Chapter 11

Solving Equilibrium Problems for Complex Systems

Aqueous solutions often contain species that interact with one another and water to yield two or more simultaneous equilibria.

Ex., for a sparingly soluble salt in water, there are three equilibria.

$$BaSo4(s) \Leftrightarrow Ba^{+2} + SO_4^{-2}$$
$$SO_4^{-2} + H_3O^+ \Leftrightarrow HSO_4^- + H_2O$$
$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

The addition of hydronium ions to this system causes the second equilibrium to be shifted to the right by the common-ion effect.

The resulting decrease in sulfate concentration causes the first equilibrium to shift to the right.

The introduction of a new equilibrium system into a solution does not change the equilibrium constants for any existing equilibria.

11 A Solving multiple-equilibrium problems using A systematic method

To solve a multiple-equilibrium problem, we must write as many independent equations as there are chemical species in the system.

We use three types of algebraic equations to solve multiple-equilibrium problems:

(1) equilibrium-constant expressions,

(2) mass-balance equations, and

(3) a single charge-balance equation.

Mass-Balance Equations

> Mass-balance equations relate the equilibrium concentrations of various species in a solution to one another and to the analytical concentrations of the various solutes.

> These equations are a direct result of the conservation of mass and moles.

Writing mass balance equations may be as straightforward as the case of a weak acid:

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

The only source of the two A^- containing species, HA and A^-, is the original solute, HA, whose analytical concentration is cHA:

$$c_{HA} = [HA] + [A^-]$$

Hydronium ions in the solution come from two sources: the dissociation of HA and the dissociation of water.

$$[H_3O^+] = [H_3O^+]_{HA} + [H_3O^+]_{H2O}$$

The concentration of hydronium from the dissociation of the acid $[H_3O^+]_{HA}$ is equal to [A-], and the hydronium concentration from water $[H_3O^+]_{H2O}$ is equal to [OH-].

$$\text{Thus, } [H_3O^+] = [A^-] + [OH^-]$$
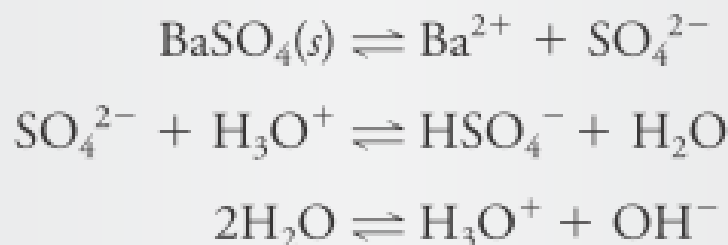
This is referred to as the *proton balance* equation because it accounts for all

EXAMPLE 11-1

Write mass-balance expressions for a 0.0100 M solution of HCl that is in equilibrium with an excess of solid $BaSO_4$.

Solution

As shown by Equations 11-1, 11-2, and 11-3, there are three equilibria in this solution:

$$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

$$SO_4^{2-} + H_3O^+ \rightleftharpoons HSO_4^- + H_2O$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Because the only source for the two sulfate species is the dissolved $BaSO_4$, the barium ion concentration must equal the total concentration of sulfate-containing species, so we can write our first mass-balance equation.

$$[Ba^{2+}] = [SO_4^{2-}] + [HSO_4^-]$$

According to the second reaction above, hydronium ions in the solution are either free H_3O^+ or they react with SO_4^{2-} to form HSO_4^-. We may express this as

$$[H_3O^+]_{tot} = [H_3O^+] + [HSO_4^-]$$

where $[H_3O^+]_{tot}$ is the hydronium concentration from all sources and $[H_3O^+]$ the free equilibrium concentration of hydronium. The protons that contribute to $[H_3O^+]_{tot}$ have two sources: aqueous HCl and the dissociation of water. In this example, we refer to the hydronium ion concentration from the complete dissociation of HCl as $[H_3O^+]_{HCl}$ and the concentration from the autoprotolysis of water as $[H_3O^+]_{H_2O}$. The total concentration of hydronium ion is then

$$[H_3O^+]_{tot} = [H_3O^+]_{HCl} + [H_3O^+]_{H_2O}$$

And from above,

$$[H_3O^+]_{tot} = [H_3O^+] + [HSO_4^-] = [H_3O^+]_{HCl} + [H_3O^+]_{H_2O}$$

But $[H_3O^+]_{HCl} = c_{HCl}$, and since the only source of hydroxide is the dissociation of water, we may also write that $[H_3O^+]_{H_2O} = [OH^-]$. By substituting these two quantities into the equation above,

