assumption in our solution for the pH of 0.10 M alanine is reasonable, using $\pm 5\%$ as the limit for the acceptable error.

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 $\text{Ag}(\text{NH}_3)_2^+$ 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 .



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

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

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.75 \times 10^{-5} \quad 6.42$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad 6.43$$

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7 \quad 6.44$$

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

$$C_{\text{NH}_3} = [\text{NH}_3] + [\text{NH}_4^+] + 2 \times [\text{Ag}(\text{NH}_3)_2^+] \quad 6.45$$

In writing this mass balance equation we multiply the concentration of $\text{Ag}(\text{NH}_3)_2^+$ by two since there are two moles of NH_3 per mole of $\text{Ag}(\text{NH}_3)_2^+$. 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 $\text{Ag}(\text{NH}_3)_2^+$; thus

$$[\text{I}^-] = [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)_2^+] \quad 6.46$$

Finally, we include a charge balance equation.

$$[\text{Ag}^+] + [\text{Ag}(\text{NH}_3)_2^+] + [\text{NH}_4^+] + [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{I}^-] \quad 6.47$$

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

Assumption One. Because the formation of the $\text{Ag}(\text{NH}_3)_2^+$ complex is so favorable (β_2 is 1.7×10^7), there is very little free Ag^+ and it is reasonable to assume that

$$[\text{Ag}^+] \ll [\text{Ag}(\text{NH}_3)_2^+]$$

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

$$[\text{NH}_4^+] \ll [\text{NH}_3]$$

Assumption Three. Because K_{sp} for AgI is significantly smaller than β_2 for $\text{Ag}(\text{NH}_3)_2^+$, the solubility of AgI is probably small enough that very little ammonia is needed for metal–ligand complexation; thus

$$[\text{Ag}(\text{NH}_3)_2^+] \ll [\text{NH}_3]$$

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 $\text{Ag}(\text{NH}_3)_2^+$, allowing us to simplify the mass balance equation for NH_3 to

$$C_{\text{NH}_3} = [\text{NH}_3] \quad 6.48$$

Finally, using assumption one, which suggests that the concentration of $\text{Ag}(\text{NH}_3)_2^+$ is much larger than the concentration of Ag^+ , we simplify the mass balance equation for I^- to

$$[\text{I}^-] = [\text{Ag}(\text{NH}_3)_2^+] \quad 6.49$$

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

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{I}^-]}{K_{\text{sp}}[\text{NH}_3]^2} \quad 6.50$$

Next we substitute [equation 6.48](#) and [equation 6.49](#) into [equation 6.50](#), obtaining

$$\beta_2 = \frac{[\text{I}^-]^2}{K_{\text{sp}}(C_{\text{NH}_3})^2} \quad 6.51$$

Solving [equation 6.51](#) for $[\text{I}^-]$ gives

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

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

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

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

Substituting the concentrations of I^- and Ag^+ into the mass balance equation for iodide ([equation 6.46](#)), gives the concentration of $\text{Ag}(\text{NH}_3)_2^+$ as

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

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

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

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

From the mass balance equation for NH_3 ([equation 6.44](#)) we see that $[\text{NH}_4^+]$ is negligible, verifying our second assumption that $[\text{NH}_4^+]$ is sig-

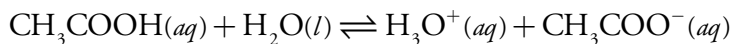
Did you notice that our solution to this problem did not make use of [equation 6.47](#), the charge balance equation? The reason for this is that we did not try to solve for the concentration of all seven species. If we need to know the complete equilibrium composition of the reaction mixture, then we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

nificantly smaller than $[\text{NH}_3]$. Our third assumption that $[\text{Ag}(\text{NH}_3)_2^+]$ is significantly smaller than $[\text{NH}_3]$ also is reasonable.

6H Buffer Solutions

Adding as little as 0.1 mL of concentrated HCl to a liter of H_2O shifts the pH from 7.0 to 3.0. Adding the same amount of HCl to a liter of a solution that is 0.1 M in acetic acid and 0.1 M in sodium acetate, however, results in a negligible change in pH. Why do these two solutions respond so differently to the addition of HCl?

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



and its corresponding acid dissociation constant

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5} \quad 6.52$$

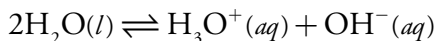
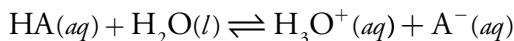
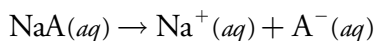
Taking the negative log of the terms in equation 6.52 and solving for pH leaves us with the result shown here.

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

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

6H.1 Systematic Solution to Buffer Problems

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



Because the concentrations of Na^+ , A^- , HA , H_3O^+ , and OH^- are unknown, we need five equations to uniquely define the solution's composition. Two of these equations are the equilibrium constant expressions for HA and H_2O .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad 6.54$$

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

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

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

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

and a charge balance equation

$$[\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{A}^-] \quad 6.57$$

Substituting equation 6.56 into equation 6.57 and solving for $[\text{A}^-]$ gives

$$[\text{A}^-] = C_{\text{NaA}} - [\text{OH}^-] + [\text{H}_3\text{O}^+] \quad 6.58$$

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

$$[\text{HA}] = C_{\text{HA}} + [\text{OH}^-] - [\text{H}_3\text{O}^+] \quad 6.59$$

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

$$\text{pH} = \text{p}K_a + \log \frac{C_{\text{NaA}} - [\text{OH}^-] + [\text{H}_3\text{O}^+]}{C_{\text{HA}} + [\text{OH}^-] - [\text{H}_3\text{O}^+]}$$

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

$$\text{pH} = \text{p}K_a + \log \frac{C_{\text{NaA}}}{C_{\text{HA}}} \quad 6.60$$

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

Lawrence Henderson (1878-1942) first developed a relationship between $[\text{H}_3\text{O}^+]$, $[\text{HA}]$, and $[\text{A}^-]$ 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 leading to equation 6.60 produce 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 $\text{p}K_a$ 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.

