

## 8

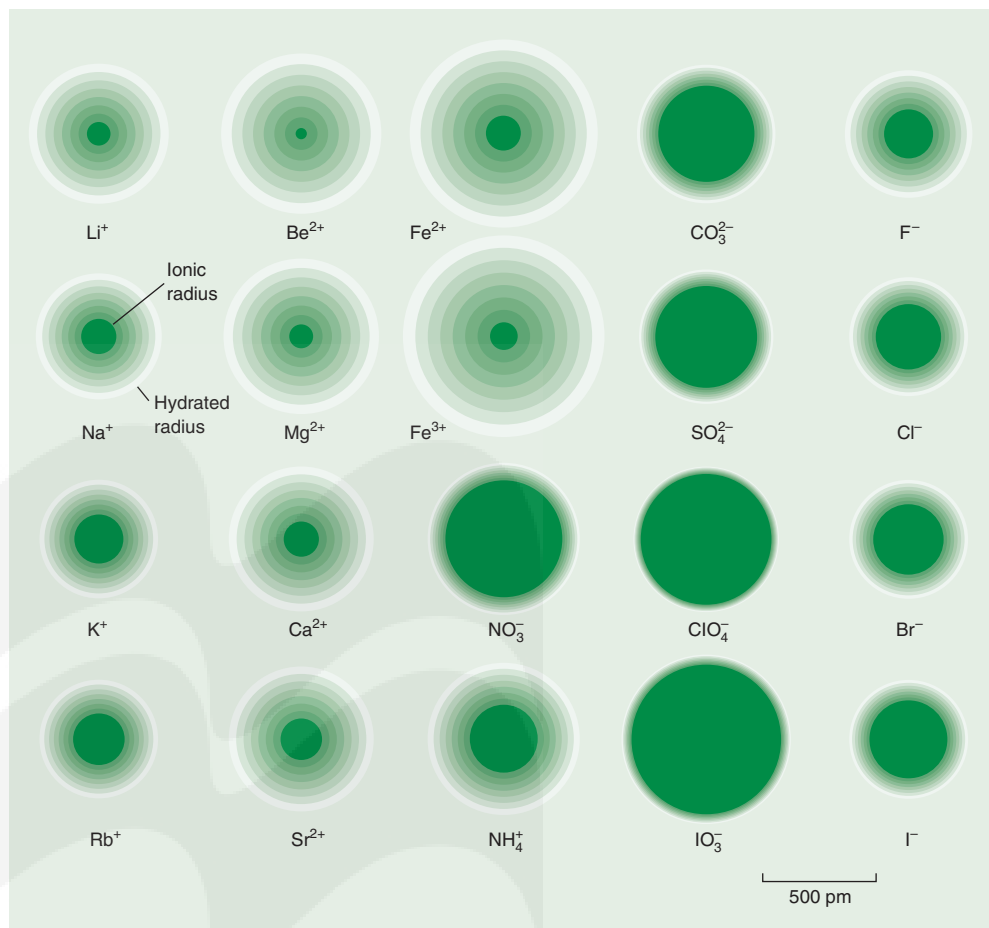
## Activity and the Systematic Treatment of Equilibrium

## HYDRATED IONS

Estimated Number of Waters of Hydration

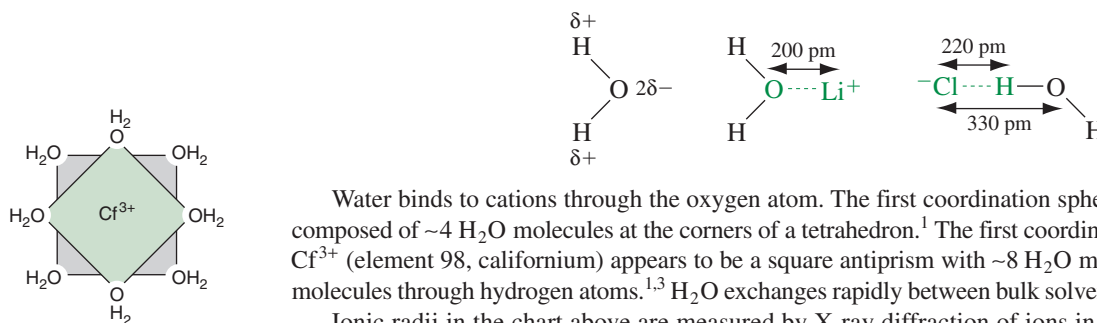
Molecule	Tightly bound H <sub>2</sub> O
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	0
C <sub>6</sub> H <sub>6</sub>	0
CH <sub>3</sub> CH <sub>2</sub> Cl	0
CH <sub>3</sub> CH <sub>2</sub> SH	0
CH <sub>3</sub> —O—CH <sub>3</sub>	1
CH <sub>3</sub> CH <sub>2</sub> OH	1
(CH <sub>3</sub> ) <sub>2</sub> C=O	1.5
CH <sub>3</sub> CH=O	1.5
CH <sub>3</sub> CO <sub>2</sub> H	2
CH <sub>3</sub> C≡N	3
$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CNHCH}_3 \end{array}$	4
CH <sub>3</sub> NO <sub>2</sub>	5
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	5
CH <sub>3</sub> NH <sub>2</sub>	6
CH <sub>3</sub> SO <sub>3</sub> H	7
NH <sub>3</sub>	9
CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	10
NH <sub>4</sub> <sup>+</sup>	12

Information from S. Fu and C. A. Lucy, "Prediction of Electrophoretic Mobilities," *Anal. Chem.* **1998**, 70, 173.



Ionic and hydrated radii of several ions. Smaller, more highly charged ions bind water molecules more tightly and behave as larger hydrated species.

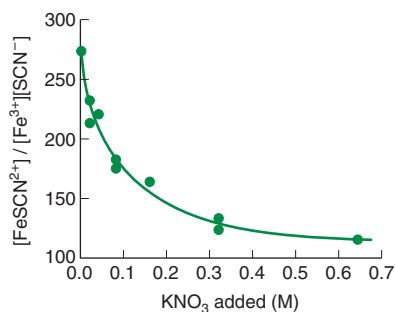
Ions and molecules in solution are surrounded by an organized sheath of solvent molecules. The oxygen atom of H<sub>2</sub>O has a partial negative charge and each hydrogen atom has half as much positive charge.



Cf<sup>3+</sup> resides in the center between planes of 4 H<sub>2</sub>O in a square antiprism geometry.

Water binds to cations through the oxygen atom. The first coordination sphere of the small cation Li<sup>+</sup> is composed of ~4 H<sub>2</sub>O molecules at the corners of a tetrahedron.<sup>1</sup> The first coordination sphere of the larger ion Cf<sup>3+</sup> (element 98, californium) appears to be a square antiprism with ~8 H<sub>2</sub>O molecules.<sup>2</sup> Cl<sup>-</sup> binds ~6 H<sub>2</sub>O molecules through hydrogen atoms.<sup>1,3</sup> H<sub>2</sub>O exchanges rapidly between bulk solvent and ion-coordination sites.

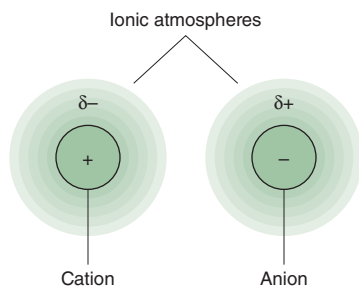
Ionic radii in the chart above are measured by X-ray diffraction of ions in crystals. Hydrated radii are estimated from diffusion coefficients of ions in solution and from the mobilities of aqueous ions in an electric field.<sup>4,5</sup> Smaller, more highly charged ions bind more water molecules and behave as larger species in solution. The *activity* of aqueous ions, which we study in this chapter, is related to the size of the hydrated species.



**FIGURE 8-1** Student data showing that the equilibrium quotient of concentrations for the reaction  $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{Fe}(\text{SCN})^{2+}$  decreases as potassium nitrate is added to the solution. Color Plate 4 shows the fading of the red color of  $\text{Fe}(\text{SCN})^{2+}$  after  $\text{KNO}_3$  has been added. Problem 13-11 gives more information on this chemical system. [Data from R. J. Stolzberg, "Discovering a Change in Equilibrium Constant with Change in Ionic Strength," *J. Chem. Ed.* **1999**, 76, 640.]

Addition of an "inert" salt increases the solubility of an ionic compound.

An anion is surrounded by excess cations.  
A cation is surrounded by excess anions.



**FIGURE 8-2** An ionic atmosphere, shown as a spherical cloud of charge  $\delta+$  or  $\delta-$ , surrounds ions in solution. The charge of the atmosphere is less than the charge of the central ion. The greater the ionic strength of the solution, the greater the charge in each ionic atmosphere.

In Chapter 6, we wrote the equilibrium constant for a reaction in the form

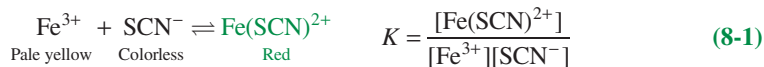


Figure 8-1, Demonstration 8-1, and Color Plate 4 show that the concentration quotient in Equation 8-1 decreases if you add the "inert" salt  $\text{KNO}_3$  to the solution. That is, the equilibrium "constant" is not really constant. This chapter explains why concentrations are replaced by *activities* in the equilibrium constant and how activities are used.

## 8-1 The Effect of Ionic Strength on Solubility of Salts

Consider a saturated solution of  $\text{CaSO}_4$  in distilled water.

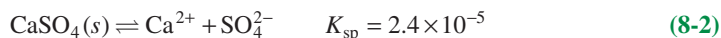


Figure 6-1 showed that the solubility is 0.015 M. The dissolved species are mainly 0.010 M  $\text{Ca}^{2+}$ , 0.010 M  $\text{SO}_4^{2-}$ , and 0.005 M  $\text{CaSO}_4(aq)$  (an ion pair).

Now an interesting effect is observed when a salt such as  $\text{KNO}_3$  is added to the solution. Neither  $\text{K}^+$  nor  $\text{NO}_3^-$  reacts with  $\text{Ca}^{2+}$  or  $\text{SO}_4^{2-}$ . Yet, when 0.050 M  $\text{KNO}_3$  is added to the saturated solution of  $\text{CaSO}_4$ , more solid dissolves until the concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  have increased by about 30%.

In general, adding an "inert" salt ( $\text{KNO}_3$ ) to a sparingly soluble salt ( $\text{CaSO}_4$ ) increases the solubility of the sparingly soluble salt. "Inert" means that  $\text{KNO}_3$  has no chemical reaction with  $\text{CaSO}_4$ . When we add salt to a solution, we say that the *ionic strength* of the solution increases. The definition of ionic strength will be given shortly.

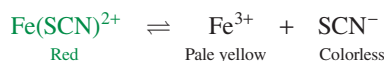
### The Explanation

Why does the solubility increase when salts are added to the solution? Consider one particular  $\text{Ca}^{2+}$  ion and one particular  $\text{SO}_4^{2-}$  ion in solution. The  $\text{SO}_4^{2-}$  ion is surrounded by  $\text{H}_2\text{O}$ , by cations ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ ), and by anions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ). However, an anion will be surrounded by more cations than anions because cations are attracted to the anion, but anions are repelled. These interactions create a region of net positive charge around any particular anion. We call this region the **ionic atmosphere** (Figure 8-2). Ions continually diffuse into and out of the ionic atmosphere. The net charge in the atmosphere, averaged over time, is less than the charge of the anion at the center. Similarly, an atmosphere of negative charge surrounds any cation in solution.

The ionic atmosphere attenuates (decreases) the attraction between ions. The cation plus its negative atmosphere has less positive charge than the cation alone. The anion plus its ionic atmosphere has less negative charge than the anion alone. The net attraction between the cation with its ionic atmosphere and the anion with its ionic atmosphere is smaller than it would be between pure cation and anion in the absence of ionic atmospheres. *The greater the ionic strength of a solution, the higher the charge in the ionic atmosphere. Each ion-plus-atmosphere contains less net charge, so there is less attraction between any particular cation and anion.*

### DEMONSTRATION 8-1 Effect of Ionic Strength on Ion Dissociation<sup>6</sup>

This experiment demonstrates the effect of ionic strength on the dissociation of the red iron(III) thiocyanate complex:



Prepare a solution of 1 mM  $\text{FeCl}_3$  by dissolving 0.27 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 1 L of water containing 3 drops of 15 M (concentrated)  $\text{HNO}_3$ . Acid slows the precipitation of  $\text{Fe}(\text{OH})_3$ , which occurs within a few days and necessitates the preparation of fresh solution for this demonstration.

To demonstrate the effect of ionic strength on the dissociation reaction, mix 300 mL of 1 mM  $\text{FeCl}_3$  with 300 mL of 1.5 mM  $\text{NH}_4\text{SCN}$  or  $\text{KSCN}$ . Divide the pale red solution into two equal portions and add 12 g of  $\text{KNO}_3$  to one of them to increase the ionic strength to 0.4 M. As  $\text{KNO}_3$  dissolves, the red  $\text{Fe}(\text{SCN})^{2+}$  complex dissociates and the color fades (Color Plate 4).

Add a few crystals of  $\text{NH}_4\text{SCN}$  or  $\text{KSCN}$  to either solution to drive the reaction toward formation of  $\text{Fe}(\text{SCN})^{2+}$ , thereby intensifying the red color. This reaction demonstrates Le Châtelier's principle—adding a product creates more reactant.

Increasing ionic strength reduces the attraction between any particular  $\text{Ca}^{2+}$  and any  $\text{SO}_4^{2-}$ , relative to their attraction for each other in distilled water. The effect is to reduce their tendency to come together, thereby *increasing* the solubility of  $\text{CaSO}_4$ .

Increasing ionic strength promotes dissociation into ions. Thus, each of the following reactions is driven to the right if the ionic strength is raised from, say, 0.01 to 0.1 M:

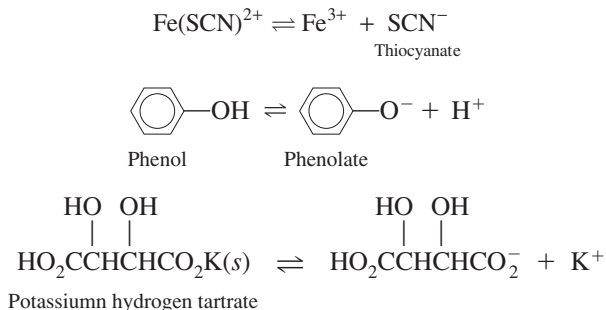


Figure 8-3 shows the effect of added salt on the solubility of potassium hydrogen tartrate.

### What Do We Mean by “Ionic Strength”?

**Ionic strength**,  $\mu$ , is a measure of the total concentration of ions in solution. The more highly charged an ion, the more it is counted.

*Ionic strength:*

$$\mu = \frac{1}{2} (c_1 z_1^2 + c_2 z_2^2 + \cdots) = \frac{1}{2} \sum c_i z_i^2 \quad (8-3)$$

where  $c_i$  is the concentration of the  $i$ th species and  $z_i$  is its charge. The sum extends over *all* ions in solution.

#### EXAMPLE Calculation of Ionic Strength

Find the ionic strength of (a) 0.10 M  $\text{NaNO}_3$ ; (b) 0.010 M  $\text{Na}_2\text{SO}_4$ ; and (c) 0.020 M  $\text{KBr}$  plus 0.010 M  $\text{Na}_2\text{SO}_4$ .

##### Solution

(a)  $\mu = \frac{1}{2} \{ [\text{Na}^+] \cdot (+1)^2 + [\text{NO}_3^-] \cdot (-1)^2 \}$   
 $= \frac{1}{2} \{ 0.10 \cdot 1 + 0.10 \cdot 1 \} = 0.10 \text{ M}$

(b)  $\mu = \frac{1}{2} \{ [\text{Na}^+] \cdot (+1)^2 + [\text{SO}_4^{2-}] \cdot (-2)^2 \}$   
 $= \frac{1}{2} \{ (0.020 \cdot 1) + (0.010 \cdot 4) \} = 0.030 \text{ M}$

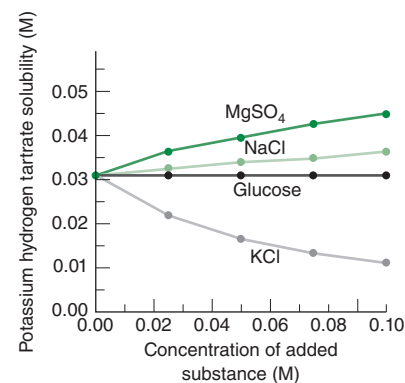
Note that  $[\text{Na}^+] = 0.020 \text{ M}$  because there are two moles of  $\text{Na}^+$  per mole of  $\text{Na}_2\text{SO}_4$ .

(c)  $\mu = \frac{1}{2} \{ [\text{K}^+] \cdot (+1)^2 + [\text{Br}^-] \cdot (-1)^2 + [\text{Na}^+] \cdot (+1)^2 + [\text{SO}_4^{2-}] \cdot (-2)^2 \}$   
 $= \frac{1}{2} \{ (0.020 \cdot 1) + (0.020 \cdot 1) + (0.020 \cdot 1) + (0.010 \cdot 4) \} = 0.050 \text{ M}$

**TEST YOURSELF** What is the ionic strength of 1 mM  $\text{CaCl}_2$ ? (*Answer:* 3 mM)

$\text{NaNO}_3$  is called a 1 : 1 electrolyte because the cation and the anion both have a charge of 1. For 1 : 1 electrolytes, ionic strength equals molarity. For other stoichiometries (such as the 2 : 1 electrolyte  $\text{Na}_2\text{SO}_4$ ), ionic strength is greater than molarity.