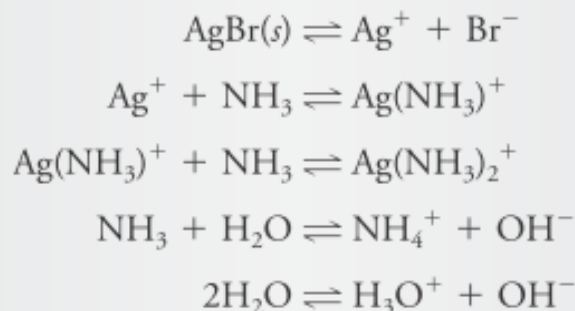$$[H_3O^+]_{tot} = [H_3O^+] + [HSO_4^-] = c_{HCl} + [OH^-]$$

and the mass-balance equation is then

$$[H_3O^+] + [HSO_4^-] = 0.0100 + [OH^-]$$

EXAMPLE 11-2

Write mass-balance expressions for the system formed when a 0.010 M NH_3 solution is saturated with the slightly soluble AgBr.

Solution

In this example, the equations for the equilibria in the solution are

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

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2{}^+$$

$$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

In this solution, AgBr is the only source of Br^-, Ag^+, $Ag(NH_3)^+$, and $Ag(NH_3)_2{}^+$. As AgBr dissolves, silver and bromide ions appear in a 1:1 ratio. While Ag^+ reacts with ammonia to form $Ag(NH_3)^+$ and $Ag(NH_3)_2{}^+$, bromide appears only as Br^-, so our first mass-balance equation is

$$[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2{}^+] = [Br^-]$$

where the bracketed terms are molar species concentrations. Also, we know that the only source of ammonia-containing species is the 0.010 M NH_3. Therefore,

$$c_{NH_3} = [NH_3] + [NH_4{}^+] + [Ag(NH_3)^+] + 2[Ag(NH_3)_2{}^+] = 0.010 \text{ M}$$

The coefficient 2 in this equation arises because $Ag(NH_3)_2{}^+$ contains two ammonia molecules. From the last two equilibria, we see that one hydroxide ion is formed for each $NH_4{}^+$ and each hydronium ion. Therefore,

11-4   Write the mass balance expression for a solution that is

(a) 0.20 M H_3AsO_4

$$0.20 = [H_3AsO_4] + [H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}]$$

(b) 0.10 M Na_2HAsO_4

$$0.10 = [H_3AsO_4] + [H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}]$$
$$2(0.10) = [Na^+] = 0.20$$

(c) 0.0500 M HClO and 0.100 M NaClO

$$0.0500 + 0.100 = [ClO^-] + [HClO]$$
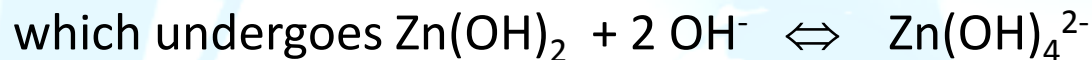$$0.100 = [Na^+]$$

(d) 0.25 M NaCl and saturated with CaF2

$$[F^-] + [HF] = 0.25 + 2[Ca^{2+}] \qquad\qquad [Na^+] = 0.25$$

(e) 0.1 M in NaOH and saturated with Zn(OH)2

which undergoes $Zn(OH)_2 + 2\ OH^- \Leftrightarrow Zn(OH)_4^{2-}$

$$0.100 = [Na^+] = [OH^-] + 2[Zn(OH)_4^{2-}]$$

(f) Saturated with BaC_2O_4

$$[Ba^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$$

(g) Saturated with CaF2

$$[Ca^{2+}] = \tfrac{1}{2}([F^-] + [HF])$$

Charge-Balance Equation

Electrolyte solutions are electrically neutral because the molar concentration of positive charge always equals the molar concentration of negative charge.

(no. moles/L) positive charge = (no. moles/L) negative charge

To obtain the charge concentration of an ion, multiply the molar concentration of the ion by its charge.

Thus, the molar concentration of positive charge in a solution due to the presence of sodium ions is the molar sodium ion concentration:

$$\underline{\frac{\text{mol positive charge}}{L}} = \underline{\frac{1 \text{ mol positive charge}}{\text{mol Na}^+}} \times \underline{\frac{\text{mol Na}^+}{L}} = 1 \times [\text{Na}^+]$$

The concentration of positive charge due to magnesium ions and phosphate ions

$$= 2 \times [\text{Mg}^{2+}] \quad \text{and} \quad = 3 \times [\text{PO}_4^{3-}]$$

- In some systems, a useful charge-balance equation cannot be written because not enough information is available or because the charge-balance equation is identical to one of the mass-balance equations.