Example 6.12

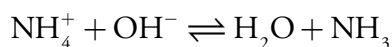
Calculate the pH of a buffer that is 0.020 M in NH_3 and 0.030 M in NH_4Cl . What is the pH after adding 1.0 mL of 0.10 M NaOH to 0.10 L of this buffer?

SOLUTION

The acid dissociation constant for NH_4^+ is 5.70×10^{-10} , or a $\text{p}K_a$ 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

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

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



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

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

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

Substituting these concentrations into the equation 6.60 gives a pH of

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

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 $C_{\text{NH}_4\text{Cl}}$, the approximations leading to equation 6.60 are reasonable.

Note that adding NaOH increases the pH from 9.06 to 9.10. As we expect, adding a base makes the pH more basic. Checking to see that the pH changes in the right direction is one way to catch a calculation error.

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 adding 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, using malonic acid ($pK_{a1} = 2.85$ and $pK_{a2} = 5.70$) we can prepare buffers with pH values of

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

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

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

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

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

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

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

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

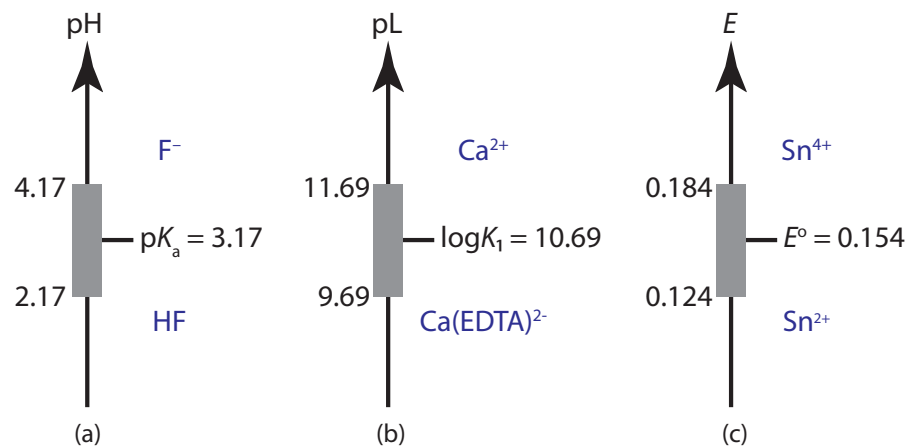


Figure 6.14 Ladder diagrams showing buffer regions for (a) an acid–base buffer for HF and F^- ; (b) a metal–ligand complexation buffer for Ca^{2+} and $Ca(EDTA)^{2-}$; and (c) an oxidation–reduction (redox) buffer for Sn^{4+} and Sn^{2+} .

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

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

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

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

6H.3 Preparing Buffers

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

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

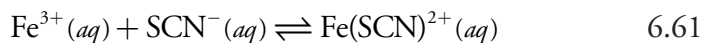
Although higher concentrations of buffering agents provide greater buffer capacity, there are reasons for using smaller concentrations, including the formation of unwanted precipitates and the tolerance of cells for high concentrations of dissolved salts.

A good “rule of thumb” when choosing a buffer is to select one whose reagents have a pK_a value close to your desired pH.

Buffer solutions are often prepared using standard “recipes” found in the chemical literature.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 containing an appropriate conjugate weak acid and weak base and measure its pH. You can then adjust the pH to the desired value by adding small portions of either a strong acid or a strong base.

6I Activity Effects

Careful measurements on the metal–ligand complex $\text{Fe}(\text{SCN})^{2+}$ suggest that 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 $\text{Fe}(\text{SCN})^{2+}$.



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 $\text{Fe}(\text{SCN})^{2+}$ and increasing the concentrations of Fe^{3+} and SCN^- . The result is a decrease in the complex’s formation constant, K_1 .

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

- 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.