Computing the ionic strength of any but the most dilute solutions is complicated because salts with ions of charge  $\geq 2$  are not fully dissociated. In Box 8-1 we find that, at a formal concentration of 0.025 M  $\text{MgSO}_4$ , 35% of  $\text{Mg}^{2+}$  is bound in the ion pair,  $\text{MgSO}_4(aq)$ . The higher the concentration and the higher the ionic charge, the more the ion pairing. Ion pairing is ubiquitous in chemistry. Box 8-2 shows how ion pairing can be employed to extract and identify ionic metabolites from single live cells.



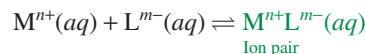
**FIGURE 8-3** Solubility of potassium hydrogen tartrate increases when the salts  $\text{MgSO}_4$  or  $\text{NaCl}$  are added. There is no effect when the neutral compound glucose is added. Addition of  $\text{KCl}$  decreases the solubility. (*Why?*) [From C. J. Marzocco, “Effect of Salts and Nonelectrolytes on the Solubility of Potassium Bitartrate,” *J. Chem. Ed.* **1998**, 75, 1628. Reprinted with permission © 1998 American Chemical Society.]

Electrolyte	Molarity	Ionic strength
1:1	M	M
2:1	M	3M
3:1	M	6M
2:2	M	4M

**BOX 8-1 Salts with Ions of Charge  $\geq 2$  Do Not Fully Dissociate<sup>7</sup>**

Salts composed of cations and anions with charges of  $\pm 1$  dissociate almost completely at concentrations  $< 0.1$  M in water. Salts containing ions with a charge  $\geq 2$  are less dissociated, even in dilute solution. Appendix J gives formation constants for *ion pairing*:

*Ion-pair formation constant:*



$$K = \frac{[ML]\gamma_{ML}}{[M]\gamma_M[L]\gamma_L}$$

where the  $\gamma_i$  are activity coefficients. With constants from Appendix J, activity coefficients from Equation 8-6, and the spreadsheet approach in Section 8-5, we calculate the following percentages of ion pairing in 0.025 F solutions:

Percentage of metal ion bound as ion pair in 0.025 F  $M_xL_y$  solution<sup>a</sup>

M \ L	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Na <sup>+</sup>	0.6%	9%
Mg <sup>2+</sup>	8%	35%

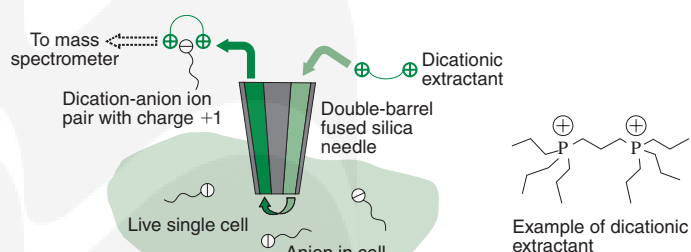
a. The size of ML was taken as 500 pm to compute its activity coefficient.

The table tells us that 0.025 F NaCl is only 0.6% associated as NaCl(aq) and Na<sub>2</sub>SO<sub>4</sub> is 9% associated as NaSO<sub>4</sub><sup>-</sup>(aq). For MgSO<sub>4</sub>, 35% is ion paired. A solution of 0.025 F MgSO<sub>4</sub> contains 0.016 M Mg<sup>2+</sup>, 0.016 M SO<sub>4</sub><sup>2-</sup>, and 0.009 M MgSO<sub>4</sub>(aq). The ionic strength of 0.025 F MgSO<sub>4</sub> is not 0.10 M but just 0.065 M. Problem 8-30 teaches you how to compute the fraction of ion pairing.

Ion pairing is not a precisely defined phenomenon. One definition is that two ions are paired if they remain within a given distance for a time longer than that needed to diffuse over that same distance.

**BOX 8-2 Ion Pairing for Single-Cell Analysis**

A cation with two positive sites (a dication) can be injected through a fine needle under a microscope into a single living cell to form tight ion pairs with anionic components of the cell and to extract those anions for identification by mass spectrometry. The dication in the figure extracted 70 identifiable metabolites, including folic acid (vitamin B<sub>9</sub>), from a single cell. Different dications might be selective for different classes of anions. The chemistry of single cells is a new frontier for biological science.



Dicationic molecule extracts anion from a live cell to make tight ion pair with net charge +1 whose exact mass is measured with a mass spectrometer. [Information from N. Pan, W. Rao, S. J. Standke, and Z. Yang, "Using Dicationic Ion-Pairing Compounds to Enhance the Single Cell Mass Spectrometry Analysis Using the Single-Probe: A Microscale Sampling and Ionization Device," *Anal. Chem.* **2016**, *88*, 6812.]

**8-2 Activity Coefficients**

Equation 8-1 does not predict any effect of ionic strength on a chemical reaction. To account for the effect of ionic strength, concentrations are replaced by **activities**:

Activity of C:

$$\mathcal{A}_C = [C]\gamma_C \quad (8-4)$$

$\uparrow$                        $\uparrow$                        $\nwarrow$   
 Activity      Concentration      Activity coefficient  
 of C              of C                      of C

Do not confuse the terms **activity** and **activity coefficient**.

The activity of species C is its concentration multiplied by its **activity coefficient**. The activity coefficient measures the deviation of behavior from ideality. If the activity coefficient were 1, then the behavior would be ideal and the equilibrium constant in Equation 8-1 would be correct.

Activity is a dimensionless quantity. Recall from Section 6-1 that [C] is really the dimensionless ratio of concentration divided by the concentration of the standard state. [C] in Equation 8-4 really means [C]/(1 M) if C is a solute or (pressure of C in bars)/(1 bar) if C is a gas. The activity of a pure solid or liquid is, by definition, unity.

The correct form of the equilibrium constant is

General form of equilibrium constant:

$$K = \frac{\mathcal{A}_C^c \mathcal{A}_D^d}{\mathcal{A}_A^a \mathcal{A}_B^b} = \frac{[C]^c \gamma_C^c [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b} \quad (8-5)$$

Equation 8-5 allows for the effect of ionic strength on a chemical equilibrium because the activity coefficients depend on ionic strength.

For Reaction 8-2, the equilibrium constant is

$$K_{sp} = \mathcal{A}_{Ca^{2+}} \mathcal{A}_{SO_4^{2-}} = [Ca^{2+}] \gamma_{Ca^{2+}} [SO_4^{2-}] \gamma_{SO_4^{2-}}$$

If the concentrations of  $Ca^{2+}$  and  $SO_4^{2-}$  are to *increase* when a second salt is added to increase ionic strength, the activity coefficients must *decrease* with increasing ionic strength.

At low ionic strength, activity coefficients approach unity, and the thermodynamic equilibrium constant (8-5) approaches the “concentration” equilibrium constant (6-2). One way to measure a thermodynamic equilibrium constant is to measure the concentration ratio (6-2) at successively lower ionic strengths and extrapolate to zero ionic strength. Commonly, tabulated equilibrium constants are not thermodynamic constants but just the concentration ratio (6-2) measured under a particular set of conditions.

Equation 8-5 is the “real” equilibrium constant. Equation 6-2 gave the concentration quotient,  $K_c$ , which did not include activity coefficients:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (6-2)$$

### EXAMPLE Exponents of Activity Coefficients

Write the solubility product expression for  $La_2(SO_4)_3(s) \rightleftharpoons 2La^{3+} + 3SO_4^{2-}$  with activity coefficients.

**Solution** Exponents of activity coefficients are the same as exponents of concentrations:

$$K_{sp} = \mathcal{A}_{La^{3+}}^2 \mathcal{A}_{SO_4^{2-}}^3 = [La^{3+}]^2 \gamma_{La^{3+}}^2 [SO_4^{2-}]^3 \gamma_{SO_4^{2-}}^3$$

**TEST YOURSELF** Write the equilibrium expression for  $Ca^{2+} + 2Cl^- \rightleftharpoons CaCl_2(aq)$  with

activity coefficients. **Answer:**  $K = \frac{\mathcal{A}_{CaCl_2}}{\mathcal{A}_{Ca^{2+}} \mathcal{A}_{Cl^-}^2} = \frac{[CaCl_2] \gamma_{CaCl_2}}{[Ca^{2+}] \gamma_{Ca^{2+}} [Cl^-]^2 \gamma_{Cl^-}^2}$

### Activity Coefficients of Ions

The ionic atmosphere model leads to the **extended Debye-Hückel equation**, relating activity coefficients to ionic strength:

Extended Debye-Hückel equation:

$$\log \gamma = \frac{-0.51z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu}/305)} \quad (\text{at } 25^\circ\text{C}) \quad (8-6)$$

In Equation 8-6,  $\gamma$  is the activity coefficient of an ion of charge  $\pm z$  and size  $\alpha$  (picometers, pm) in an aqueous solution of ionic strength  $\mu$ . The equation works fairly well for  $\mu \leq 0.1$  M. To find activity coefficients for ionic strengths above 0.1 M (up to molalities of 2–6 mol/kg for many salts), more complicated *Pitzer equations* are usually used.<sup>8</sup>

Table 8-1 lists sizes ( $\alpha$ ) and activity coefficients of many ions. All ions of the same size and charge appear in the same group and have the same activity coefficients. For example,  $Ba^{2+}$  and succinate ion  $[-O_2CCH_2CH_2CO_2^-]$ , listed as  $(CH_2CO_2^-)_2$  each have a size of 500 pm and are listed among the charge  $\pm 2$  ions. At an ionic strength of 0.001 M, both of these ions have an activity coefficient of 0.868.

The ion size  $\alpha$  in Equation 8-6 is an empirical parameter that provides agreement between measured activity coefficients and ionic strength up to  $\mu \approx 0.1$  M. In theory,  $\alpha$  is the diameter of the hydrated ion.<sup>9</sup> However, sizes in Table 8-1 cannot be taken literally. For example, the diameter of  $Cs^+$  ion in crystals is 340 pm. The hydrated  $Cs^+$  ion must be larger than the ion in the crystal, but the size of  $Cs^+$  in Table 8-1 is only 250 pm.

Even though ion sizes in Table 8-1 are empirical parameters, trends among sizes are sensible. Small, highly charged ions bind solvent more tightly and have larger effective sizes than do larger or less highly charged ions. For example, the order of sizes in Table 8-1 is  $Li^+ > Na^+ > K^+ > Rb^+$ , even though crystallographic radii are  $Li^+ < Na^+ < K^+ < Rb^+$ .

1 pm (picometer) =  $10^{-12}$  m

Ionic and hydrated ion sizes are shown at the opening of this chapter.



TABLE 8-1		Activity coefficients for aqueous solutions at 25°C				
Ion	Ion size ( $\alpha$ , pm)	Ionic strength ( $\mu$ , M)				
		0.001	0.005	0.01	0.05	0.1
Charge = $\pm 1$						
H <sup>+</sup>	900	0.967	0.933	0.914	0.86	0.83
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCO <sub>2</sub> <sup>-</sup> , (C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> N <sup>+</sup>	800	0.966	0.931	0.912	0.85	0.82
(O <sub>2</sub> N) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> O <sup>-</sup> , (C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> NH <sup>+</sup> , CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup>	700	0.965	0.930	0.909	0.845	0.81
Li <sup>+</sup> , C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup> , HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup> , ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup> , C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> CH <sub>2</sub> ) <sub>4</sub> N <sup>+</sup> , (C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	600	0.965	0.929	0.907	0.835	0.80
Cl <sub>2</sub> CHCO <sub>2</sub> <sup>-</sup> , Cl <sub>3</sub> CCO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> NH <sup>+</sup> , (C <sub>3</sub> H <sub>7</sub> )NH <sub>3</sub> <sup>+</sup>	500	0.964	0.928	0.904	0.83	0.79
Na <sup>+</sup> , CdCl <sup>+</sup> , ClO <sub>2</sub> <sup>-</sup> , IO <sub>3</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HSO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> , Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup> , CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> , ClCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup> , (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> , H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	450	0.964	0.928	0.902	0.82	0.775
<sup>+</sup> H <sub>3</sub> NCH <sub>2</sub> CO <sub>2</sub> H, (CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup> , CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	400	0.964	0.927	0.901	0.815	0.77
OH <sup>-</sup> , F <sup>-</sup> , SCN <sup>-</sup> , OCN <sup>-</sup> , HS <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> , IO <sub>4</sub> <sup>-</sup> , MnO <sub>4</sub> <sup>-</sup> , HCO <sub>2</sub> <sup>-</sup> , H <sub>2</sub> citrate <sup>-</sup> , CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> , (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	350	0.964	0.926	0.900	0.81	0.76
K <sup>+</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , CN <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	300	0.964	0.925	0.899	0.805	0.755
Rb <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Tl <sup>+</sup> , Ag <sup>+</sup>	250	0.964	0.924	0.898	0.80	0.75
Charge = $\pm 2$						
Mg <sup>2+</sup> , Be <sup>2+</sup>	800	0.872	0.755	0.69	0.52	0.45
CH <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> , (CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub>	700	0.872	0.755	0.685	0.50	0.425
Ca <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , Sn <sup>2+</sup> , Mn <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , C <sub>6</sub> H <sub>4</sub> (CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> , H <sub>2</sub> C(CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> , (CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub>	600	0.870	0.749	0.675	0.485	0.405
Sr <sup>2+</sup> , Ba <sup>2+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , S <sup>2-</sup> , S <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , WO <sub>4</sub> <sup>2-</sup> , H <sub>2</sub> C(CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> , (CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> , (CHOHCO <sub>2</sub> <sup>-</sup> ) <sub>2</sub>	500	0.868	0.744	0.67	0.465	0.38
Pb <sup>2+</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>3</sub> <sup>2-</sup> , MoO <sub>4</sub> <sup>2-</sup> , Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup> , Fe(CN) <sub>5</sub> NO <sup>2-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , Hcitrate <sup>2-</sup>	450	0.867	0.742	0.665	0.455	0.37
Hg <sub>2</sub> <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>6</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> , SeO <sub>4</sub> <sup>2-</sup> , CrO <sub>4</sub> <sup>2-</sup> , HPO <sub>4</sub> <sup>2-</sup>	400	0.867	0.740	0.660	0.445	0.355
Charge = $\pm 3$						
Al <sup>3+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , Sc <sup>3+</sup> , Y <sup>3+</sup> , In <sup>3+</sup> , lanthanides <sup>a</sup>	900	0.738	0.54	0.445	0.245	0.18
citrate <sup>3-</sup>	500	0.728	0.51	0.405	0.18	0.115
PO <sub>4</sub> <sup>3-</sup> , Fe(CN) <sub>6</sub> <sup>3-</sup> , Cr(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup> , Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup> , Co(NH <sub>3</sub> ) <sub>5</sub> H <sub>2</sub> O <sup>3+</sup>	400	0.725	0.505	0.395	0.16	0.095
Charge = $\pm 4$						
Th <sup>4+</sup> , Zr <sup>4+</sup> , Ce <sup>4+</sup> , Sn <sup>4+</sup>	1 100	0.588	0.35	0.255	0.10	0.065
Fe(CN) <sub>6</sub> <sup>4-</sup>	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.

SOURCE: Data from J. Kielland, J. Am. Chem. Soc. **1937**, 59, 1675.

### Effect of Ionic Strength, Ion Charge, and Ion Size on the Activity Coefficient

Over the range of ionic strengths from 0 to 0.1 M, the effect of each variable on activity coefficients is as follows:

1. As ionic strength increases, the activity coefficient decreases (Figure 8-4). The activity coefficient ( $\gamma$ ) approaches unity as the ionic strength ( $\mu$ ) approaches 0.
2. As the magnitude of the charge of the ion increases, its activity coefficient departs further from unity. Activity corrections are more important for ions with a charge of  $\pm 3$  than for ions with a charge of  $\pm 1$  (Figure 8-4).
3. The smaller the ion size ( $\alpha$ ), the more important activity effects become.

**EXAMPLE Using Table 8-1**

Find the activity coefficient of  $\text{Ca}^{2+}$  in a solution of 3.3 mM  $\text{CaCl}_2$ .

**Solution** The ionic strength is

$$\begin{aligned}\mu &= \frac{1}{2} \{ [\text{Ca}^{2+}] \cdot 2^2 + [\text{Cl}^-] \cdot (-1)^2 \} \\ &= \frac{1}{2} \{ (0.0033) \cdot 4 + (0.0066) \cdot 1 \} = 0.010 \text{ M}\end{aligned}$$

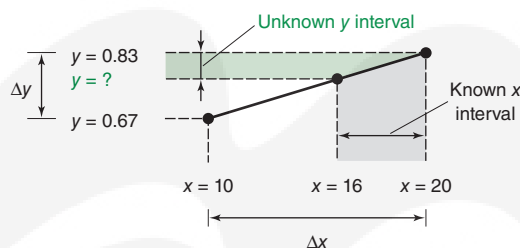
In Table 8-1,  $\text{Ca}^{2+}$  is listed under the charge  $\pm 2$  and has a size of 600 pm. Thus  $\gamma = 0.675$  when  $\mu = 0.010 \text{ M}$ .

**TEST YOURSELF** Find  $\gamma$  for  $\text{Cl}^-$  in 0.33 mM  $\text{CaCl}_2$ . (*Answer:* 0.964)

**How to Interpolate**

If you need to find an activity coefficient for an ionic strength that is between values in Table 8-1, you can use Equation 8-6. Alternatively, in the absence of a spreadsheet, you can interpolate in Table 8-1. In *linear interpolation*, we assume that values between two entries of a table lie on a straight line. For example, consider a table in which  $y = 0.67$  when  $x = 10$  and  $y = 0.83$  when  $x = 20$ . What is the value of  $y$  when  $x = 16$ ?

x value	y value
10	0.67
16	?
20	0.83



To interpolate a value of  $y$ , we can set up a proportion:

*Interpolation:*

$$\frac{\text{Unknown } y \text{ interval}}{\Delta y} = \frac{\text{known } x \text{ interval}}{\Delta x} \quad (8-7)$$

$$\frac{0.83 - y}{0.83 - 0.67} = \frac{20 - 16}{20 - 10} \Rightarrow y = 0.76_6$$

For  $x = 16$ , our estimate of  $y$  is 0.76<sub>6</sub>.

**EXAMPLE Interpolating Activity Coefficients**

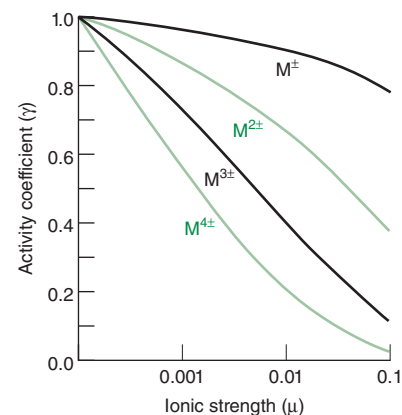
Calculate the activity coefficient of  $\text{H}^+$  when  $\mu = 0.025 \text{ M}$ .

**Solution**  $\text{H}^+$  is the first entry in Table 8-1.

$\mu$	$\gamma$ for $\text{H}^+$
0.01	0.914
0.025	?
0.05	0.86

The linear interpolation is set up as follows:

$$\begin{aligned}\frac{\text{Unknown } \gamma \text{ interval}}{\Delta \gamma} &= \frac{\text{known } \mu \text{ interval}}{\Delta \mu} \\ \frac{0.86 - \gamma}{0.86 - 0.914} &= \frac{0.05 - 0.025}{0.05 - 0.01} \\ \gamma &= 0.89_4\end{aligned}$$



**FIGURE 8-4** Activity coefficients for differently charged ions with a constant ionic size ( $\alpha$ ) of 500 pm. At zero ionic strength,  $\gamma = 1$ . The greater the charge of the ion, the more rapidly  $\gamma$  decreases as ionic strength increases. Note that the abscissa is logarithmic.

**Interpolation** is the estimation of a number that lies *between* two values in a table. Estimating a number that lies *beyond* values in a table is called **extrapolation**.

This calculation is equivalent to saying:

"16 is 60% of the way from 10 to 20. Therefore, the  $y$  value will be 60% of the way from 0.67 to 0.83."

**Another Solution** A better, but slightly more tedious, calculation uses Equation 8-6, with the ion size  $\alpha = 900$  pm listed for  $\text{H}^+$  in Table 8-1:

$$\log \gamma_{\text{H}^+} = \frac{(-0.51)(1^2)\sqrt{0.025}}{1 + (900\sqrt{0.025}/305)} = -0.054_{98}$$

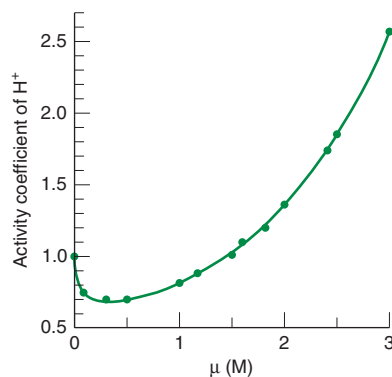
$$\gamma_{\text{H}^+} = 10^{-0.054_{98}} = 0.88_1$$

**TEST YOURSELF** By interpolation, find  $\gamma$  for  $\text{H}^+$  when  $\mu = 0.06$  M. (*Answer:* 0.85<sub>4</sub>)

For neutral species,  $\mathcal{A}_C \approx [C]$ . A more accurate relation is  $\log \gamma = k\mu$ , where  $k \approx 0$  for ion pairs,  $k \approx 0.11$  for  $\text{NH}_3$  and  $\text{CO}_2$ , and  $k \approx 0.2$  for organic molecules. For an ionic strength of  $\mu = 0.1$  M,  $\gamma \approx 1.00$  for ion pairs,  $\gamma \approx 1.03$  for  $\text{NH}_3$ , and  $\gamma \approx 1.05$  for organic molecules.

For gases,  $\mathcal{A} \approx P(\text{bar})$ .

At high ionic strength,  $\gamma$  increases with increasing  $\mu$ .



**FIGURE 8-5** Activity coefficient of  $\text{H}^+$  in solutions containing 0.0100 M  $\text{HClO}_4$  and varying amounts of  $\text{NaClO}_4$ . [Data from L. Pezza, M. Molina, M. de Moraes, C. B. Melios, and J. O. Tognolli, "Ionic Medium Effects on Equilibrium Constants: Part I. Proton, Copper(II), Cadmium(II), Lead(II) and Acetate Activity Coefficients in Aqueous Solution," *Talanta* **1996**, 43, 1689.] The authoritative source on electrolyte solutions is H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions* (New York: Reinhold, 1958 ed.).

For a deeper discussion of what pH really means and how the pH of primary standard solutions is measured, see B. Lunelli and F. Scagnolari, "pH Basics," *J. Chem. Ed.* **2009**, 86, 246.

## Activity Coefficients of Nonionic Compounds

Neutral molecules, such as benzene and acetic acid, have no ionic atmosphere because they have no charge. To a good approximation, their activity coefficients are unity when the ionic strength is less than 0.1 M. In this book, we set  $\gamma = 1$  for neutral molecules. That is, *the activity of a neutral molecule will be assumed to be equal to its concentration*.

For gases such as  $\text{H}_2$ , the activity is written

$$\mathcal{A}_{\text{H}_2} = P_{\text{H}_2} \gamma_{\text{H}_2}$$

where  $P_{\text{H}_2}$  is pressure in bars. The activity of a gas is called its *fugacity*, and the activity coefficient is called the *fugacity coefficient*. Deviation of gas behavior from the ideal gas law results in deviation of the fugacity coefficient from unity. For gases at or below 1 bar,  $\gamma \approx 1$ . Therefore, for gases, we will set  $\mathcal{A} = P(\text{bar})$ .

## High Ionic Strengths

Above an ionic strength of  $\sim 1$  M, activity coefficients of most ions increase, as shown for  $\text{H}^+$  in  $\text{NaClO}_4$  solutions in Figure 8-5. We should not be too surprised that activity coefficients in concentrated salt solutions are not the same as those in dilute aqueous solution. The "solvent" is no longer  $\text{H}_2\text{O}$  but, rather, a mixture of  $\text{H}_2\text{O}$  and  $\text{NaClO}_4$ . Hereafter, we limit our attention to dilute aqueous solutions.

### EXAMPLE Using Activity Coefficients

Find the concentration of  $\text{Ca}^{2+}$  in equilibrium with 0.050 M  $\text{NaF}$  saturated with  $\text{CaF}_2$ . The solubility of  $\text{CaF}_2$  is small, so the concentration of  $\text{F}^-$  is 0.050 M from  $\text{NaF}$ .

**Solution** We find  $[\text{Ca}^{2+}]$  from the solubility product expression, including activity coefficients. The ionic strength of 0.050 M  $\text{NaF}$  is 0.050 M. At  $\mu = 0.050$  M in Table 8-1, we find  $\gamma_{\text{Ca}^{2+}} = 0.485$  and  $\gamma_{\text{F}^-} = 0.81$ .

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

$$3.2 \times 10^{-11} = [\text{Ca}^{2+}] (0.485) (0.050)^2 (0.81)^2$$

$$[\text{Ca}^{2+}] = 4.0 \times 10^{-8} \text{ M}$$

The value of  $K_{\text{sp}}$  came from Appendix F. Note that  $\gamma_{\text{F}^-}$  is squared.

**TEST YOURSELF** Find  $[\text{Hg}_2^{2+}]$  in equilibrium with 0.010 M  $\text{KCl}$  saturated with  $\text{Hg}_2\text{Cl}_2$ . (*Answer:*  $2.2 \times 10^{-14}$  M)

## 8-3 pH Revisited

The definition  $\text{pH} \approx -\log[\text{H}^+]$  in Chapter 6 is not exact. A better definition is

$$\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log[\text{H}^+] \gamma_{\text{H}^+} \quad (8-8)$$

When we measure pH with a pH meter, we are attempting to measure the negative logarithm of the hydrogen ion *activity*, not its concentration.



**EXAMPLE** pH of Pure Water at 25°C

Let's calculate the pH of pure water by using activity coefficients.

**Solution** The relevant equilibrium is



$$K_w = \mathcal{A}_{\text{H}^+} \mathcal{A}_{\text{OH}^-} = [\text{H}^+] \gamma_{\text{H}^+} [\text{OH}^-] \gamma_{\text{OH}^-} \quad (8-10)$$

$\text{H}^+$  and  $\text{OH}^-$  are produced in a 1 : 1 mole ratio, so their concentrations must be equal. Calling each concentration  $x$ , we write

$$K_w = 1.0 \times 10^{-14} = (x) \gamma_{\text{H}^+} (x) \gamma_{\text{OH}^-}$$

But the ionic strength of pure water is so small that it is reasonable to guess that  $\gamma_{\text{H}^+} = \gamma_{\text{OH}^-} = 1$ . Using these values in the preceding equation gives

$$1.0 \times 10^{-14} = (x)(1)(x)(1) = x^2 \Rightarrow x = 1.0 \times 10^{-7} \text{ M}$$

The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are both  $1.0 \times 10^{-7} \text{ M}$ . The ionic strength is  $1.0 \times 10^{-7} \text{ M}$ , so each activity coefficient is very close to 1.00. The pH is

$$\text{pH} = -\log[\text{H}^+] \gamma_{\text{H}^+} = -\log(1.0 \times 10^{-7})(1.00) = 7.00$$

**EXAMPLE** pH of Water Containing a Salt

Now let's calculate the pH of water containing 0.10 M KCl at 25°C.

**Solution** Reaction 8-9 tells us that  $[\text{H}^+] = [\text{OH}^-]$ . However, the ionic strength of 0.10 M KCl is 0.10 M. The activity coefficients of  $\text{H}^+$  and  $\text{OH}^-$  in Table 8-1 are 0.83 and 0.76, respectively, when  $\mu = 0.10 \text{ M}$ . Putting these values into Equation 8-10 gives

$$\begin{aligned} K_w &= [\text{H}^+] \gamma_{\text{H}^+} [\text{OH}^-] \gamma_{\text{OH}^-} \\ 1.0 \times 10^{-14} &= (x)(0.83)(x)(0.76) \\ x &= 1.26 \times 10^{-7} \text{ M} \end{aligned}$$

The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are equal and are both greater than  $1.0 \times 10^{-7} \text{ M}$ . The activities of  $\text{H}^+$  and  $\text{OH}^-$  are not equal in this solution:

$$\begin{aligned} \mathcal{A}_{\text{H}^+} &= [\text{H}^+] \gamma_{\text{H}^+} = (1.26 \times 10^{-7})(0.83) = 1.05 \times 10^{-7} \\ \mathcal{A}_{\text{OH}^-} &= [\text{OH}^-] \gamma_{\text{OH}^-} = (1.26 \times 10^{-7})(0.76) = 0.96 \times 10^{-7} \end{aligned}$$

Finally, we calculate  $\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log(1.05 \times 10^{-7}) = 6.98$ .

**TEST YOURSELF** Find  $[\text{H}^+]$  and the pH of 0.05 M  $\text{LiNO}_3$ . (**Answer:**  $1.20 \times 10^{-7} \text{ M}$ , 6.99)

The pH of water changes from 7.00 to 6.98 when we add 0.10 M KCl. KCl is not an acid or a base. The pH changes because KCl affects the activities of  $\text{H}^+$  and  $\text{OH}^-$ . The pH change of 0.02 units lies at the limit of accuracy of pH measurements and is hardly important. However, the *concentration* of  $\text{H}^+$  in 0.10 M KCl ( $1.26 \times 10^{-7} \text{ M}$ ) is 26% greater than the concentration of  $\text{H}^+$  in pure water ( $1.00 \times 10^{-7} \text{ M}$ ).

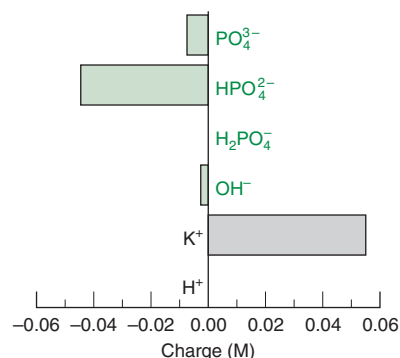
**8-4** Systematic Treatment of Equilibrium

The *systematic treatment of equilibrium* is a way to deal with all types of chemical equilibria, regardless of their complexity. After setting up general equations, we often introduce specific conditions or judicious approximations that allow simplification. Even simplified calculations are usually tedious, so we make liberal use of spreadsheets for numerical solutions.

The systematic procedure is to write as many independent algebraic equations as there are unknowns (species) in the problem. The equations are generated by writing all the chemical equilibrium conditions plus two more: the balances of charge and of mass. There is only one charge balance in a given system, but there could be several mass balances.

Solutions must have zero total charge.

The coefficient of each term in the charge balance equals the magnitude of the charge on each ion.



**FIGURE 8-6** Charge contributed by each ion in 1.00 L of solution containing 0.025 0 mol  $\text{KH}_2\text{PO}_4$  plus 0.030 0 mol  $\text{KOH}$ . The total positive charge equals the total negative charge.

$\Sigma[\text{positive charges}] = \Sigma[\text{negative charges}]$

Activity coefficients do not appear in the charge balance. The charge contributed by 0.1 M  $\text{H}^+$  is exactly 0.1 M. Think about this.

The mass balance is a statement of the conservation of matter. It really refers to conservation of atoms, not to mass.

## Charge Balance

The **charge balance** is an algebraic statement of electroneutrality: *The sum of the positive charges in solution equals the sum of the negative charges in solution.*

Suppose that a solution contains the following ionic species:  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{K}^+$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ . The charge balance is

$$[\text{H}^+] + [\text{K}^+] = [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] \quad (8-11)$$

This statement says that the total charge contributed by  $\text{H}^+$  and  $\text{K}^+$  equals the magnitude of the charge contributed by all of the anions on the right side of the equation. *The coefficient in front of each species always equals the magnitude of the charge on the ion.* This statement is true because a mole of, say,  $\text{PO}_4^{3-}$  contributes three moles of negative charge. If  $[\text{PO}_4^{3-}] = 0.01 \text{ M}$ , the negative charge is  $3[\text{PO}_4^{3-}] = 3(0.01) = 0.03 \text{ M}$ .

Equation 8-11 appears unbalanced to many people. “The right side of the equation has much more charge than the left side!” you might think. But you would be wrong.

For example, consider a solution prepared by weighing out 0.025 0 mol of  $\text{KH}_2\text{PO}_4$  plus 0.030 0 mol of  $\text{KOH}$  and diluting to 1.00 L. The concentrations of the species at equilibrium are calculated to be

$$\begin{aligned} [\text{H}^+] &= 3.9 \times 10^{-12} \text{ M} & [\text{H}_2\text{PO}_4^-] &= 1.4 \times 10^{-6} \text{ M} \\ [\text{K}^+] &= 0.055 0 \text{ M} & [\text{HPO}_4^{2-}] &= 0.022 56 \text{ M} \\ [\text{OH}^-] &= 0.002 56 \text{ M} & [\text{PO}_4^{3-}] &= 0.002 44 \text{ M} \end{aligned}$$

This calculation, which you should be able to do when you have finished studying acids and bases, takes into account the reaction of  $\text{OH}^-$  with  $\text{H}_2\text{PO}_4^-$  to produce  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .

Are the charges balanced? Yes, indeed. Plugging into Equation 8-11, we find

$$\begin{aligned} [\text{H}^+] + [\text{K}^+] &= [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] \\ 3.9 \times 10^{-12} + 0.055 0 &= 0.002 56 + 1.4 \times 10^{-6} + 2(0.022 56) + 3(0.002 44) \\ 0.055 0 \text{ M} &= 0.055 0 \text{ M} \end{aligned}$$

The total positive charge is 0.055 0 M, and the total negative charge also is 0.055 0 M (Figure 8-6). Charges must balance in every solution. Otherwise, a beaker with excess positive charge would glide across the lab bench and smash into a beaker with excess negative charge.

The general form of the charge balance for any solution is

$$\text{Charge balance: } n_1[\text{C}_1] + n_2[\text{C}_2] + \dots = m_1[\text{A}_1] + m_2[\text{A}_2] + \dots \quad (8-12)$$

where  $[\text{C}]$  is the concentration of a cation,  $n$  is the charge of the cation,  $[\text{A}]$  is the concentration of an anion, and  $m$  is the magnitude of the charge of the anion.