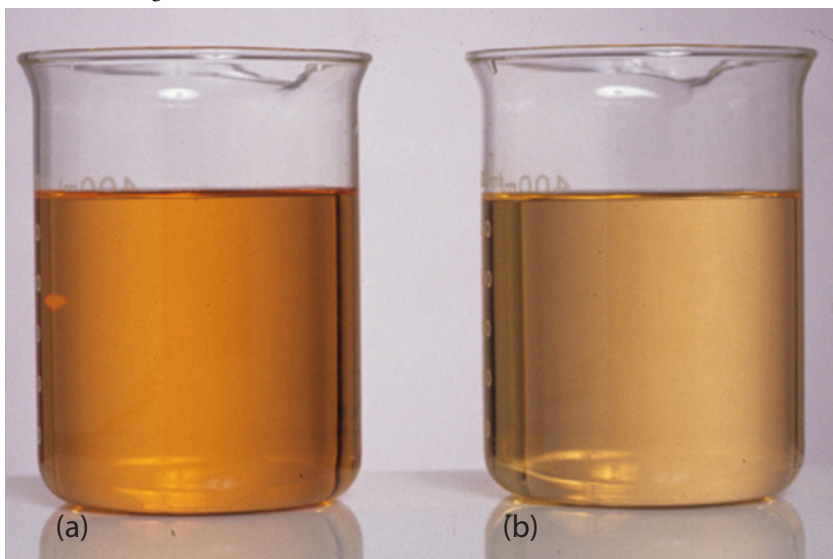


Figure 6.15 The effect of a inert salt on a reaction’s equilibrium position is shown by the solutions in these two beakers. The beaker on the left contains equal volumes of 1.0 mM FeCl_3 and 1.5 mM KSCN . The solution’s color is due to the formation of the metal–ligand complex $\text{Fe}(\text{SCN})^{2+}$. 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 $\text{Fe}(\text{SCN})^{2+}$ as a result of the equilibrium in reaction 6.61 shifting to the left.

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

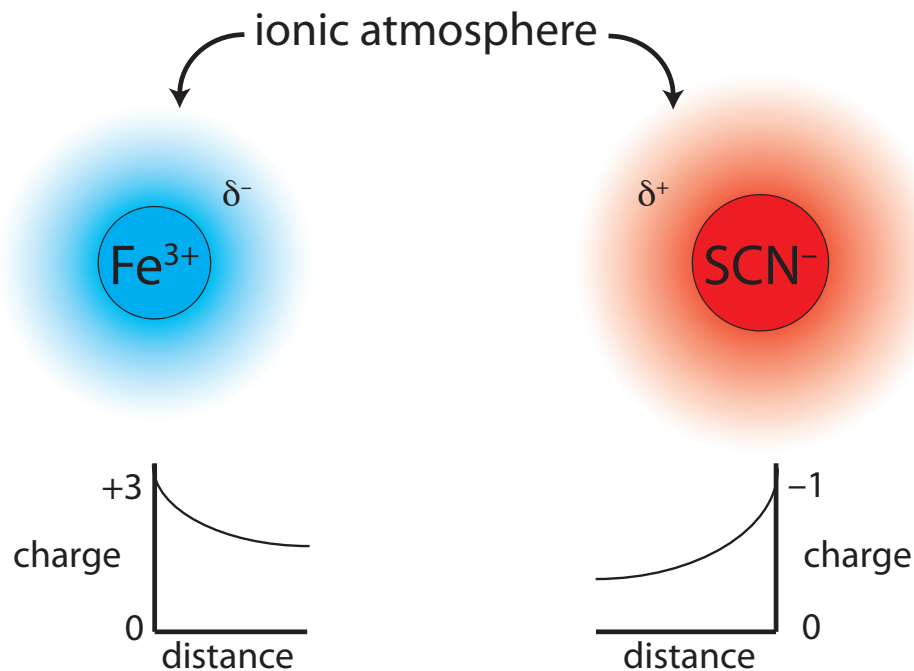


Figure 6.16 Ions of Fe^{3+} and SCN^- are surrounded by ionic atmospheres with net charges of δ^- and δ^+ . Because of these ionic atmospheres, each ion's apparent charge at the edge of its ionic atmosphere is less than the ion's actual charge.

Why should adding an inert electrolyte affect a reaction's equilibrium position? We can explain the effect of KNO_3 on the formation of $\text{Fe}(\text{SCN})^{2+}$ by considering the reaction on a microscopic scale. The solution in [Figure 6.15b](#) contains a variety of cations and anions— Fe^{3+} , SCN^- , K^+ , NO_3^- , H_3O^+ , and OH^- . Although the solution is homogeneous, on average, there are slightly more anions in regions near Fe^{3+} ions, and slightly more cations in regions near SCN^- ions. As shown in [Figure 6.16](#), each Fe^{3+} ion and SCN^- ion is surrounded by an ionic atmosphere of opposite charge (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 the $\text{Fe}(\text{SCN})^{2+}$ 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 $\text{Fe}(\text{SCN})^{2+}$, 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

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

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

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 calculating the ionic strength of these two solutions, be aware that an equilibrium reaction may well generate ions that affect the solution's ionic strength.

Example 6.13

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

SOLUTION

The ionic strength for 0.10 M NaCl is

$$\begin{aligned} &= \frac{1}{2} \left\{ [\text{Na}^+] \times (+1)^2 + [\text{Cl}^-] \times (-1)^2 \right\} \\ &= \frac{1}{2} \left\{ (0.10) \times (+1)^2 + (0.10) \times (-1)^2 \right\} \\ &= 0.10 \text{ M} \end{aligned}$$

For 0.10 M Na_2SO_4 the ionic strength is

$$\begin{aligned} &= \frac{1}{2} \left\{ [\text{Na}^+] \times (+1)^2 + [\text{SO}_4^{2-}] \times (-2)^2 \right\} \\ &= \frac{1}{2} \left\{ (0.10) \times (+1)^2 + (0.20) \times (-2)^2 \right\} \\ &= 0.30 \text{ M} \end{aligned}$$

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 $\text{Fe}(\text{SCN})^{2+}$. This creates a contradiction. Earlier in this chapter we showed that there is a relationship between a reaction's standard-state free energy, ΔG° , and its equilibrium constant, K .

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

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 $\text{Fe}(\text{SCN})^{2+}$, [reaction 6.61](#) must have an underlying *thermodynamic* formation constant that is independent of ionic strength.