### EXAMPLE Writing a Charge Balance

Write the charge balance for a solution containing  $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{ClO}_4^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{CN}^-$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HCN}$ ,  $\text{NH}_3$ , and  $\text{NH}_4^+$ .

**Solution** Neutral species ( $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HCN}$ , and  $\text{NH}_3$ ) contribute no charge, so the charge balance is

$$[\text{H}^+] + 3[\text{Fe}^{3+}] + 2[\text{Mg}^{2+}] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{ClO}_4^-] + 3[\text{Fe}(\text{CN})_6^{3-}] + [\text{CN}^-]$$

**TEST YOURSELF** What would be the charge balance if you add  $\text{MgCl}_2$  to the solution and it dissociates into  $\text{Mg}^{2+} + 2\text{Cl}^-$ ? (**Answer:**  $[\text{H}^+] + 3[\text{Fe}^{3+}] + 2[\text{Mg}^{2+}] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{ClO}_4^-] + 3[\text{Fe}(\text{CN})_6^{3-}] + [\text{CN}^-] + [\text{Cl}^-]$ )

## Mass Balance

The **mass balance**, also called the *material balance*, is a statement of the conservation of matter. The mass balance states that *the quantity of all species in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution.* It is easier to see this relation through examples than by a general statement.

Suppose that a solution is prepared by dissolving 0.050 mol of acetic acid in water to give a total volume of 1.00 L. Acetic acid partially dissociates into acetate:



The mass balance states that the quantity of dissociated and undissociated acetic acid in the solution must equal the amount of acetic acid put into the solution.

Mass balance for acetic acid in water:

$$0.050 \text{ M} = \underset{\text{What we put into the solution}}{[\text{CH}_3\text{CO}_2\text{H}]} + \underset{\text{Undissociated product}}{[\text{CH}_3\text{CO}_2^-]} + \underset{\text{Dissociated product}}{[\text{H}^+]}$$

When a compound dissociates in several ways, the mass balance must include all the products. Phosphoric acid ( $\text{H}_3\text{PO}_4$ ), for example, dissociates to  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ . The mass balance for phosphorus atoms in a solution prepared by dissolving 0.025 0 mol of  $\text{H}_3\text{PO}_4$  in 1.00 L is

$$0.025 \text{ 0 M} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

*Activity coefficients do not appear in the mass balance. The concentration of each species counts exactly the number of atoms of that species.*

### EXAMPLE Mass Balance When the Total Concentration Is Known

Write the mass balances for  $\text{K}^+$  and for phosphate in a solution prepared by mixing 0.025 0 mol  $\text{KH}_2\text{PO}_4$  plus 0.030 0 mol  $\text{KOH}$  and diluting to 1.00 L.

**Solution** The total  $\text{K}^+$  is 0.025 0 M + 0.030 0 M, so one mass balance is

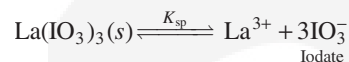
$$[\text{K}^+] = 0.055 \text{ 0 M}$$

The total of *all forms* of phosphate is 0.025 0 M, so the mass balance for phosphate is

$$[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 0.025 \text{ 0 M}$$

**TEST YOURSELF** Write two mass balances for a 1.00-L solution containing 0.100 mol of sodium acetate. (**Answer:**  $[\text{Na}^+] = 0.100 \text{ M}$ ;  $[\text{CH}_3\text{CO}_2\text{H}] + [\text{CH}_3\text{CO}_2^-] = 0.100 \text{ M}$ )

Now consider a solution prepared by dissolving  $\text{La}(\text{IO}_3)_3$  in water.



We do not know how much  $\text{La}^{3+}$  or  $\text{IO}_3^-$  is dissolved, but we do know that there must be three iodate ions for each lanthanum ion dissolved. That is, the iodate concentration must be three times the lanthanum concentration. If  $\text{La}^{3+}$  and  $\text{IO}_3^-$  are the only species derived from  $\text{La}(\text{IO}_3)_3$ , then the mass balance is

$$[\text{IO}_3^-] = 3[\text{La}^{3+}]$$

If the solution also contains the ion pair  $\text{LaIO}_3^{2+}$  and the hydrolysis product  $\text{LaOH}^{2+}$ , the mass balance would be

$$\begin{aligned} [\text{Total iodate}] &= 3[\text{total lanthanum}] \\ [\text{IO}_3^-] + [\text{LaIO}_3^{2+}] &= 3\{[\text{La}^{3+}] + [\text{LaIO}_3^{2+}] + [\text{LaOH}^{2+}]\} \end{aligned}$$

### EXAMPLE Mass Balance When the Total Concentration Is Unknown

Write the mass balance for a saturated solution of the slightly soluble salt  $\text{Ag}_3\text{PO}_4$ , which produces  $\text{PO}_4^{3-}$  and  $3\text{Ag}^+$  when it dissolves.

**Solution** If the phosphate in solution remained as  $\text{PO}_4^{3-}$ , we could write

$$[\text{Ag}^+] = 3[\text{PO}_4^{3-}]$$

because three silver ions are produced for each phosphate ion. However, phosphate reacts with water to give  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{H}_3\text{PO}_4$ , so the mass balance is

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

Atoms of Ag = 3 (atoms of P)

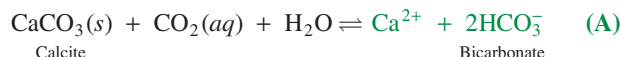
Box 8-3 illustrates the operation of a mass balance in natural waters.

That is, the number of atoms of  $\text{Ag}^+$  must equal three times the total number of atoms of phosphorus, regardless of how many species contain phosphorus.

**TEST YOURSELF** Write the mass balance for a saturated solution of  $\text{Ba}(\text{HSO}_4)_2$  if the species in solution are  $\text{Ba}^{2+}$ ,  $\text{BaSO}_4(aq)$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{BaOH}^+$ . (**Answer:**  $2 \times \text{total barium} = \text{total sulfate}$ , or  $2([\text{Ba}^{2+}] + [\text{BaSO}_4(aq)] + [\text{BaOH}^+]) = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{BaSO}_4(aq)]$ )

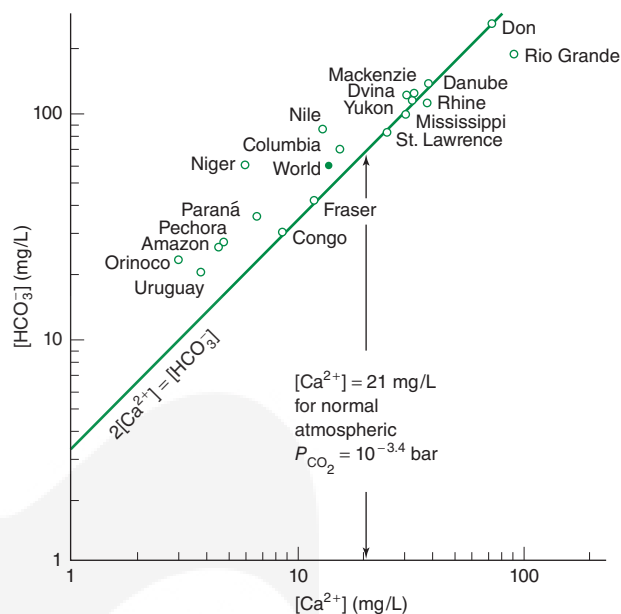
### BOX 8-3 Calcium Carbonate Mass Balance in Rivers

$\text{Ca}^{2+}$  is the most common cation in rivers and lakes. It comes from dissolution of the mineral calcite by the action of  $\text{CO}_2$  to produce 2 moles of  $\text{HCO}_3^-$  for each mole of  $\text{Ca}^{2+}$ :



Near neutral pH, most of the product is bicarbonate, not  $\text{CO}_3^{2-}$  or  $\text{H}_2\text{CO}_3$ . The mass balance for the dissolution of calcite is therefore  $[\text{HCO}_3^-] \approx 2[\text{Ca}^{2+}]$ . Indeed, measurements of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in many rivers conform to this mass balance, shown by the straight line on the graph. Rivers such as the Danube, the Mississippi, and the Congo, which lie on the line  $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$ , appear to be saturated with calcium carbonate. If the river water were in equilibrium with atmospheric  $\text{CO}_2$  ( $P_{\text{CO}_2} = 10^{-3.4}$  bar), the concentration of  $\text{Ca}^{2+}$  would be 21 mg/L (see Problem 8-34). Rivers with more than 21 mg of  $\text{Ca}^{2+}$  per liter have a higher concentration of dissolved  $\text{CO}_2$  produced by respiration or from inflow of groundwaters with a high  $\text{CO}_2$  content. Rivers such as the Nile, the Niger, and the Amazon, for which  $2[\text{Ca}^{2+}] < [\text{HCO}_3^-]$ , are not saturated with  $\text{CaCO}_3$ .

Between 1960 and 2016, atmospheric  $\text{CO}_2$  increased by 28%—mostly from our burning of fossil fuel. This increase drives Reaction A to the right and threatens the existence of coral reefs,<sup>10</sup> which are living structures consisting largely of  $\text{CaCO}_3$ . Coral reefs are a unique habitat for many aquatic species. Continued buildup of atmospheric  $\text{CO}_2$  threatens certain plankton and other forms of sea life with  $\text{CaCO}_3$  shells,<sup>11</sup> a loss that, in turn, threatens higher members of the food chain.



Concentrations of bicarbonate and calcium in many rivers conform to the mass balance  $[\text{HCO}_3^-] \approx 2[\text{Ca}^{2+}]$ . [Data from W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 3rd ed. (New York: Wiley-Interscience, 1996), p. 189; and H. D. Holland, *The Chemistry of the Atmosphere and Oceans* (New York: Wiley-Interscience, 1978).]

### Systematic Treatment of Equilibrium

Now that we have considered the charge and mass balances, we are ready for the systematic treatment of equilibrium.<sup>12</sup> Here is the general prescription:

- Step 1** Write the *pertinent reactions*.
- Step 2** Write the *charge balance equation*.
- Step 3** Write *mass balance equations*. There may be more than one.
- Step 4** Write the *equilibrium constant expression* for each chemical reaction. This step is the only one in which activity coefficients appear.
- Step 5** *Count the equations and unknowns*. There should be as many equations as unknowns (chemical species). If not, you must either find more equilibria or fix some concentrations at known values.
- Step 6** *Solve for all unknowns*.

Steps 1 and 6 are the heart of the problem. Guessing what chemical equilibria exist in a given solution requires a fair degree of chemical intuition. In this book, you will usually be given help with step 1. Unless we know all the relevant equilibria, it is not possible to calculate the composition of a solution correctly. Because we do not know all the chemical reactions, we undoubtedly oversimplify many equilibrium problems. Step 6—solving the equations—is likely to be your biggest challenge. With  $n$  equations and  $n$  unknowns, the problem can be solved, at least in principle. In the simplest cases, you can do this by hand, but, for most problems, approximations are made or a spreadsheet is employed.

## 8-5 Applying the Systematic Treatment of Equilibrium

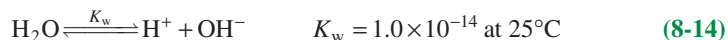
Now we examine some problems to learn to apply the systematic treatment of equilibrium and to illustrate what can be done by hand and when a spreadsheet is really helpful.

### A Solution of Ammonia

Let's find the concentrations of species in an aqueous solution containing 0.010 0 mol  $\text{NH}_3$  in 1.000 L. The primary equilibrium is



A second equilibrium in every aqueous solution is



Our goal is to find  $[\text{NH}_3]$ ,  $[\text{NH}_4^+]$ ,  $[\text{H}^+]$ , and  $[\text{OH}^-]$ .

**Step 1** Pertinent reactions. They are 8-13 and 8-14.

**Step 2** Charge balance. The sum of positive charge equals the sum of negative charge:

$$[\text{NH}_4^+] + [\text{H}^+] = [\text{OH}^-] \quad (8-15)$$

**Step 3** Mass balance. All of the ammonia delivered to the solution is either in the form  $\text{NH}_3$  or  $\text{NH}_4^+$ . These two must add up to 0.010 0 M.

$$[\text{NH}_3] + [\text{NH}_4^+] = 0.010\,0\,\text{M} \equiv F \quad (8-16)$$

where F stands for formal concentration.

**Step 4** Equilibrium expressions

$$K_b = \frac{[\text{NH}_4^+]\gamma_{\text{NH}_4^+}[\text{OH}^-]\gamma_{\text{OH}^-}}{[\text{NH}_3]\gamma_{\text{NH}_3}} = 10^{-4.755} \quad (8-17)$$

$$K_w = [\text{H}^+]\gamma_{\text{H}^+}[\text{OH}^-]\gamma_{\text{OH}^-} = 10^{-14.00} \quad (8-18)$$

The symbol  $\equiv$  means "is defined as."

We use pK in spreadsheet 8-7. pK is the negative logarithm of an equilibrium constant. For  $K_b = 10^{-4.755}$ ,  $\text{p}K_b = 4.755$ .

*This is the only step in which activity coefficients enter the problem.*

**Step 5** Count equations and unknowns. We have four equations, 8-15 to 8-18, and four unknowns ( $[\text{NH}_3]$ ,  $[\text{NH}_4^+]$ ,  $[\text{H}^+]$ , and  $[\text{OH}^-]$ ). We have enough information to solve the problem.

We need  $n$  equations to solve for  $n$  unknowns.

**Step 6** Solve.

This "simple" problem is complicated. Let's start by ignoring activity coefficients; we return to them later in the  $\text{Mg}(\text{OH})_2$  example. *Our approach is to eliminate one variable at a time until only one unknown is left.* For an acid-base problem, I choose to express each concentration in terms of  $[\text{H}^+]$ . A substitution we can always make is  $[\text{OH}^-] = K_w/[\text{H}^+]$ . Putting this expression for  $[\text{OH}^-]$  into the charge balance 8-15 gives

$$[\text{NH}_4^+] + [\text{H}^+] = \frac{K_w}{[\text{H}^+]}$$

from which we can solve for  $[\text{NH}_4^+]$ :

$$[\text{NH}_4^+] = \frac{K_w}{[\text{H}^+]} - [\text{H}^+] \quad (8-19)$$

The mass balance tells us that  $[\text{NH}_3] = F - [\text{NH}_4^+]$ . We can substitute the expression for  $[\text{NH}_4^+]$  from Equation 8-19 into the mass balance to express  $[\text{NH}_3]$  in terms of  $[\text{H}^+]$ :

$$[\text{NH}_3] = F - [\text{NH}_4^+] = F - \left( \frac{K_w}{[\text{H}^+]} - [\text{H}^+] \right) \quad (8-20)$$

Equation 8-19 gives  $[\text{NH}_4^+]$  in terms of  $[\text{H}^+]$ . Equation 8-20 gives  $[\text{NH}_3]$  in terms of  $[\text{H}^+]$ .

We can generate an equation in which the only unknown is  $[\text{H}^+]$  by substituting our expressions for  $[\text{NH}_4^+]$ ,  $[\text{NH}_3]$ , and  $[\text{OH}^-]$  into the  $K_b$  equilibrium (still ignoring activity coefficients):

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{\left( \frac{K_w}{[\text{H}^+]} - [\text{H}^+] \right) \left( \frac{K_w}{[\text{H}^+]} \right)}{\left( F - \frac{K_w}{[\text{H}^+]} + [\text{H}^+] \right)} \quad (8-21)$$

**FIGURE 8-7** Spreadsheet to find concentrations of species in aqueous  $\text{NH}_3$  using Excel Goal Seek. Cell B3 contains  $\text{p}K_b = -\log K_b$ . If  $\text{p}K_b = 4.755$ ,  $K_b = 10^{-4.755}$ .

	A	B	C	D	E
1	Using Goal Seek for Ammonia Equilibrium				
2					
3	$\text{p}K_b =$	4.755	$K_b =$	1.76E-05	$= 10^{\wedge}\text{B3}$
4	$\text{p}K_w =$	14.00	$K_w =$	1.00E-14	$= 10^{\wedge}\text{B4}$
5	$F =$	0.01			
6					
7	$\text{pH} =$	9	Initial value is estimate		
8	$[\text{H}^+] =$	1.00E-09	$= 10^{\wedge}\text{B7}$		
9	$[\text{NH}_4^+] = K_w/[\text{H}^+] - [\text{H}^+] =$	1.00E-05	$= \text{D4/B8-B8}$		
10	$[\text{OH}^-] = K_w/[\text{H}^+] =$	1.00E-05	$= \text{D4/B8}$		
11	$[\text{NH}_3] = F - K_w/[\text{H}^+] + [\text{H}^+] =$	9.99E-03	$= \text{B5-D4/B8+B8}$		
12	$Q = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] =$	1.00E-08	$= \text{B9*B10/B11}$		
13	$K_b - [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] =$	1.76E-05	$= \text{D3-B12}$		

Equation 8-21 is horrible, but  $[\text{H}^+]$  is the only unknown. Excel has a built-in procedure called Goal Seek that solves equations with one unknown. Set up the spreadsheet in Figure 8-7, which uses Equations 8-19 and 8-20 for  $[\text{NH}_4^+]$  and  $[\text{NH}_3]$ , plus  $[\text{OH}^-] = K_w/[\text{H}^+]$  in cells B9, B11, and B10. Cell B5 contains the formal concentration of ammonia,  $F = 0.01 \text{ M}$ . Cell B7 contains an estimate (a guess in this case) for  $\text{pH}$  from which  $[\text{H}^+]$  is computed in cell B8. Ammonia is a base, so we guess a basic  $\text{pH} = 9$ . Cell B12 evaluates the reaction quotient  $Q = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$  with whatever (incorrect) concentrations are in cells B9:B11. Cell B13 shows the difference  $K_b - [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$ . If concentrations in cells B9:B11 are correct, then  $K_b - [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$  would be 0.

We will use Goal Seek to adjust the  $\text{pH}$  in cell B7 until the difference  $K_b - [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$  in cell B13 is as close to 0 as Excel can make it. Before calling Goal Seek in Excel 2016, go to the File tab, click Options, and select Formulas. In Calculation Options, set Maximum Change to  $1\text{E-}14$  and click OK. When the difference in cell B13 is less than  $1\text{E-}14$ , Excel will consider it to be “zero.”

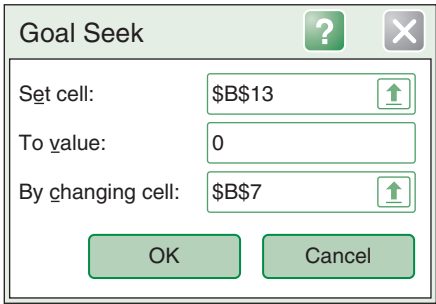
Back in the spreadsheet, select the Data tab and click What If Analysis in Forecast. Select Goal Seek. In the Goal Seek window in Figure 8-8a, set cell B13 To value 0 By changing cell B7. Click OK and Excel varies the value in B7 until the value in B13 is close to 0. The final  $\text{pH}$  appears in cell B7 in Figure 8-8b. Concentrations of all species appear in cells B8:B11. That was pretty easy once we set up the spreadsheet!

The concentrations of  $[\text{NH}_4^+]$  and  $[\text{NH}_3]$  in cells B9 and B11 after executing Goal Seek in Figure 8-8b confirm that ammonia is a weak base. The fraction that has reacted with water is just 4.1%:

$$\text{Fraction reacted} = \frac{[\text{NH}_4^+]}{[\text{NH}_3] + [\text{NH}_4^+]} = \frac{[4.11 \times 10^{-4} \text{ M}]}{[9.59 \times 10^{-3} \text{ M}] + [4.11 \times 10^{-4} \text{ M}]} = 4.1\%$$

You should now appreciate that applying the systematic treatment of equilibrium to even the simplest of problems is not simple. In most equilibrium problems, we make simplifying approximations to reach a good answer with a reasonable effort. After solving a problem, we must always verify that our approximations are valid.

Here is an approximation to simplify the ammonia problem. Ammonia is a base, so we expect that  $[\text{OH}^-] \gg [\text{H}^+]$ . For example, suppose the  $\text{pH}$  comes out to 9. Then  $[\text{H}^+] = 10^{-9} \text{ M}$  and  $[\text{OH}^-] (= K_w/[\text{H}^+]) = 10^{-14}/10^{-9} = 10^{-5} \text{ M}$ . That is,  $[\text{OH}^-] \gg [\text{H}^+]$ . In the first term



	A	B
7	$\text{pH} =$	10.61339622
8	$[\text{H}^+] =$	2.44E-11
9	$[\text{NH}_4^+] = K_w/[\text{H}^+] - [\text{H}^+] =$	4.11E-04
10	$[\text{OH}^-] = K_w/[\text{H}^+] =$	4.11E-04
11	$[\text{NH}_3] = F - K_w/[\text{H}^+] + [\text{H}^+] =$	9.59E-03
12	$Q = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] =$	1.76E-05
13	$K_b - [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] =$	5.14E-18

**FIGURE 8-8** (a) Goal Seek window and (b) concentrations after executing Goal Seek.



of the numerator of Equation 8-21, we can neglect  $[\text{H}^+]$  in comparison with  $K_w/[\text{H}^+]$ . In the denominator, we can also neglect  $[\text{H}^+]$  in comparison with  $K_w/[\text{H}^+]$ . With these approximations, Equation 8-21 becomes

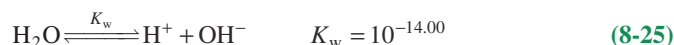
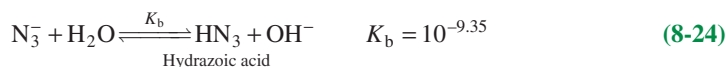
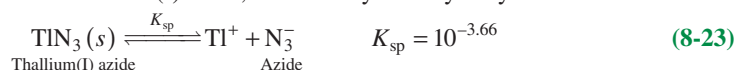
$$K_b = \frac{\left(\frac{K_w}{[\text{H}^+]} - [\text{H}^+]\right)\left(\frac{K_w}{[\text{H}^+]}\right)}{\left(F - \frac{K_w}{[\text{H}^+]} + [\text{H}^+]\right)} = \frac{\left(\frac{K_w}{[\text{H}^+]}\right)\left(\frac{K_w}{[\text{H}^+]}\right)}{\left(F - \frac{K_w}{[\text{H}^+]}\right)} = \frac{[\text{OH}^-]^2}{F - [\text{OH}^-]} \quad (8-22)$$

Equation 8-22 is quadratic with one variable  $[\text{OH}^-]$ . We can use algebra to solve for  $[\text{OH}^-]$ . We will deal with equations of this type extensively in the next chapter on acids and bases.

Now we introduce a more general spreadsheet approach that does not require us to reduce an equilibrium problem to one equation in one unknown.

### Solubility and Hydrolysis of Thallium Azide

Consider the dissolution of thallium(I) azide, followed by base hydrolysis of azide:



Our goal is to find  $[\text{Ti}^+]$ ,  $[\text{N}_3^-]$ ,  $[\text{HN}_3]$ ,  $[\text{H}^+]$ , and  $[\text{OH}^-]$ .

**Step 1** Pertinent reactions. The three reactions are 8-23 to 8-25.

**Step 2** Charge balance. The sum of positive charge equals the sum of negative charge:

$$[\text{Ti}^+] + [\text{H}^+] = [\text{N}_3^-] + [\text{OH}^-] \quad (8-26)$$

**Step 3** Mass balance. Dissolution of  $\text{TlN}_3$  gives an equal number of  $\text{Ti}^+$  and  $\text{N}_3^-$ . Some azide becomes hydrazoic acid. The concentration of  $\text{Ti}^+$  equals the sum of concentrations of  $\text{N}_3^-$  and  $\text{HN}_3$ .

$$[\text{Ti}^+] = [\text{N}_3^-] + [\text{HN}_3] \quad (8-27)$$

**Step 4** Equilibrium expressions

$$K_{\text{sp}} = [\text{Ti}^+]\gamma_{\text{Ti}^+}[\text{N}_3^-]\gamma_{\text{N}_3^-} = 10^{-3.66} \quad (8-28)$$

$$K_b = \frac{[\text{HN}_3]\gamma_{\text{HN}_3}[\text{OH}^-]\gamma_{\text{OH}^-}}{[\text{N}_3^-]\gamma_{\text{N}_3^-}} = 10^{-9.35} \quad (8-29)$$

$$K_w = [\text{H}^+]\gamma_{\text{H}^+}[\text{OH}^-]\gamma_{\text{OH}^-} = 10^{-14.00} \quad (8-30)$$

**Step 5** Count equations and unknowns. There are five equations, 8-26 to 8-30, and five unknowns ( $[\text{Ti}^+]$ ,  $[\text{N}_3^-]$ ,  $[\text{HN}_3]$ ,  $[\text{H}^+]$ , and  $[\text{OH}^-]$ ), so we have enough information to solve the problem.

**Step 6** Solve. We now introduce a spreadsheet method with broad application to equilibrium problems.<sup>13</sup> We ignore activity coefficients for now, but will eventually deal with them.

With five unknowns and three equilibria 8-28 to 8-30, the spreadsheet method begins with an *estimate* for two of the unknown concentrations:

Number of concentrations to estimate =

$$(\text{number of unknowns}) - (\text{number of equilibria}) = 5 - 3 = 2 \quad (8-31)$$

We then write expressions for the remaining three concentrations in terms of the two estimated concentrations. It is desirable to estimate concentrations of species that appear in two or more equilibria. In Equations 8-28 to 8-30, the species  $\text{N}_3^-$  and  $\text{OH}^-$  each appear twice, so we will estimate their concentrations. From these estimates, we find the remaining concentrations from the equilibrium expressions:

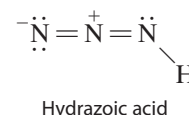
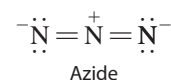
$$[\text{Ti}^+][\text{N}_3^-] = K_{\text{sp}} \Rightarrow [\text{Ti}^+] = K_{\text{sp}}/[\text{N}_3^-] \quad (8-32)$$

$$\frac{[\text{HN}_3][\text{OH}^-]}{[\text{N}_3^-]} = K_b \Rightarrow [\text{HN}_3] = \frac{K_b[\text{N}_3^-]}{[\text{OH}^-]} \quad (8-33)$$

$$[\text{H}^+][\text{OH}^-] = K_w \Rightarrow [\text{H}^+] = K_w/[\text{OH}^-] \quad (8-34)$$

The solution to quadratic equation 8-22 is  $[\text{OH}^-] = 4.11 \times 10^{-4} \text{ M}$ , giving  $[\text{H}^+] = K_w/[\text{OH}^-] = 2.44 \times 10^{-11} \text{ M}$ , confirming the approximation that  $[\text{OH}^-] \gg [\text{H}^+]$ .

Azide is a linear ion with two equivalent  $\text{N}=\text{N}$  bonds:



We continue to neglect activity coefficients until the next example.

**FIGURE 8-9** Thallium azide solubility spreadsheet without activity coefficients. Initial estimates  $\text{pN}_3^- = 2$  and  $\text{pOH}^- = 4$  appear in cells B6 and B7. From these two numbers, the spreadsheet computes concentrations in cells C6:C10. Solver then varies  $\text{pN}_3^-$  and  $\text{pOH}^-$  in cells B6 and B7 until the charge and mass balances in cell F8 are satisfied.

	A	B	C	D	E	F
1	Thallium azide equilibria					
2	1. Estimate values of $\text{pC} = -\log[C]$ for $\text{N}_3^-$ and $\text{OH}^-$ in cells B6 and B7					
3	2. Use Solver to adjust the values of $\text{pC}$ in cells B6 and B7 to minimize the sum in cell F8					
4						
5	Species	$\text{pC}$	$\text{C} (= 10^{-\text{pC}})$		Mass and charge balances	$10^6 \cdot b_i$
6	$\text{N}_3^-$	2	1.00000E-02	$\text{C6} = 10^{-\text{B6}}$	$b_1 = [\text{Ti}^+] - [\text{N}_3^-] - [\text{HN}_3]$	1.19E+06
7	$\text{OH}^-$	4	1.00000E-04	$\text{C7} = 10^{-\text{B7}}$	$b_2 = [\text{Ti}^+] + [\text{H}^+] - [\text{N}_3^-] - [\text{OH}^-]$	1.18E+06
8	$\text{Ti}^+$		2.18776E-02	$\text{C8} = \text{D12}/\text{C6}$	$\Sigma (10^6 \cdot b_i)^2 =$	2.80E+12
9	$\text{HN}_3$		4.46684E-08	$\text{C9} = \text{D13} \cdot \text{C6}/\text{C7}$	$\text{F6} = 1\text{e6} \cdot (\text{C8} - \text{C6} - \text{C9})$	
10	$\text{H}^+$		1.00000E-10	$\text{C10} = \text{D14}/\text{C7}$	$\text{F7} = 1\text{e6} \cdot (\text{C8} + \text{C10} - \text{C6} - \text{C7})$	
11					$\text{F8} = \text{F6}^2 + \text{F7}^2$	
12	$\text{pK}_{\text{sp}} =$	3.66	$\text{K}_{\text{sp}} =$	2.1878E-04	$= 10^{-\text{B12}}$	
13	$\text{pK}_b =$	9.35	$\text{K}_b =$	4.4668E-10	$= 10^{-\text{B13}}$	
14	$\text{pK}_w =$	14.00	$\text{K}_w =$	1.0000E-14	$= 10^{-\text{B14}}$	

Figure 8-9 sets out the work of finding five unknown concentrations in cells C6:C10. Type this spreadsheet, entering the required constants in cells B12:B14 and the formulas in cells C6:C10, F6:F8, and D12:D14.

Now we need to *estimate* concentrations for  $\text{N}_3^-$  and  $\text{OH}^-$ . Concentrations of different species in equilibrium could range over many orders of magnitude, which creates difficulties in computer arithmetic. Therefore, we express the concentrations of  $\text{N}_3^-$  and  $\text{OH}^-$  by their negative logarithms in cells B6 and B7. To estimate  $[\text{N}_3^-] = 10^{-2} \text{ M}$ , enter 2 in cell B6.

Just as  $\text{pH} = -\log[\text{H}^+]$ , we define  $\text{pC}$  as the negative logarithm of a concentration:

$$\text{pC} \equiv -\log C \quad (8-35)$$

where  $C$  is a concentration. Similarly,  $\text{pK}$  is the negative logarithm of an equilibrium constant. For example,  $\text{pK}_w = -\log K_w$ . If  $K_w = 1.00 \times 10^{-14}$ ,  $\text{pK}_w = 14.00$ .

How do you estimate  $[\text{N}_3^-]$  and  $[\text{OH}^-]$ ? The value of  $K_{\text{sp}}$  for  $\text{TiN}_3$  is  $10^{-3.66}$ . If there were no reaction of  $\text{N}_3^-$  with water, the concentrations would be  $[\text{Ti}^+] = [\text{N}_3^-] = \sqrt{K_{\text{sp}}} = 10^{-3.66/2} = 10^{-1.83} \text{ M}$ . We only need an estimate for  $[\text{N}_3^-]$ , so  $\text{pN}_3^- \approx 2$  is good enough in cell B6, giving  $[\text{N}_3^-] = 10^{-2} \text{ M}$  in cell C6. But  $\text{N}_3^-$  reacts with  $\text{H}_2\text{O}$  to make  $\text{OH}^-$  by Reaction 8-24. With no calculation whatsoever, we can estimate that  $[\text{OH}^-]$  might be  $\sim 10^{-4} \text{ M}$  in a weakly basic solution. Therefore, enter  $\text{pOH}^- = 4$  in cell B7. From  $[\text{N}_3^-]$  and  $[\text{OH}^-]$  in cells C6 and C7, the spreadsheet computes  $[\text{Ti}^+]$ ,  $[\text{HN}_3]$ , and  $[\text{H}^+]$  in cells C8:C10 from Equations 8-32 to 8-34. None of these values is correct. They are just starting estimates from which Excel can compute better values.

The charge balance (8-26) can be rearranged to the form

$$b_1 \equiv [\text{Ti}^+] + [\text{H}^+] - [\text{N}_3^-] - [\text{OH}^-] = 0 \quad (8-26a)$$

and the mass balance (8-27) can be rearranged to the form

$$b_2 \equiv [\text{Ti}^+] - [\text{N}_3^-] - [\text{HN}_3] = 0 \quad (8-27a)$$

The sums labeled  $b_1$  and  $b_2$  in Equations 8-26a and 8-27a would both be 0 if the concentrations are correct. These sums are not 0 in our initial spreadsheet because the concentrations  $[\text{N}_3^-]$  and  $[\text{OH}^-]$  are not correct.

To find correct concentrations, we choose to minimize the sum  $\Sigma b_i^2 = b_1^2 + b_2^2$ , which is always a positive number. Our criterion for correct concentrations is that they satisfy the mass and charge balances (as well as the equilibrium expressions).

We minimize the sum of the squares of the mass and charge balances by using Excel Solver. When optimum concentrations are found, the sum will be a small number such as  $10^{-15}$ . Solver sometimes does not work well when the sum is too small, so we preemptively multiply the charge and mass balances by  $10^6$  in Figure 8-9 before using Solver. Cell F6 contains  $10^6 \cdot b_1$  and cell F7 contains  $10^6 \cdot b_2$ . Cell F8 is the sum  $(10^6 \cdot b_1)^2 + (10^6 \cdot b_2)^2$ .