The apparent formation constant for $\text{Fe}(\text{SCN})^{2+}$, 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 $\text{Fe}(\text{SCN})^{2+}$, therefore, is

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

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

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

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

where z_A is the ion's charge, α_A is the effective diameter of the hydrated ion 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. An ion's effective hydrated radius is the radius of the ion plus those water molecules closely bound to the ion. The effective radius is greater for smaller, more highly charged ions than it is for larger, less highly charged ions.

Table 6.2 Effective Diameters (a) for Selected Ions

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+} , CO_3^{2-} , SO_3^{2-}	0.45
Hg_2^{2+} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CrO_4^{2-} , HPO_4^{2-}	0.40
Al^{3+} , Fe^{3+} , Cr^{3+}	0.9
PO_4^{3-} , $\text{Fe}(\text{CN})_6^{3-}$	0.4
Zr^{4+} , Ce^{4+} , Sn^{4+}	1.1
$\text{Fe}(\text{CN})_6^{4-}$	0.5

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

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

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

INCLUDING ACTIVITY COEFFICIENTS WHEN SOLVING EQUILIBRIUM PROBLEMS

Earlier in this chapter we calculated the solubility of $\text{Pb}(\text{IO}_3)_2$ 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 $\text{Pb}(\text{IO}_3)_2$ in deionized water, we do not need to account for ionic strength.

But what if we need to know the solubility of $\text{Pb}(\text{IO}_3)_2$ in a solution containing other, inert ions? In this case we need to include activity coefficients in our calculation.

Example 6.14

Calculate the solubility of $\text{Pb}(\text{IO}_3)_2$ in a matrix of 0.020 M $\text{Mg}(\text{NO}_3)_2$.

SOLUTION

We begin by calculating the solution's ionic strength. Since $\text{Pb}(\text{IO}_3)_2$ is only sparingly soluble, we will assume that we can ignore its contribution to the ionic strength; thus

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

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

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

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

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

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

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

$$\gamma_{\text{IO}_3^-} = 0.810$$

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

Concentrations	$\text{Pb}(\text{IO}_3)_2(s)$	\rightleftharpoons	$\text{Pb}^{2+}(aq)$	+	$2\text{IO}_3^-(aq)$
Initial	solid		0		0
Change	solid		+ x		+ $2x$
Equilibrium	solid		x		$2x$

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

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

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

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

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

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

Practice Exercise 6.13

Calculate the molar solubility of 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.

The solution's equilibrium composition is

$$[\text{Pb}^{2+}] = 6.0 \times 10^{-5} \text{ M}$$

$$[\text{IO}_3^-] = 1.2 \times 10^{-4} \text{ M}$$

$$[\text{Mg}^{2+}] = 0.020 \text{ M}$$

$$[\text{NO}_3^-] = 0.040 \text{ M}$$

Because the concentrations of 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^- ? 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^- , 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

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

Now we see that the correct definition is

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

Failing to account for the effect of ionic strength can lead to a significant error in the reported concentration of 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, in developing and carrying out analytical methods, we are more interested in controlling pH than in calculating $[\text{H}_3\text{O}^+]$. As a result, the difference between the two definitions of pH is rarely a significant concern.

6J Using Excel and R to Solve Equilibrium Problems

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

6J.1 Excel

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

EXAMPLE 1: SOLUBILITY OF $\text{Pb}(\text{IO}_3)_2$ IN 0.10 M $\text{Pb}(\text{NO}_3)_2$

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, none are computationally easy. One approach is to iterate in on the answer by finding two values of x , one of which leads to a result larger than 2.5×10^{-13} and one of which 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 Excel's Solver function works.

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

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

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

Figure 6.17 Spreadsheet demonstrating the use of Excel's Solver function to find the root of a cubic equation. The spreadsheet in (a) shows the cubic equation in cell B2 and the initial guess for the value of x in cell B1; Excel replaces the formula with its equivalent value. The spreadsheet in (b) shows the results of running Excel's Solver function.

	A	B
(a)		
1	x =	0
2	function	= 4*b1^3 + 0.4*b1^2 - 2.5e-13
(b)		
1	x =	7.90565E-07
2	function	-5.71156E-19

cell B1. We expect x to be small—because $\text{Pb}(\text{IO}_3)_2$ is not very soluble—so setting our initial guess to 0 seems reasonable. Finally, we access the Solver function by selecting **Solver...** from the **Tools** menu, which opens the *Solver Parameters* window.

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

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

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

where *expected value* is the target cell's desired value (0 in this case), *calculated value* is the function's current value (cell B1 in this case), and *precision* is the value we enter in the box for *Precision*. Because our initial guess of $x=0$ gives a calculated result of 2.5×10^{-13} , accepting the Solver's default precision of 1×10^{-6} stops the search after one cycle. To be safe, 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 $\text{Pb}(\text{IO}_3)_2$.

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

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

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

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

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

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

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

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

$$\begin{aligned} [\text{H}_3\text{O}^+]^3 + K_a [\text{H}_3\text{O}^+]^2 \\ - (K_a C_{\text{HA}} + K_w) [\text{H}_3\text{O}^+] - K_a K_w = 0 \end{aligned} \quad 6.64$$

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

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

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

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

Practice Exercise 6.14

Using Excel, calculate the solubility of AgI in 0.10 M NH_3 without making any assumptions. See our [earlier treatment of this problem](#) for the relevant equilibrium reactions and constants.

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

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* and 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—such as solving an equilibrium problem with lots of unknowns—the Solver function becomes less reliable in finding a solution.

	A	B	C	D
1	pH =	3.00	2.00	1.00
2	[H ₃ O ⁺] =	= 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

(a)

	A	B	C	D
1	pH =	3.00	2.00	1.00
2	[H ₃ O ⁺] =	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

(b)

	A	B	C	D
1	pH =	1.59	1.58	1.57
2	[H ₃ O ⁺] =	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

(c)

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 [H₃O⁺] in the first row, and the formulas that you must 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.

6J.2 R

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

EXAMPLE 1: SOLUBILITY OF Pb(IO₃)₂ IN 0.10 M Pb(NO₃)₂

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

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

where x is the equilibrium concentration of Pb^{2+} . Although there are several approaches for solving cubic equations, none are computationally easy. One approach to solving the problem is to iterate in on the answer by finding two values of x , one of which leads to a result larger than 2.5×10^{-13} and one of which 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

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

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

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

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

$$> \text{eqn} = \text{function}(x) \ 4*x^3 + 0.4*x^2 - 2.5e-13$$

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.

$$> \text{uniroot}(\text{eqn}, \text{lower} = 0, \text{upper} = 0.1, \text{tol} = 1e-18)$$

We expect x to be small—because $\text{Pb}(\text{IO}_3)_2$ is not very soluble—so setting the lower limit to 0 is a reasonable choice. The choice for the upper limit is less critical. To ensure that the solution has sufficient precision, the tolerance should be smaller than the expected root. Figure 6.19 shows the resulting output. The value *\$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 $\text{Pb}(\text{IO}_3)_2$. The other results are the equation's value for the root, the number of iterations needed to find the root, and the root's estimated precision.