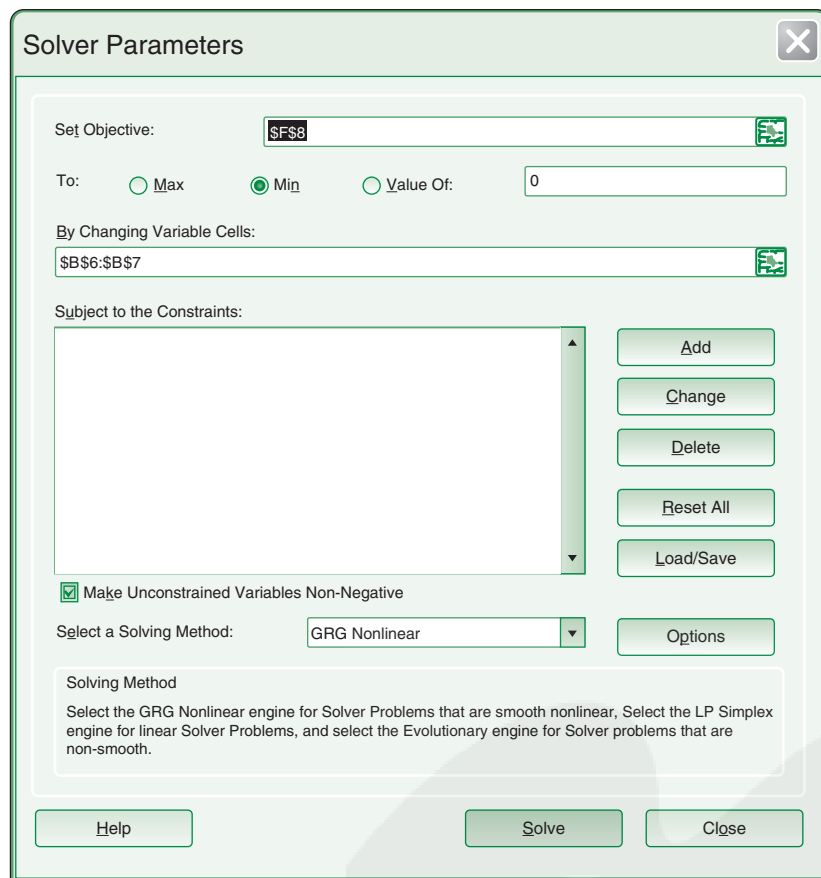
In the Excel 2016 Data ribbon on a PC, find Solver in the Analyze section. If Solver is not already loaded, click the File menu and select Excel Options and Add-Ins. Select Solver Add-in, click GO, and then OK to load Solver. On a Mac, Excel 2016 Solver is located in the Tools menu. Click Tools and then click Add-Ins. Select Solver and click OK to load it. Solver is then run from the Data tab.

The p function is the negative logarithm of a quantity:

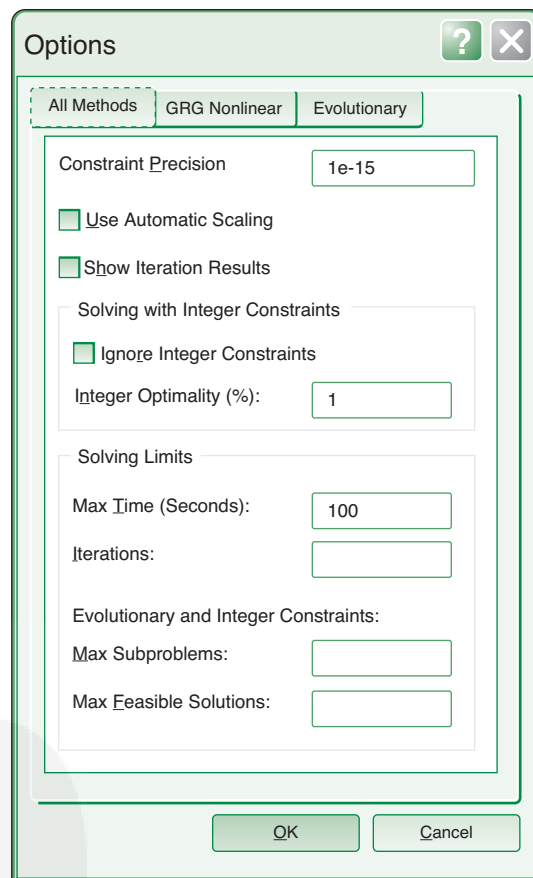
$$\text{pC} \equiv -\log C \quad \text{pK} \equiv -\log K$$

$$\text{If } K = 10^{-3.66}, \text{pK} = 3.66$$

*An important check.* In an empty cell in Figure 8-11, compute the quotient  $K_b = [\text{HN}_3][\text{OH}^-]/[\text{N}_3^-] = \text{C9} \cdot \text{C7}/\text{C6}$ . No matter what values are in cells C9, C7, and C6, the quotient must be  $K_b = 4.467\text{E}-10$ . If it is not, check the formulas for each concentration.



(a)



(b)

**FIGURE 8-10** Solver Parameters and Solver Options windows.

Click Solver. In the Solver Parameters window (Figure 8-10a), click Options. In Solver Options (Figure 8-10b), select the All Methods tab. Set Constraint Precision =  $1\text{e-}15$ , Max time = 100 s. Still in the Solver Options window, select the GRG Nonlinear tab. In Derivatives, select Central. Other parameters can be left with default values. Click OK.

In the Solver Parameters window in Figure 8-10a, Set Objective F8 To Min By Changing Variable Cells B6:B7 (Figure 8-10a). Select a Solving Method should be GRG Nonlinear. You just instructed Solver to vary  $\text{pN}_3^-$  and  $\text{pOH}^-$  in cells B6:B7 until the combined charge and mass balance in cell F8 is close to zero. Click Solve, and Solver returns new values for  $\text{pN}_3^-$  and  $\text{pOH}^-$  in cells B6:B7. Note the sum in cell F8. Run Solver again to see if cell F8 decreases. Continue to run Solver until cell F8 remains constant. If F8 is very small (such as  $1\text{e-}10$ ), you probably have a good solution. Try different starting values in cells B6 and B7 to show that Solver reaches the same solution. In some problems, after optimizing both variables, try optimizing one variable at a time (B6 or B7) to see if the solution improves, giving a smaller value in cell F8.

My final result is shown in Figure 8-11. Your numbers will probably be different. If your concentrations in cells C6:C10 agree with Figure 8-11 within three decimal places, your results are good enough.

We had estimated that  $[\text{N}_3^-] = 10^{-2} \text{ M}$  and  $[\text{OH}^-] = 10^{-4} \text{ M}$ . Solver tells us that  $[\text{N}_3^-] = 0.0148 \text{ M}$  and  $[\text{OH}^-] = 2.57 \times 10^{-6} \text{ M}$ . Figure 8-11 also tells us that  $[\text{HN}_3] = 2.57 \times 10^{-6} \text{ M}$ , which is nearly equal to  $[\text{OH}^-]$ . Hydrolysis 8-24 produces one  $\text{HN}_3$  for each  $\text{OH}^-$ . The fraction of azide that hydrolyzes is  $[\text{HN}_3]/([\text{N}_3^-] + [\text{HN}_3]) = 0.017\%$ . This fraction is sensible because  $\text{N}_3^-$  is a weak base with  $K_b = 10^{-9.35}$ .

Let's review the systematic equilibrium procedure:

1. We listed three chemical reactions that we think would occur when  $\text{TiN}_3(\text{s})$  dissolves in water and wrote their equilibrium constant expressions.
2. We wrote the charge and mass balances.
3. We checked to be sure that we have as many equations as there are unknowns.

**FIGURE 8-11** Thallium azide solubility spreadsheet after Solver has finished its work.

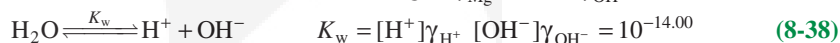
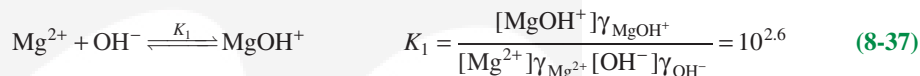
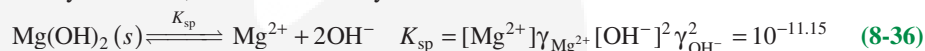
	A	B	C	D	E	F
1	Thallium azide equilibria					
2	1. Estimate values of $pC = -\log[C]$ for $N_3^-$ and $OH^-$ in cells B6 and B7					
3	2. Use Solver to adjust the values of $pC$ in cells B6 and B7 to minimize the sum in cell F8					
4						
5	Species	pC	C (= $10^{-pC}$ )		Mass and charge balances	$10^6 b_i$
6	$N_3^-$	1.83003771	1.47898E-02	$C6 = 10^{-B6}$	$b_1 = [Ti^+] - [N_3^-] - [HN_3]$	-1.03E-09
7	$OH^-$	5.58969041	2.57223E-06	$C7 = 10^{-B7}$	$b_2 = [Ti^+] + [H^+] - [N_3^-] - [OH^-]$	-1.01E-09
8	$Ti^+$		1.47924E-02	$C8 = D12/C6$	$\Sigma(10^6 b_i)^2 =$	2.09E-18
9	$HN_3$		2.56834E-06	$C9 = D13 * C6 / C7$	$F6 = 1e6 * (C8 - C6 - C9)$	
10	$H^+$		3.88768E-09	$C10 = D14 / C7$	$F7 = 1e6 * (C8 + C10 - C6 - C7)$	
11					$F8 = F6^2 + F7^2$	
12	$pK_{sp} =$	3.66	$K_{sp} =$	2.1878E-04	$= 10^{-B12}$	
13	$pK_b =$	9.35	$K_b =$	4.4668E-10	$= 10^{-B13}$	
14	$pK_w =$	14.00	$K_w =$	1.0000E-14	$= 10^{-B14}$	

- We estimated (number of unknowns) – (number of equilibria) = 5 – 3 = 2 of the concentrations. We chose  $[N_3^-]$  and  $[OH^-]$  because these species appear in multiple equilibria. We expressed concentrations as  $pC = -\log C$  to aid computer arithmetic.
- From  $[N_3^-]$  and  $[OH^-]$  and the equilibrium expressions, we computed  $[Ti^+]$ ,  $[HN_3]$ , and  $[H^+]$ .
- We then wrote the mass balance in the form  $b_1 \equiv [Ti^+] - [N_3^-] - [HN_3] = 0$  and the charge balance in the form  $b_2 \equiv [Ti^+] + [H^+] - [N_3^-] - [OH^-] = 0$ .
- We multiplied  $b_1$  and  $b_2$  by  $10^6$  in anticipation that Solver would work better if we prevent  $b_1$  and  $b_2$  from becoming too small for accurate computer arithmetic.
- We then asked Solver to vary  $pN_3^-$  and  $pOH^-$  to minimize  $(10^6 * b_1)^2 + (10^6 * b_2)^2$  to satisfy the mass and charge balances.
- As a check, vary the initial values of  $pN_3^-$  and  $pOH^-$  to see that Solver generates the same solution.



### Solubility of Magnesium Hydroxide with Activity Coefficients

Let's find the concentrations of species in a saturated solution of  $Mg(OH)_2$ , given the following chemistry. This time, we include activity coefficients.<sup>14</sup>



**Step 1** Pertinent reactions are listed above.

**Step 2** Charge balance:

$$2[Mg^{2+}] + [MgOH^+] + [H^+] = [OH^-] \quad (8-39)$$

**Step 3** Mass balance. This is a little tricky. From Reaction 8-36, we could say that the concentrations of all species containing  $OH^-$  equal two times the concentrations of all magnesium species. However, Reaction 8-38 also creates 1  $OH^-$  for each  $H^+$ . The mass balance accounts for both sources of  $OH^-$ :

$$\underbrace{[OH^-] + [MgOH^+]}_{\text{Species containing } OH^-} = 2 \underbrace{[Mg^{2+}] + [MgOH^+]}_{\text{Species containing } Mg^{2+}} + [H^+] \quad (8-40)$$

After all this thinking, Equation 8-40 is equivalent to Equation 8-39.

**Step 4** Equilibrium constant expressions are in Equations 8-36 through 8-38.

**Step 5** Count equations and unknowns. We have four equations (8-36 to 8-39) and four unknowns:  $[Mg^{2+}]$ ,  $[MgOH^+]$ ,  $[H^+]$ , and  $[OH^-]$ .

**Step 6** Solve. We will use the spreadsheet approach introduced in the  $TiN_3$  problem, but including activity coefficients this time. With four unknowns and three equilibria, we will estimate one concentration:

Number of concentrations to estimate =

$$(\text{number of unknowns}) - (\text{number of equilibria}) = 4 - 3 = 1$$

$K_1$  is the same equilibrium constant as  $\beta_1$  in Box 6-2 and Appendix I.

	A	B	C	D	E	F	G	H
1	Magnesium hydroxide equilibria							
2	1. Estimate pMg in cell B8							
3	2. Use Solver to adjust B8 to minimize sum in cell H15							
4	Ionic strength							
5	$\mu$	3.793E-04				Extended	Activity	
6				Size		Debye-Hückel	Coefficient	
7	Species	pC	C (M)	$\alpha$ (pm)	Charge	$\log \gamma$	$\gamma$	
8	Mg <sup>2+</sup>	3.9115263	1.226E-04	800	2	-3.780E-02	9.166E-01	G8 = 10^F8
9	OH <sup>-</sup>		2.567E-04	350	-1	-9.715E-03	9.779E-01	
10	MgOH <sup>+</sup>		1.148E-05	500	1	-9.625E-03	9.781E-01	
11	H <sup>+</sup>		4.071E-11	900	1	-9.392E-03	9.786E-01	
12								
13	pK <sub>sp</sub> =	11.15	K <sub>sp</sub> =	7.08E-12		Mass and charge balances:		10 <sup>6</sup> *b <sub>i</sub>
14	pK <sub>1</sub> =	-2.60	K <sub>1</sub> =	3.98E+02	b <sub>1</sub> = 2[Mg <sup>2+</sup> ] + [MgOH <sup>+</sup> ] + [H <sup>+</sup> ] - [OH <sup>-</sup> ]			0.00E+00
15	pK <sub>w</sub> =	14.00	K <sub>w</sub> =	1.00E-14			(10 <sup>6</sup> *b <sub>i</sub> ) <sup>2</sup> =	0.00E+00
16						H14 = 1e6*(2*C8+C10+C11-C9)		
17	Ion size estimate:						H15 = H14^2	
18	MgOH <sup>+</sup> size ≈ 500 pm						C8 = 10^-B8	
19						C9 = SQRT(D13/(C8*G8))/G9		
20	Initial value:					C10 = D14*C8*G8*C9*G9/G10		
21	pMg =	4					C11 = D15/(C9*G9*G11)	
22					F8 = -0.51*E8^2*SQRT(\$B\$5)/(1+D8*SQRT(\$B\$5)/305)			
23					B5 = 0.5*(E8^2*C8+E9^2*C9+E10^2*C10+E11^2*C11)			

**FIGURE 8-12** Magnesium hydroxide solubility spreadsheet with activity coefficients after Solver has operated.

The strategy is to estimate one concentration and then let Excel Solver optimize that concentration for us. The correct ionic strength is a by-product of the optimization.

Mg<sup>2+</sup> appears in two equilibria and OH<sup>-</sup> appears in three. It would be fine to estimate either concentration. I choose Mg<sup>2+</sup>. For the sake of *estimating* [Mg<sup>2+</sup>], let's just consider the solubility equilibrium 8-36 and neglect activity coefficients. Reaction 8-36 creates 2 OH<sup>-</sup> for each Mg<sup>2+</sup>. If  $x = [\text{Mg}^{2+}]$ , then  $[\text{OH}^-] = 2x$ . The  $K_{\text{sp}}$  expression gives

$$K_{\text{sp}} \approx [\text{Mg}^{2+}]_x [\text{OH}^-]_{2x}^2 = 7.1 \times 10^{-12}$$

$$(x)(2x)^2 = 4x^3 = 7.1 \times 10^{-12} \Rightarrow x = \left( \frac{7.1 \times 10^{-12}}{4} \right)^{1/3} = 1.2 \times 10^{-4} \text{ M}$$

The solution is  $x = [\text{Mg}^{2+}] = 1.2 \times 10^{-4} \text{ M}$  or  $\text{pMg}^{2+} = -\log(1.2 \times 10^{-4}) = 3.9$ . I choose to *estimate*  $\text{pMg}^{2+} = 4$  for the initial value.

Create the spreadsheet in Figure 8-12 with the value 0 in cell B5 and  $\text{pMg}^{2+} = 4$  in cell B8. Cell C8 contains [Mg<sup>2+</sup>] computed from  $[\text{Mg}^{2+}] = 10^{-\text{B8}}$ . Formulas are listed at the lower right of the spreadsheet. Cells C9:C11 compute [OH<sup>-</sup>], [MgOH<sup>+</sup>], and [H<sup>+</sup>] from the equilibrium expressions 8-36 to 8-38, including activity coefficients.

Now we wish to compute the ionic strength in cell B5 from the concentrations in cells C8:C11. However, concentrations depend on the ionic strength. We say there is a *circular reference*, because concentrations depend on ionic strength and ionic strength depends on concentrations. You must enable Excel to handle the circular reference. In Excel 2016, select the File tab and select Options. In the Options window, select Formulas. In Calculation Options, check "Enable iterative calculation" and set Maximum Change to 1e-15. Click OK and your spreadsheet is ready to handle circular references. Now, change the value 0 in cell B5 to the formula " $= 0.5 * (\text{E8}^2 * \text{C8} + \text{E9}^2 * \text{C9} + \text{E10}^2 * \text{C10} + \text{E11}^2 * \text{C11})$ " shown at the bottom of the spreadsheet.

Ion sizes for Mg<sup>2+</sup>, OH<sup>-</sup>, and H<sup>+</sup> appear in Table 8-1. We do not know the size of MgOH<sup>+</sup>. Mg<sup>2+</sup> is probably best represented as Mg(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> and MgOH<sup>+</sup> is Mg(OH<sub>2</sub>)<sub>5</sub>(OH)<sup>+</sup>. Mg(OH<sub>2</sub>)<sub>5</sub>(OH)<sup>+</sup> should be similar in size to Mg(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup>, except that Mg(OH<sub>2</sub>)<sub>5</sub>(OH)<sup>+</sup> has a charge of +1 and Mg(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> has a charge of +2. Recall that the greater the charge of an ion, the stronger it attracts solvent molecules and the larger is its hydrated radius. The size of Mg<sup>2+</sup> = Mg(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> in Table 8-1 is 800 pm. I *guess* that the size of Mg(OH<sub>2</sub>)<sub>5</sub>(OH)<sup>+</sup> is 500 pm. At the end of the equilibrium problem, you could change the size of Mg(OH<sub>2</sub>)<sub>5</sub>(OH)<sup>+</sup> to see if there is much effect on the answer (there is not).