EXAMPLE 2: pH OF 1.0 M HF

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

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

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

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

For example, entering

```
> eqn(2)
```

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

```
$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.

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

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

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

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

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

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

Another option is to use write a function to solve simultaneously the four equations for the variables [HF], [F⁻], [H₃O⁺], and [OH⁻]. 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 [H₃O⁺], 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

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

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

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

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

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 are done entering 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)	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.

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

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

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

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

Practice Exercise 6.15

Using R, calculate the solubility of AgI in 0.10 M 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 have developed several tools for evaluating the composition of a system at equilibrium. These tools differ in how accurately they allow us to answer questions involving equilibrium chemistry. They also differ in their ease of use. An important part of having several tools available to you is knowing when to use them. If you need to know whether a reaction is favorable, or to estimate the pH of a solution, then a ladder diagram will meet your needs. On the other hand, if you require a more

accurate estimate of a compound's solubility, then a rigorous calculation that includes activity coefficients is necessary.

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

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

6L Key Terms

acid	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

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

6M Chapter Summary

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

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

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

When a ligand donates one or more pairs of electron to a metal ion, the result is a metal–ligand complex. Two types of equilibrium constants are used to describe metal–ligand complexation—stepwise formation constants and overall formation constants. There are two stepwise formation constants for the metal–ligand complex ML_2 , each describing the addition of one ligand; thus, K_1 represents the addition of the first ligand to M, and K_2 represents the addition of the second ligand to ML. Alternatively, we can use a cumulative, or overall formation constant, β_2 , for the metal–ligand complex ML_2 , in which both ligands are added to M.

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

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

You should be able to describe a system at equilibrium both qualitatively and quantitatively. You can develop a rigorous solution to an equilibrium problem by combining equilibrium constant expressions with appropriate mass balance and charge balance equations. Using this systematic approach, you can solve some quite complicated equilibrium problems. If a less rigor-

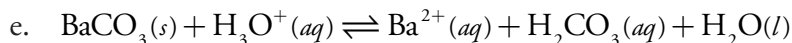
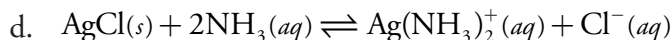
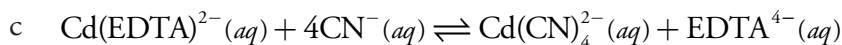
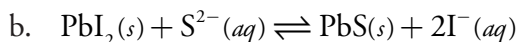
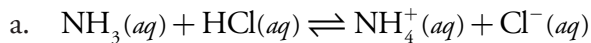
ous answer is acceptable, then a ladder diagram may help you estimate the equilibrium system's composition.

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

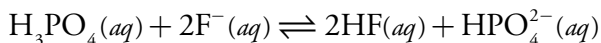
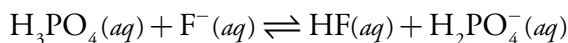
A quantitative solution to an equilibrium problem may give an answer that does not agree with experimental results if we do not consider the effect of ionic strength. The true, thermodynamic equilibrium constant is a function of activities, a , not concentrations. A species' activity is related to its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

6N Problems

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

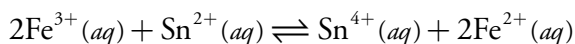


2. Using a ladder diagram, explain why the first reaction is favorable and the second reaction is unfavorable.



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

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



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

[Appendix 10: Solubility Products](#)

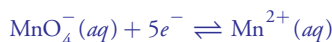
[Appendix 11: Acid Dissociation Constants](#)

[Appendix 12: Metal-Ligand Formation Constants](#)

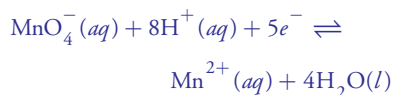
[Appendix 13: Standard State Reduction Potentials](#)

These redox reactions in this problem are not balanced. You will need to balance the reactions before calculating their standard state potentials. Although you may recall how to do this from another course, there is a much easier approach that you can use here. Identify the oxidizing agent and the reducing agent and divide the reaction into two unbalanced half-reactions. Using [Appendix 13](#), find the appropriate balanced half-reactions. Add the two half-reactions together and simplify the stoichiometry to arrive at the balanced redox reaction.

As an example, in (a) the oxidizing agent is MnO_4^- and its unbalanced half-reaction is



The corresponding balanced half-reaction from [Appendix 13](#) is



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

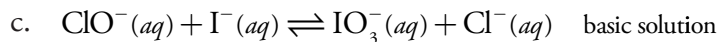
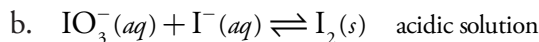
[Appendix 10: Solubility Products](#)

[Appendix 11: Acid Dissociation Constants](#)

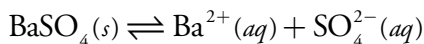
[Appendix 12: Metal-Ligand Formation Constants](#)

[Appendix 13: Standard State Reduction Potentials](#)

4. Calculate the standard state potential and the equilibrium constant for each of the following redox reactions. Assume that $[\text{H}_3\text{O}^+]$ is 1.0 M for acidic solutions, and that $[\text{OH}^-]$ is 1.0 M for basic solutions.



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.

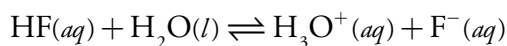
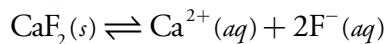


How do the following affect the solubility of BaSO_4 and, therefore, the accuracy of the analytical method?

- decreasing the solution's pH
 - adding more BaCl_2
 - increasing the volume of the solution by adding H_2O
6. Write a charge balance equation and mass balance equations for the following solutions. Some solutions may have more than one mass balance equation.
- 0.10 M NaCl
 - 0.10 M HCl
 - 0.10 M HF
 - 0.10 M NaH_2PO_4
 - MgCO₃ (saturated solution)
 - 0.10 M $\text{Ag}(\text{CN})_2^-$
 - 0.10 M HCl and 0.050 M NaNO₂
7. Using the systematic approach to equilibrium problems, calculate the pH of the following solutions. Be sure to state and justify any assumptions you make in solving the problems.
- 0.050 M HClO₄
 - 1.00×10^{-7} M HCl
 - 0.025 M HClO
 - 0.010 M HCOOH
 - 0.050 M Ba(OH)₂
 - 0.010 M C₅H₅N

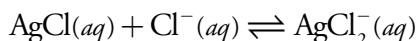
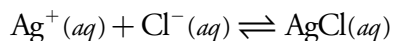
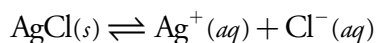
8. Construct ladder diagrams for the following diprotic weak acids (H_2L) and estimate the pH of 0.10 M solutions of H_2L , HL^- and L^{2-} .
- maleic acid
 - malonic acid
 - succinic acid
9. Using the systematic approach to solving equilibrium problems, calculate the pH of the diprotic weak acid in problem 8. Be sure to state and justify any assumptions you make in solving the problems.
10. Ignoring activity effects, calculate the concentration of Hg_2^{2+} in the following solutions. Be sure to state and justify any assumption you make in solving the problems.
- a saturated solution of Hg_2Br_2
 - 0.025 M $Hg_2(NO_3)_2$ saturated with Hg_2Br_2
 - 0.050 M NaBr saturated with Hg_2Br_2

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



Calculate the solubility of CaF_2 in a solution buffered to a pH of 7.00. Use a ladder diagram to help simplify the calculations. How would your approach to this problem change if the pH is buffered to 2.00? What is the solubility of CaF_2 at this pH? Be sure to state and justify any assumptions you make in solving the problems.

12. Calculate the solubility of $Mg(OH)_2$ in a solution buffered to a pH of 7.00. How does this compare to its solubility in unbuffered deionized water? Be sure to state and justify any assumptions you make in solving the problem.
13. Calculate the solubility of Ag_3PO_4 in a solution buffered to a pH of 7.00. Be sure to state and justify any assumptions you make in solving the problem.
14. Determine the equilibrium composition of saturated solution of $AgCl$. Assume that the solubility of $AgCl$ is influenced by the following reactions.



Be sure to state and justify any assumptions you make in solving the problem.

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

[Appendix 10: Solubility Products](#)

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[Appendix 13: Standard State Reduction Potentials](#)

15. Calculate the ionic strength of the following solutions
- 0.050 M NaCl
 - 0.025 M CuCl₂
 - 0.10 M Na₂SO₄
16. Repeat the calculations in problem 10, this time correcting for the effect of ionic strength. Be sure to state and justify any assumptions you make in solving the problems.
17. Over what pH range do you expect Ca₃(PO₄)₂ to have its minimum solubility?
18. Construct ladder diagrams for the following systems, each consisting of two or three equilibria. Using your ladder diagrams, what reactions are likely to occur in each system?
- HF and H₃PO₄
 - Ag(CN)₂⁻, Ni(CN)₄²⁻ and Fe(CN)₆³⁻
 - Cr₂O₇²⁻/Cr³⁺ and Fe³⁺/Fe²⁺
19. Calculate the pH of the following acid–base buffers. Be sure to state and justify any assumptions you make in solving the problems.
- 100 mL of 0.025 M formic acid and 0.015 M sodium formate
 - 50.00 mL of 0.12 M NH₃ and 5.30 mL of 1.0 M HCl
 - 5.00 g of Na₂CO₃ and 5.00 g of NaHCO₃ diluted to 100 mL
20. Calculate the pH of the buffers in problem 19 after adding 5.0 mL of 0.10 M HCl. Be sure to state and justify any assumptions you make in solving the problems.
21. Calculate the pH of the buffers in problem 19 after adding 5.0 mL of 0.10 M NaOH. Be sure to state and justify any assumptions you make in solving the problems.
22. Consider the following hypothetical complexation reaction between a metal, M, and a ligand, L
- $$M(aq) + L(aq) \rightleftharpoons ML(aq)$$
- with a formation constant of 1.5×10^8 . Derive an equation, similar to the Henderson–Hasselbalch equation, relating pM to the concentrations of L and ML. What is the pM for a solution containing 0.010 mol of M and 0.020 mol of L? What is pM be if you add 0.002 mol of M to this solution? Be sure to state and justify any assumptions you make in solving the problem.
23. A redox buffer contains an oxidizing agent and its conjugate reducing agent. Calculate the potential of a solution containing 0.010 mol of Fe³⁺ and 0.015 mol of Fe²⁺. What is the potential if you add sufficient

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

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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.
- the solubility of CaF_2 in deionized water
 - the solubility of AgCl in deionized water (see Problem 14 for the relevant equilibria)
 - the pH of 0.10 M fumaric acid
25. Beginning with the relevant equilibrium reactions, derive equation 6.64 for the rigorous solution to the pH of 0.1 M HF.

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

[Appendix 10: Solubility Products](#)

[Appendix 11: Acid Dissociation Constants](#)

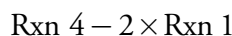
[Appendix 12: Metal-Ligand Formation Constants](#)

[Appendix 13: Standard State Reduction Potentials](#)

60 Solutions to Practice Exercises

Practice Exercise 6.1

The overall reaction is equivalent to



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

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

Click [here](#) to return to the chapter.

Practice Exercise 6.2

The K_b for hydrogen oxalate is

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

and the K_b for oxalate is

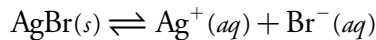
$$K_{b,\text{C}_2\text{O}_4^{2-}} = \frac{K_w}{K_{a,\text{HC}_2\text{O}_4^-}} = \frac{1.00 \times 10^{-14}}{5.42 \times 10^{-5}} = 1.85 \times 10^{-10}$$

As we expect, the K_b value for $\text{C}_2\text{O}_4^{2-}$ is larger than that for HC_2O_4^- .

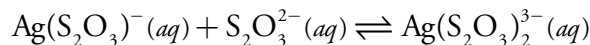
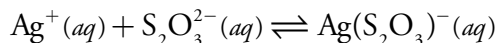
Click [here](#) to return to the chapter.

Practice Exercise 6.3

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



The remaining two reactions are the stepwise formation of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, which we characterize by K_1 and K_2 .



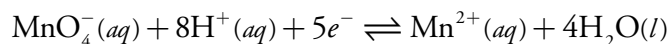
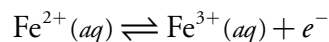
Using values for K_{sp} , K_1 , and K_2 from [Appendix 10](#) and [Appendix 11](#), we find that the equilibrium constant for our reaction is

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

Click [here](#) to return to the chapter.

Practice Exercise 6.4

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



From [Appendix 13](#), the standard state reduction potentials for these half-reactions are

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \text{ V} \quad E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$$

(a) The standard state potential for the reaction is

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

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

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

Solving for K gives its value as

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

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

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

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

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

Click [here](#) to return to the chapter.

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 to the side. The predominate form at a pH of 7.00 is HCO_3^- .

Click [here](#) to return to the chapter.

Practice Exercise 6.6

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

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

$$\text{moles } p\text{-nitrophenol} = 0.040 \text{ mol}$$

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

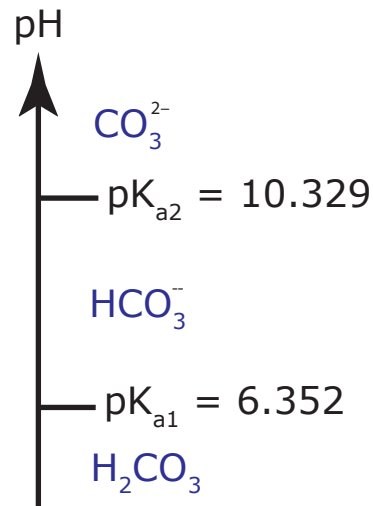
Click [here](#) to return to the chapter.

Practice Exercise 6.7

As Hg_2Cl_2 dissolves, two Cl^- are produced for each ion of Hg_2^{2+} . If we assume that 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	$\text{Hg}_2\text{Cl}_2(s)$	\rightleftharpoons	$\text{Hg}_2^{2+}(aq)$	+	$2\text{Cl}^-(aq)$
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



$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (x)(2x)^2 = 4x^3 = 1.2 \times 10^{-18}$$

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

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

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