Column F of Figure 8-12 computes  $\log \gamma$  from the extended Debye-Hückel equation 8-6 with the formula in cell H22. Column G computes activity coefficients  $\gamma = 10^{(\log \gamma)}$ . These activity coefficients appear in the equilibrium expressions used to find concentrations in cells C9:C11 with formulas in cells H19:H21.

The charge balance in cell H14 is  $b_1 = 2[\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{H}^+] - [\text{OH}^-]$ . In this particular problem, the mass balance is identical to the charge balance, so we do not use the mass balance. As in Figure 8-9 for  $\text{TiN}_3$  equilibria, we choose to multiply the sum of charges in cell H14 by  $10^6$  to prevent possible arithmetic errors with very small numbers in Excel. The function we minimize in cell H15 is

$$\text{Function to minimize:} \quad \sum (10^6 * b_i)^2 = (10^6 * b_1)^2$$

So, finally, here we go. Compose the spreadsheet in Figure 8-12. Use an initial estimate  $\text{pMg}^{2+} = 4$  in cell B8. On the Data tab, select Solver and then Options. On the All Methods tab, set Constraint Precision =  $1\text{e-}15$ . On the GRG Nonlinear tab, for Derivatives select Central. Click OK. In the Solver Parameters window, Set Objective H15 To Min By Changing Variable Cells B8. Click Solve. Solver varies  $\text{pMg}^{2+}$  in B8 until  $\sum (10^6 * b_i)^2$  is a minimum in cell H15.

Final results shown in Figure 8-12 are

$$\begin{aligned} [\text{Mg}^{2+}] &= 1.23 \times 10^{-4} \text{ M} & [\text{OH}^-] &= 2.57 \times 10^{-4} \text{ M} \\ [\text{MgOH}^+] &= 1.15 \times 10^{-5} \text{ M} & [\text{H}^+] &= 4.07 \times 10^{-11} \text{ M} \\ \mu &= 3.79 \times 10^{-4} \text{ M} \end{aligned}$$

Approximately 10% of the  $\text{Mg}^{2+}$  undergoes hydrolysis to  $\text{MgOH}^+$ . The pH of the solution is

$$\text{pH} = -\log[\text{H}^+] \gamma_{\text{H}^+} = -\log(4.07 \times 10^{-11})(0.979) = 10.40$$

The spreadsheet in Figure 8-12 provides a tool with which you can tackle a variety of modest equilibrium problems including activity coefficients.

Solver works best when your initial estimates are close to the actual values and when you do not ask Solver to find too many variables at once. Always try some different initial estimates to see if Solver reaches the same conclusion. Try executing Solver successively with values from one run input to the next run to see if the solution improves, as judged by the  $\sum b_i^2$  becoming smaller. If Solver is unable to find two or more variables in a complex problem, solve for one or two variables at a time while holding others fixed.

### We Will Usually Omit Activity Coefficients

Although it is proper to write equilibrium constants in terms of activities, the complexity of manipulating activity coefficients is a nuisance. In most of this book, we will omit activity coefficients unless there is a particular point to be made.

## Terms to Understand

activity	extended Debye-Hückel	ionic strength	pH
activity coefficient	equation	mass balance	pK
charge balance	ionic atmosphere		

## Summary

The thermodynamic equilibrium constant for the reaction  $aA + bB \rightleftharpoons cC + dD$  is  $K = \mathcal{A}_C^c \mathcal{A}_D^d / (\mathcal{A}_A^a \mathcal{A}_B^b)$ , where  $\mathcal{A}_i$  is the activity of the  $i$ th species. The activity is the product of the concentration ( $c$ ) and the activity coefficient ( $\gamma$ ):  $\mathcal{A}_i = c_i \gamma_i$ . For nonionic compounds and gases,  $\gamma_i \approx 1$ . For ionic species, the activity coefficient depends on the ionic strength, defined as  $\mu = \frac{1}{2} \sum c_i z_i^2$ , where  $z_i$  is the charge of an ion. For low ionic strengths ( $\leq 0.1 \text{ M}$ ) the activity coefficient decreases as ionic strength increases. Dissociation of ionic compounds increases with ionic strength because the ionic atmosphere of each ion diminishes the attraction of ions for one another.

You should be able to estimate activity coefficients by interpolation in Table 8-1. pH is defined in terms of the activity of  $\text{H}^+$ :  $\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log[\text{H}^+] \gamma_{\text{H}^+}$ . By analogy, pK is the negative logarithm of an equilibrium constant.

In the systematic treatment of equilibrium, write pertinent equilibrium expressions, as well as the charge and mass balances. The charge balance states that the sum of all positive charges in solution equals the sum of all negative charges. The mass balance states that the moles of all forms of an element in solution must equal the moles of that element delivered to the solution. Be sure that you have as many



equations as unknowns and then solve for the concentrations by using algebra with approximations, or spreadsheets with the Solver routine. For Solver, we *estimate* (number of unknowns) – (number of equilibria)

initial pC values and then let Solver find the pC values (and ionic strength) that minimize the sum of squares of the charge and mass balances. The ionic strength value is a by-product of the optimization.

## Exercises

**8-A.** Assuming complete dissociation of the salts, calculate the ionic strength of (a) 0.2 mM KNO<sub>3</sub>; (b) 0.2 mM Cs<sub>2</sub>CrO<sub>4</sub>; (c) 0.2 mM MgCl<sub>2</sub> plus 0.3 mM AlCl<sub>3</sub>.

**8-B.** Find the activity (not the activity coefficient) of the (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N<sup>+</sup> (tetrapropylammonium) ion in a solution containing 0.005 0 M (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N<sup>+</sup>Br<sup>−</sup> plus 0.005 0 M (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>Cl<sup>−</sup>.

**8-C.** Using activities, find [Ag<sup>+</sup>] in 0.060 M KSCN saturated with AgSCN(s).

**8-D.** Using activities, calculate the pH and concentration of H<sup>+</sup> in 0.050 M LiBr at 25°C.

**8-E.** A 40.0-mL solution of 0.040 0 M Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> was titrated with 60.0 mL of 0.100 M KI to precipitate Hg<sub>2</sub>I<sub>2</sub> (*K*<sub>sp</sub> = 4.6 × 10<sup>−29</sup>).

(a) Show that 32.0 mL of KI are needed to reach the equivalence point.

(b) When 60.0 mL of KI have been added, virtually all Hg<sub>2</sub><sup>2+</sup> has precipitated, along with 3.20 mmol of I<sup>−</sup>. Considering all ions remaining in the solution, calculate the ionic strength when 60.0 mL of KI have been added.

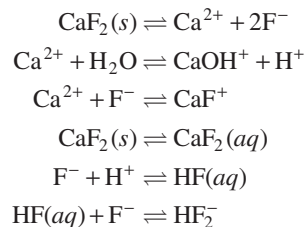
(c) Using activities, calculate pHg<sub>2</sub><sup>2+</sup> (= −log *a*<sub>Hg<sub>2</sub><sup>2+</sup></sub>) for (b).

**8-F. (a)** Write the mass balance for CaCl<sub>2</sub> in water if the species are Ca<sup>2+</sup> and Cl<sup>−</sup>.

(b) Write the mass balance if the species are Ca<sup>2+</sup>, Cl<sup>−</sup>, CaCl<sup>+</sup>, and CaOH<sup>+</sup>.

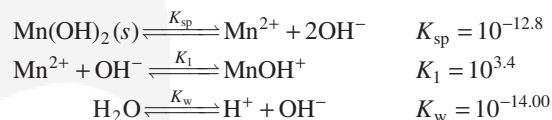
(c) Write the charge balance for (b).

**8-G.** Write the charge and mass balances for dissolving CaF<sub>2</sub> in water if the reactions are



**8-H.** Write charge and mass balances for aqueous Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> if the species are Ca<sup>2+</sup>, CaOH<sup>+</sup>, CaPO<sub>4</sub><sup>−</sup>, PO<sub>4</sub><sup>3−</sup>, HPO<sub>4</sub><sup>2−</sup>, H<sub>2</sub>PO<sub>4</sub><sup>−</sup>, and H<sub>3</sub>PO<sub>4</sub>.

**8-I.** (a) Using activities, find the concentrations of species in 0.10 M NaClO<sub>4</sub> saturated with Mn(OH)<sub>2</sub>. Modify the spreadsheet in Figure 8-12 by fixing μ = 0.1 in cell B5 and changing equilibrium constants and ion sizes. Suppose that the size of MnOH<sup>+</sup> is 400 pm and the chemistry is



(b) Solve the same problem if there is no NaClO<sub>4</sub> in the solution.

(c) Why is the solubility of Mn(OH)<sub>2</sub> greater in NaClO<sub>4</sub>? Find [total dissolved Mn in 0.1 M NaClO<sub>4</sub>]/[total dissolved Mn without NaClO<sub>4</sub>].

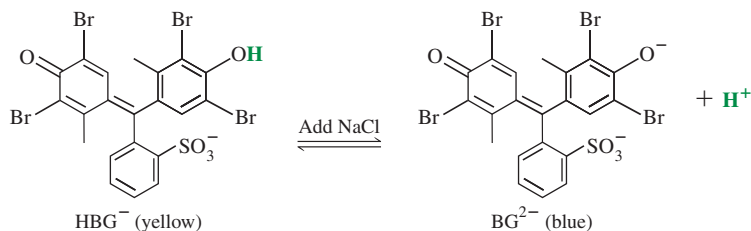
## Problems

### Activity Coefficients

**8-1.** Explain why the solubility of an ionic compound increases as the ionic strength of the solution increases (at least up to ~0.5 M).

**8-2.** Which statements are true? In the ionic strength range 0–0.1 M, activity coefficients decrease with (a) increasing ionic strength; (b) increasing ionic charge; (c) decreasing hydrated radius.

**8-3.** Color Plate 5 shows how the color of the acid-base indicator bromocresol green (H<sub>2</sub>BG) changes as NaCl is added to an aqueous solution of (H<sup>+</sup>)(HBG<sup>−</sup>). Explain why the color changes from pale green to pale blue as NaCl is added.



H<sup>+</sup> counterion is not shown.  
A counterion is the other ion in a solution needed for charge neutrality.

**8-4.** Calculate the ionic strength of (a) 0.008 7 M KOH and (b) 0.000 2 M La(IO<sub>3</sub>)<sub>3</sub> (assuming complete dissociation at this low concentration and no hydrolysis reaction to make LaOH<sup>2+</sup>).

**8-5.** Find the activity coefficient of each ion at the indicated ionic strength:

- |   |               |
|---|---------------|
| (a) SO <sub>4</sub> <sup>2−</sup>                                   | (μ = 0.01 M)  |
| (b) Sc <sup>3+</sup>  | (μ = 0.005 M) |
| (c) Eu <sup>3+</sup>  | (μ = 0.1 M)   |
| (d) (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> NH <sup>+</sup> | (μ = 0.05 M)  |

**8-6.** Interpolate in Table 8-1 to find the activity coefficient of H<sup>+</sup> when μ = 0.030 M.

**8-7.** Calculate the activity coefficient of Zn<sup>2+</sup> when μ = 0.083 M by using (a) Equation 8-6; (b) linear interpolation in Table 8-1.

**8-8.** Calculate the activity coefficient of Al<sup>3+</sup> when μ = 0.083 M by linear interpolation in Table 8-1.

**8-9.** The equilibrium constant for dissolution of a nonionic compound, such as diethyl ether (CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>), in water can be written



At low ionic strength,  $\gamma \approx 1$  for neutral compounds. At high ionic strength, most neutral molecules can be *salted out* of aqueous solution. That is, when a high concentration (typically  $> 1$  M) of a salt such as NaCl is added to an aqueous solution, neutral molecules usually become *less* soluble. Does the activity coefficient,  $\gamma_{\text{ether}}$ , increase or decrease at high ionic strength?

**8-10.** Including activity coefficients, find  $[\text{Hg}_2^{2+}]$  in saturated  $\text{Hg}_2\text{Br}_2$  in 0.001 00 M KBr.

**8-11.** Including activity coefficients, find the concentration of  $\text{Ba}^{2+}$  in a 0.100 M  $(\text{CH}_3)_4\text{NIO}_3$  solution saturated with  $\text{Ba}(\text{IO}_3)_2$ .

**8-12.** Find the activity coefficient of  $\text{H}^+$  in a solution containing 0.010 M HCl plus 0.040 M  $\text{KClO}_4$ . What is the pH of the solution?

**8-13.** Using activities, calculate the pH of a solution containing 0.010 M NaOH plus 0.012 0 M  $\text{LiNO}_3$ . What would be the pH if you neglected activities?

**8-14.** The temperature-dependent form of the extended Debye-Hückel equation 8-6 is

$$\log \gamma = \frac{(-1.825 \times 10^6)(\epsilon T)^{-3/2} z^2 \sqrt{\mu}}{1 + \alpha \sqrt{\mu} / (2.00 \sqrt{\epsilon T})}$$

where  $\epsilon$  is the (dimensionless) dielectric constant<sup>†</sup> of water,  $T$  is temperature (K),  $z$  is the charge of the ion,  $\mu$  is ionic strength (mol/L), and  $\alpha$  is the ion size parameter (pm). The dependence of  $\epsilon$  on temperature is

$$\epsilon = 79.755e^{(-4.6 \times 10^{-3})(T-293.15)}$$

Calculate the activity coefficient of  $\text{SO}_4^{2-}$  at 50.00°C when  $\mu = 0.100$  M. Compare your value with the one in Table 8-1.

**8-15. Activity coefficient of a neutral molecule.** We use the approximation that the activity coefficient ( $\gamma$ ) of neutral molecules is 1.00. A more accurate relation is  $\log \gamma = k\mu$ , where  $\mu$  is ionic strength and  $k \approx 0.11$  for  $\text{NH}_3$  and  $\text{CO}_2$  and  $k \approx 0.2$  for organic molecules. With activity coefficients for HA,  $\text{A}^-$ , and  $\text{H}^+$ , predict the value of the quotient below for benzoic acid ( $\text{HA} \equiv \text{C}_6\text{H}_5\text{CO}_2\text{H}$ ). The observed quotient is  $0.63 \pm 0.03$ .<sup>15</sup>

$$\text{Concentration quotient} = \frac{\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \text{ (at } \mu = 0\text{)}}{\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \text{ (at } \mu = 0.1 \text{ M)}}$$

## Systematic Treatment of Equilibrium

**8-16.** State the meaning of the charge and mass balance equations.

**8-17.** Why do activity coefficients not appear in the charge and mass balance equations?

<sup>†</sup> The dimensionless *dielectric constant*,  $\epsilon$ , measures how well a solvent can separate oppositely charged ions. The force of attraction (newtons) between ions of charge  $q_1$  and  $q_2$  (coulombs) separated by distance  $r$  (meters) is

$$\text{Force} = -(8.988 \times 10^9) \frac{q_1 q_2}{\epsilon r^2}$$

The larger the value of  $\epsilon$ , the smaller the attraction between ions. Water, with  $\epsilon \approx 80$ , separates ions very well. Here are some values of  $\epsilon$ : methanol, 33; ethanol, 24; benzene, 2; vacuum and air, 1. Ionic compounds dissolved in solvents less polar than water may exist predominantly as ion pairs, not separate ions.

**8-18.** Write the charge balance for a solution containing  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ca}(\text{HCO}_3)^+$ ,  $\text{Ca}(\text{OH})^+$ ,  $\text{K}^+$ , and  $\text{ClO}_4^-$ .

**8-19.** Write the charge balance for a solution of  $\text{H}_2\text{SO}_4$  in water if the  $\text{H}_2\text{SO}_4$  ionizes to  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ .

**8-20.** Write the charge balance for an aqueous solution of arsenic acid,  $\text{H}_3\text{AsO}_4$ , in which the acid can dissociate to  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ . Look up the structure of arsenic acid in Appendix G and write the structure of  $\text{HAsO}_4^{2-}$ .

**8-21. (a)** Write the charge and mass balances for a solution made by dissolving  $\text{MgBr}_2$  to give  $\text{Mg}^{2+}$ ,  $\text{Br}^-$ ,  $\text{MgBr}^+$ , and  $\text{MgOH}^+$ .


**(b)** Modify the mass balance if the solution was made by dissolving 0.2 mol  $\text{MgBr}_2$  in 1 L.


**8-22.** What would happen if charge balance did not exist in a solution? The force between two charges was given in the footnote to Problem 8-14. Find the force between two beakers separated by 1.5 m of air if one contains 250 mL with  $1.0 \times 10^{-6}$  M excess negative charge and the other has 250 mL with  $1.0 \times 10^{-6}$  M excess positive charge. There are  $9.648 \times 10^4$  coulombs per mole of charge. Convert force from N into pounds (0.224 8 pounds/N). Could two elephants hold the beakers apart?

**8-23.** For a 0.1 M aqueous solution of sodium acetate,  $\text{Na}^+\text{CH}_3\text{CO}_2^-$ , one mass balance is simply  $[\text{Na}^+] = 0.1$  M. Write a mass balance involving acetate.

**8-24.** Consider the dissolution of the compound  $\text{X}_2\text{Y}_3$ , which gives  $\text{X}_2\text{Y}_2^{2+}$ ,  $\text{X}_2\text{Y}^{4+}$ ,  $\text{X}_2\text{Y}_3(\text{aq})$ , and  $\text{Y}^{2-}$ . Use the mass balance to find an expression for  $[\text{Y}^{2-}]$  in terms of the other concentrations. Simplify your answer as much as possible.


**8-25.** Write a mass balance for a solution of  $\text{Fe}_2(\text{SO}_4)_3$  if the species are  $\text{Fe}^{3+}$ ,  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Fe}(\text{OH})^+$ ,  $\text{Fe}_2(\text{OH})_2^{4+}$ ,  $\text{FeSO}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{HSO}_4^-$ .

**8-26.**  *Ammonia equilibrium solved with Goal Seek.* Modify Figure 8-7 to find the concentrations of species in 0.05 M  $\text{NH}_3$ . The only change required is the value of F. How do the pH and fraction of ammonia hydrolysis ( $= [\text{NH}_4^+] / ([\text{NH}_4^+] + [\text{NH}_3])$ ) change when the formal concentration of  $\text{NH}_3$  increases from 0.01 to 0.05 M?

**8-27.**  *Ammonia equilibrium treated by Solver.* We now use the Solver spreadsheet introduced in Figure 8-9 for  $\text{TiN}_3$  solubility to find the concentrations of species in 0.01 M ammonia solution, neglecting activity coefficients. In the systematic treatment of equilibrium for  $\text{NH}_3$  hydrolysis, we have four unknowns ( $[\text{NH}_3]$ ,  $[\text{NH}_4^+]$ ,  $[\text{H}^+]$ , and  $[\text{OH}^-]$ ) and two equilibria (8-13 and 8-14). Therefore, we will estimate the concentrations of (4 unknowns) – (2 equilibria) = 2 species, for which I choose  $\text{NH}_4^+$  and  $\text{OH}^-$ . Set up the spreadsheet shown below, in which the estimates  $\text{pNH}_4^+ = 3$  and  $\text{pOH}^- = 3$  appear in cells B6 and B7. (Estimates come from the  $K_b$  equilibrium 8-17 with  $[\text{NH}_4^+] = [\text{OH}^-] = \sqrt{K_b[\text{NH}_3]} \approx \sqrt{10^{-4.755}[0.01]} \Rightarrow \text{pNH}_4^+ = \text{pOH}^- \approx 3$ . Estimates do not have to be very good for Solver to work.) The formula in cell C8 is  $[\text{NH}_3] = [\text{NH}_4^+][\text{OH}^-]/K_b$  and the formula in C9 is  $[\text{H}^+] = K_w/[\text{OH}^-]$ . The mass balance  $b_1$  appears in cell F6 and the charge balance  $b_2$  appears in cell F7. Cell F8 has the sum  $b_1^2 + b_2^2$ . As described for  $\text{TiN}_3$  on page 185, open the Solver window and set the Solver Options. Then use Solver to Set Objective F8 To Min By Changing Variable Cells B6:B7. What are the concentrations of the species? What fraction of ammonia ( $= [\text{NH}_4^+] / ([\text{NH}_4^+] + [\text{NH}_3])$ ) is hydrolyzed? Your answers should agree with those from Goal Seek in Figure 8-8.

	A	B	C	D	E	F
1	Ammonia equilibrium					F =
2	1. Estimate values of pC = -log[C] for NH <sub>4</sub> <sup>+</sup> and OH <sup>-</sup> in cells B6 and B7					0.01
3	2. Use Solver to adjust the values of pC to minimize the sum in cell F8					
4						
5	Species	pC			Mass and charge balances	10 <sup>6</sup> *b <sub>i</sub>
6	NH <sub>4</sub> <sup>+</sup>	3.00000000	1.0000E-03	C6 = 10^-B6	b <sub>1</sub> = F - [NH <sub>4</sub> <sup>+</sup> ] - [NH <sub>3</sub> ]	-4.79E+04
7	OH <sup>-</sup>	3.00000000	1.0000E-03	C7 = 10^-B7	b <sub>2</sub> = [NH <sub>4</sub> <sup>+</sup> ] + [H <sup>+</sup> ] - [OH <sup>-</sup> ]	1.00E-05
8	NH <sub>3</sub>		5.6885E-02	C8 = C6*C7/D12	Σ(10 <sup>6</sup> *b <sub>i</sub> ) <sup>2</sup> =	2.29E+09
9	H <sup>+</sup>		1.0000E-11	C9 = D13/C7	F6 = 1e6*(F2-C6-C8)	
10					F7 = 1e6*(C6+C9-C7)	
11					F8 = F6^2+F7^2	
12	pK <sub>b</sub> =	4.755	K <sub>b</sub> =	1.76E-05	= 10^-B12	
13	pK <sub>w</sub> =	14.00	K <sub>w</sub> =	1.00E-14	= 10^-B13	


Spreadsheet for Problem 8-27.


**8-28.**  Sodium acetate hydrolysis treated by Solver with activity coefficients.

(a) Following the NH<sub>3</sub> example in Section 8-5, write the equilibria and charge and mass balances needed to find the composition of 0.01 M sodium acetate (Na<sup>+</sup>A<sup>-</sup>). Include activity coefficients where appropriate. The two reactions are hydrolysis (pK<sub>b</sub> = 9.244) and ionization of H<sub>2</sub>O.

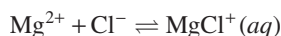
(b) Including activity coefficients, set up a spreadsheet analogous to Figure 8-12 to find the concentrations of all species. Assign an initial ionic strength = 0.01 M. After the spreadsheet is set up, change the ionic strength from the numerical value 0.01 to the formula for ionic strength. The process of beginning with a numerical value and changing to a formula is necessary because of a circular reference between ionic strength and concentrations. There are four unknowns and two equilibria, so use Solver to find 4 - 2 = 2 concentrations. Find pA<sup>-</sup> and pOH<sup>-</sup> to minimize the charge and mass balances. Find [A<sup>-</sup>], [OH<sup>-</sup>], [HA], and [H<sup>+</sup>]. Find the ionic strength, pH = -log([H<sup>+</sup>]γ<sub>H<sup>+</sup></sub>), and the fraction of hydrolysis = [HA]/F.

**8-29. (a)** Following the example of Mg(OH)<sub>2</sub> in Section 8-5, write the equations, including activity coefficients, needed to find the solubility of Ca(OH)<sub>2</sub>.<sup>16</sup> Find equilibrium constants in Appendixes F and I.

(b)  Suppose that the size of CaOH<sup>+</sup> is 500 pm. Including activity coefficients, compute concentrations of all species, fraction of hydrolysis (= [CaOH<sup>+</sup>]/([Ca<sup>2+</sup>] + [CaOH<sup>+</sup>])), and total dissolved calcium (= [Ca<sup>2+</sup>] + [CaOH<sup>+</sup>]). Compare your answer to the solubility of Ca(OH)<sub>2</sub> ≈ 0.0198 M at 25°C.<sup>17</sup>

**8-30.**  Systematic treatment of equilibrium for ion pairing. Let's derive the fraction of ion pairing for the salts in Box 8-1, which are 0.025 F NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, and MgSO<sub>4</sub>. Each case is somewhat different. All solutions will be near neutral pH because hydrolysis reactions of Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, and Cl<sup>-</sup> have small equilibrium constants. Therefore, we assume that [H<sup>+</sup>] = [OH<sup>-</sup>] and omit these species from the calculations. We work MgCl<sub>2</sub> as an example and then you are asked to work each of the others. The ion-pair equilibrium constant, K<sub>ip</sub>, comes from Appendix J.

Pertinent reaction:



$$K_{\text{ip}} = \frac{[\text{MgCl}^+(\text{aq})]\gamma_{\text{MgCl}^+}}{[\text{Mg}^{2+}]\gamma_{\text{Mg}^{2+}}[\text{Cl}^-]\gamma_{\text{Cl}^-}} \quad \log K_{\text{ip}} = 0.6 \quad \text{p}K_{\text{ip}} = -0.6 \quad (\text{A})$$

Charge balance (omit [H<sup>+</sup>] and [OH<sup>-</sup>], whose concentrations are small compared with [Mg<sup>2+</sup>], [MgCl<sup>+</sup>], and [Cl<sup>-</sup>]):

$$2[\text{Mg}^{2+}] + [\text{MgCl}^+] = [\text{Cl}^-] \quad (\text{B})$$

Mass balances:

$$[\text{Mg}^{2+}] + [\text{MgCl}^+] = F = 0.025 \text{ M} \quad (\text{C})$$

$$[\text{Cl}^-] + [\text{MgCl}^+] = 2F = 0.050 \text{ M} \quad (\text{D})$$

Only two of Equations (B), (C), and (D) are independent. If you double (C) and subtract (D), you will produce (B). We choose (C) and (D) as independent equations.


Equilibrium constant expression: Equation (A)

Count: 3 equations (A, C, D) and 3 unknowns ([Mg<sup>2+</sup>], [MgCl<sup>+</sup>], [Cl<sup>-</sup>])

Solve: We will use Solver to find (number of unknowns) - (number of equilibria) = 3 - 1 = 2 unknown concentrations.

In the spreadsheet on the next page, F = 0.025 M appears in cell G2. We estimate pMg<sup>2+</sup> and pCl<sup>-</sup> in cells B8 and B9. The ionic strength in cell B5 is given by the formula in cell H22. Excel must be set to allow for circular references as described on page 187. Sizes of Mg<sup>2+</sup> and Cl<sup>-</sup> are from Table 8-1 and the size of MgCl<sup>+</sup> is a guess. Activity coefficients are computed in columns F and G. Mass balances b<sub>1</sub> = F - [Mg<sup>2+</sup>] - [MgCl<sup>+</sup>], and b<sub>2</sub> = 2F - [Cl<sup>-</sup>] - [MgCl<sup>+</sup>] appear in cells H13 and H14, and the sum of their squares is in cell H15. The charge balance is not used because it is not independent of the two mass balances. Solver is invoked to minimize cell H15 by varying pMg<sup>2+</sup> and pCl<sup>-</sup> in cells B8 and B9. From optimized concentrations, the ion-pair fraction = [MgCl<sup>+</sup>]/F = 0.0815 is computed in cell D13. This fraction is shown in the table in Box 8-1. As a check, total Mg, total Cl, and K<sub>ip</sub> are correctly computed in cells B21:B23.

The Problem: Create a spreadsheet like the one for MgCl<sub>2</sub> to find the concentrations, ionic strength, and ion-pair fraction in 0.025 F NaCl. The ion-pair formation constant from Appendix J is log K<sub>ip</sub> = 10<sup>-0.5</sup> for the reaction Na<sup>+</sup> + Cl<sup>-</sup> ⇌ NaCl(aq). Mass balances are [Na<sup>+</sup>] + [NaCl(aq)] = F and [Na<sup>+</sup>] = [Cl<sup>-</sup>] (which is also the charge balance). Estimate pNa<sup>+</sup> and pCl<sup>-</sup> for input and then vary pNa<sup>+</sup> and pCl<sup>-</sup> to minimize the sum of squares of the two mass balances.

**8-31.**  Ion pairing. As in Problem 8-30, find the concentrations, ionic strength, and ion-pair fraction in 0.025 F Na<sub>2</sub>SO<sub>4</sub>. Assume that the size of NaSO<sub>4</sub><sup>-</sup> is 500 pm.

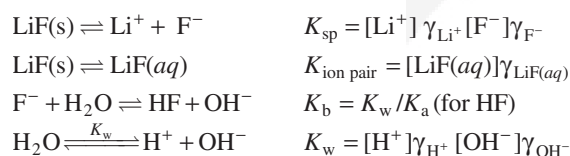
	A	B	C	D	E	F	G	H		
1	Magnesium chloride ion pairing with activities									
2	1. Estimate pMg <sup>2+</sup> and Cl <sup>-</sup> in cells B8 and B9				Formal conc = F =		0.025	M		
3	2. Use Solver to adjust B8 and B9 to minimize sum in cell H16				[Mg <sup>2+</sup> ] + [MgCl <sup>+</sup> (aq)] = F					
4	Ionic strength					[Cl <sup>-</sup> ] + [MgCl <sup>+</sup> (aq)] = 2F				
5	μ	7.093E-02				Extended	Activity			
6				Size		Debye-Hückel	Coefficient			
7	Species	pC	C (M)	α (pm)	Charge	log γ	γ			
8	Mg <sup>2+</sup>	1.638971597	2.296E-02	800	2	-3.199E-01	0.479	G8 = 10^F8		
9	Cl <sup>-</sup>	1.319093767	4.796E-02	300	-1	-1.076E-01	0.780			
10	MgCl <sup>+</sup> (aq)		2.037E-03	500	1	-9.455E-02	0.804			
11										
12	pK <sub>ip</sub> =	-0.60	K <sub>ip</sub> =	3.98E+00	Mass balances:			10 <sup>6</sup> ·b <sub>1</sub>		
13	Ion pair fraction = [MgCl <sup>+</sup> (aq)]/F =			0.0815	b <sub>1</sub> = F - [Mg <sup>2+</sup> ] - [MgCl <sup>+</sup> (aq)]			5.55E-07		
14			D13 = C10/G2		b <sub>2</sub> = 2F - [Cl <sup>-</sup> ] - [MgCl <sup>+</sup> (aq)]			3.26E-07		
15	Ion size estimate:						Σ(10 <sup>6</sup> ·b <sub>i</sub> ) <sup>2</sup> =	4.14E-13		
16	MgCl <sup>+</sup> (aq) =	500					H13 = 1e6* (G2-C8-C10)			
17	Initial value:						H14 = 1e6*(2*G2-C9-C10)			
18	pMg <sup>2+</sup> =	1.7					H15 = H13^2 + H14^2			
19	pCl <sup>-</sup> =	1.4					C8 = 10^-B8	C9 = 10^-B9		
20	Check:						C10 = D12*C8*G8*C9*G9/G10			
21	Total Mg =	0.02500	= C8+C10	F8 = -0.51*E8^2*SQRT(\$B\$5)/(1+D8*SQRT(\$B\$5)/305)						
22	Total Cl =	0.05000	= C9+C10		B5 = 0.5*(E8^2*C8+E9^2*C9+E10^2*C10)					
23	K <sub>ip</sub> =	3.981E+00	= C10*G10/(C8*G8*C9*G9)							

Spreadsheet for Problem 8-30. You can find this spreadsheet on SaplingPlus or at macmillanlearning.com.

**8-32. (a)** *Ion pairing.* As in Problem 8-30, find the concentrations, ionic strength, and ion-pair fraction in 0.025 F  $\text{MgSO}_4$ .

**(b)** Two possibly important reactions that we did not consider are acid hydrolysis  $\text{Mg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{MgOH}^+ + \text{H}^+$  and base hydrolysis of  $\text{SO}_4^{2-}$ . Write these two reactions and find their equilibrium constants in Appendices I and G. With the assumed pH near 7.0, and neglecting activity coefficients, show that both reactions are negligible.

**8-33.** *Solubility with activity.* Find the concentrations of the major species in a saturated aqueous solution of LiF. Consider these reactions:

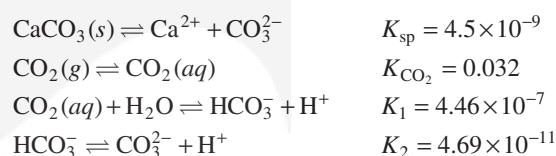


**(a)** Look up the equilibrium constants in the appendixes and write their  $\text{pK}$  values. The ion pair reaction is the sum of  $\text{LiF(s)} \rightleftharpoons \text{Li}^+ + \text{F}^-$  from Appendix F and  $\text{Li}^+ + \text{F}^- \rightleftharpoons \text{LiF(aq)}$  from Appendix J. Write the equilibrium constant expressions and the charge and mass balances.

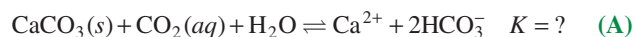
**(b)** Create a spreadsheet that uses activities to find the concentrations of all species and the ionic strength. Use  $\text{pF}^-$  and  $\text{pOH}^-$  as

independent variables to estimate. It does not work to choose  $\text{pF}^-$  and  $\text{pLi}^+$  because either concentration fixes that of the other through the relation  $K_{\text{sp}} = [\text{Li}^+] \gamma_{\text{Li}^+} [\text{F}^-] \gamma_{\text{F}^-}$ .

**8-34. Heterogeneous equilibria and calcite solubility.** If river water in Box 8-3 is saturated with calcite ( $\text{CaCO}_3$ ),  $[\text{Ca}^{2+}]$  is governed by the following equilibria:



**(a)** Combine these reactions to find the equilibrium constant for the reaction



**(b)** The mass balance for Reaction A is  $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$ . Find  $[\text{Ca}^{2+}]$  (in mol/L and in mg/L) in equilibrium with atmospheric  $\text{CO}_2$  if  $P_{\text{CO}_2} = 4.0 \times 10^{-4} \text{ bar} = 10^{-3.4} \text{ bar}$ . Locate this point on the line in Box 8-3.

**(c)** The concentration of  $\text{Ca}^{2+}$  in the Don River is 80 mg/L. What effective  $P_{\text{CO}_2}$  is in equilibrium with this much  $\text{Ca}^{2+}$ ? How can the river have this much  $\text{CO}_2$ ?