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

Click [here](#) to return to the chapter.

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

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

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

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

This simplifies our problems to

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

which gives the value of x as

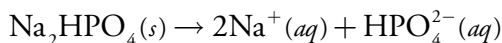
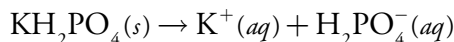
$$x = 1.2 \times 10^{-16} \text{ M}$$

The difference between the actual concentration of Cl^- , which is $(0.10 + x)$ M, and our assumption that it is 0.10 M introduces an error of $1.2 \times 10^{-14}\%$. This is a negligible error. The molar solubility of 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 [solution](#) to [Practice Exercise 6.7](#)).

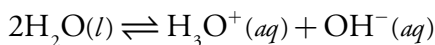
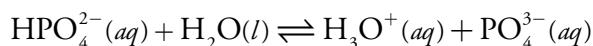
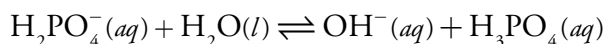
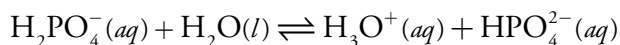
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Practice Exercise 6.9

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



and the acid–base dissociation reactions for H_2PO_4^- , HPO_4^{2-} , and H_2O .



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

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

but the mass balance equation for the phosphate takes a little bit of thought. Both 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.

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

The charge balance equation is

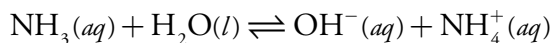
$$[\text{H}_3\text{O}^+] + [\text{K}^+] + [\text{Na}^+] =$$

$$[\text{H}_2\text{PO}_4^-] + 2 \times [\text{HPO}_4^{2-}] + 3 \times [\text{PO}_4^{3-}] + [\text{OH}^-]$$

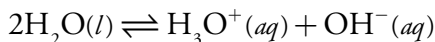
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Practice Exercise 6.10

In determining the pH of 0.050 M NH_3 , we need to consider two equilibrium reactions—the base dissociation reaction for NH_3



and water's dissociation reaction.



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

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

the K_w equation for H_2O

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

a mass balance on ammonia

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

and a charge balance equation

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

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

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

which simplifies the charge balance equation to

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

Because NH_3 is a weak base, our second assumption is

$$[\text{NH}_3] \gg [\text{NH}_4^+]$$

which simplifies the mass balance equation to

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

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

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

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

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{9.35 \times 10^{-4}} = 1.07 \times 10^{-11}$$

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

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

Because the concentration of NH_4^+ is 1.9% of C_{NH_3} , our second assumption also is reasonable. Given that $[\text{H}_3\text{O}^+]$ 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.

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

$$\text{Assumption Two: } K_{\text{a1}}K_{\text{w}} \ll K_{\text{a1}}K_{\text{a2}}C_{\text{HL}}$$

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

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

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

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

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

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

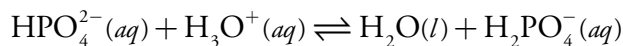
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Practice Exercise 6.12

The acid dissociation constant for H_2PO_4^- is 6.32×10^{-8} , or a $\text{p}K_{\text{a}}$ 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

$$\text{pH} = 7.199 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7.199 + \log \frac{0.050}{0.10} = 6.898 \approx 6.90$$

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



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

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

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

Substituting these concentrations into equation 6.60 gives a pH of

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

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

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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 $\mu = 0.10 \text{ M}$. 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^- .

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

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

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

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

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

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

$$K_{\text{sp}} = a_{\text{Hg}_2^{2+}} a_{\text{Cl}^-}^2 = \gamma_{\text{Hg}_2^{2+}} [\text{Hg}_2^{2+}] \gamma_{\text{Cl}^-}^2 [\text{Cl}^-]^2 = 1.2 \times 10^{-18}$$

$$1.2 \times 10^{-18} = (0.351)(x)(0.75)^2(0.10 + x)^2$$

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

$$1.2 \times 10^{-18} = (0.351)(x)(0.75)^2(0.10)^2$$

Solving for x gives its value as 6.1×10^{-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 $5 \times$ smaller than its actual value.

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Practice Exercise 6.14

To solve this problem, 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. See our earlier treatment of this problem for the relevant equilibrium reactions and equilibrium constants. 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 $[\text{Ag}^+]$, using the mass balance on iodide and silver to obtain $[\text{Ag}(\text{NH}_3)_2^+]$, using β_2 to calculate $[\text{NH}_3]$, using the mass balance on ammonia to find $[\text{NH}_4^+]$, using K_{b} to calculate

$[\text{OH}^-]$, and using K_w to calculate $[\text{H}_3\text{O}^+]$. The system's charge balance equation provides a means for determining the calculation's error.

$$[\text{Ag}^+] + [\text{Ag}(\text{NH}_3)_2^+] + [\text{NH}_4^+] + [\text{H}_3\text{O}^+] - [\text{I}^-] - [\text{OH}^-] = 0$$

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 $[\text{Ag}^+] = [\text{I}^-]$, the concentration of iodide is

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

corresponding 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 species in solution using the definition of pI to calculate $[\text{I}^-]$, using the K_{sp} to obtain $[\text{Ag}^+]$, using the mass balance on iodide and silver to obtain $[\text{Ag}(\text{NH}_3)_2^+]$, using β_2 to calculate $[\text{NH}_3]$, using the mass balance on ammonia to find $[\text{NH}_4^+]$, using K_b to calculate $[\text{OH}^-]$, and using K_w to calculate $[\text{H}_3\text{O}^+]$. The system's charge balance equation provides a means for determining the calculation's error.

$$[\text{Ag}^+] + [\text{Ag}(\text{NH}_3)_2^+] + [\text{NH}_4^+] + [\text{H}_3\text{O}^+] - [\text{I}^-] - [\text{OH}^-] = 0$$

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 $[\text{Ag}^+] = [\text{I}^-]$, the concentration of iodide is

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

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

```
> 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 $3.8 \times 10^{-6} \text{ mol/L}$, which agrees with our earlier solution to this problem.

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