- For a 0.100 M solution of sodium chloride, the charge-balance equation can be written as:

$$\text{mol/L positive charge} = [Na^+] + [H_3O^+] = 0.100 + 1 \times 10^{-7}$$

$$\text{mol/L negative charge} = [Cl^-] + [OH^-] = 0.100 + 1 \times 10^{-7}$$

The charge-balance equation can be written by equating the concentrations of positive and negative charges:

$$[Na^+] + [H_3O^+] = [Cl^-] + [OH^-] = 0.100 + 1 \times 10^{-7}$$

e.g.   - $MgCl_2$ = 0.1 M

Positive charge $2\,[Mg^{+2}] + [H_3O^+] = 2 \times 0.1 + 1 \times 10^{-7}$

Negative charge $[Cl-1] + [OH\,-] = = 2 \times 0.1 + 1 \times 10^{-7}$

$2\,[Mg^{+2}] + [H_3O^+] = [Cl^-] + [OH\,^-] = 0.2 + 1 \times 10^{-7}$ since $[H_3O^+] = [OH\,^-]$

$2\,[Mg^{+2}] = [Cl^-] = 0.200\ M$

EXAMPLE 11-3

Write a charge-balance equation for the system in Example 11-2.
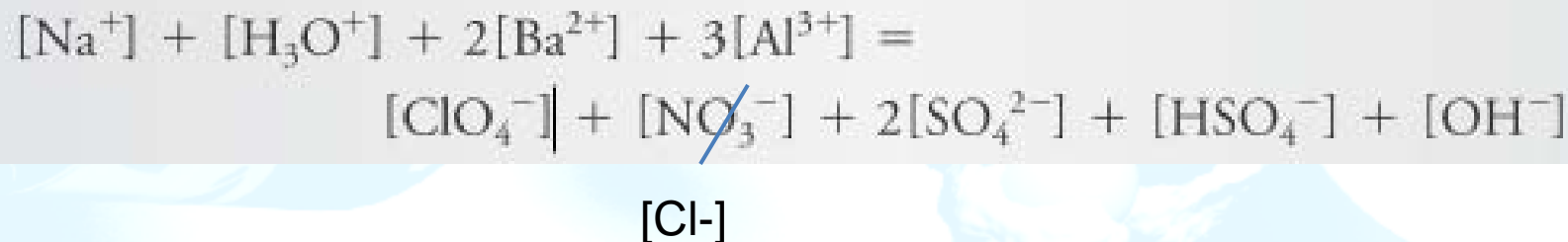
(0.1 M NH3 solution saturated with AgBr)

Solution

$$[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] + [H_3O^+] + [NH_4^+] = [OH^-] + [Br^-]$$

EXAMPLE 11-4

Write a charge-balance equation for an aqueous solution that contains NaCl, $Ba(ClO_4)_2$, and $Al_2(SO_4)_3$.

Solution

$$[Na^+] + [H_3O^+] + 2[Ba^{2+}] + 3[Al^{3+}] =$$
$$[ClO_4^-] + [NO_3^-] + 2[SO_4^{2-}] + [HSO_4^-] + [OH^-]$$

[Cl-]

Write the charge balance equations for Q-11-4

(a) $[H_3O^+] = [OH^-] + [H_2AsO_4^-] + 2[HAsO_4^{2-}] + 3[AsO_4^{3-}]$

(b) $[Na^+] + [H_3O^+] = [OH^-] + [H_2AsO_4^-] + 2[HAsO_4^{2-}] + 3[AsO_4^{3-}]$

(c) $[Na^+] + [H_3O^+] = [OH^-] + [ClO^-]$

(d) $[Na^+] + [H_3O^+] + 2[Ca^{2+}] = [F^-] + [OH^-]$

(e) $2[Zn^{2+}] + [Na^+] + [H_3O^+] = [OH^-] + 2[Zn(OH)_4^{2-}]$

(f) $2[Ba^{2+}] + [H_3O^+] = [OH^-] + 2[C_2O_4^{2-}] + [HC_2O_4^-]$

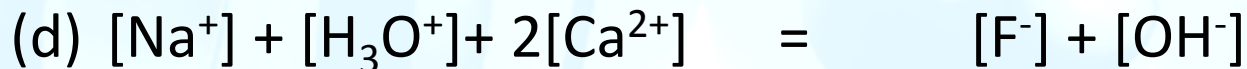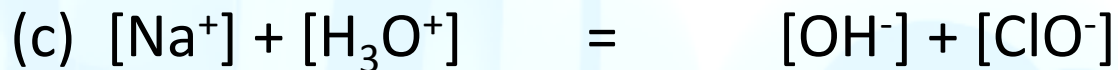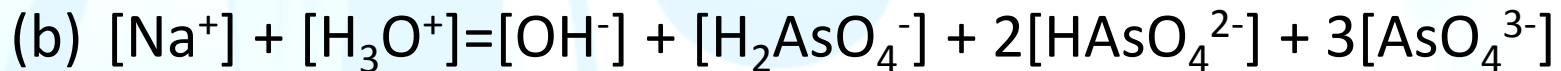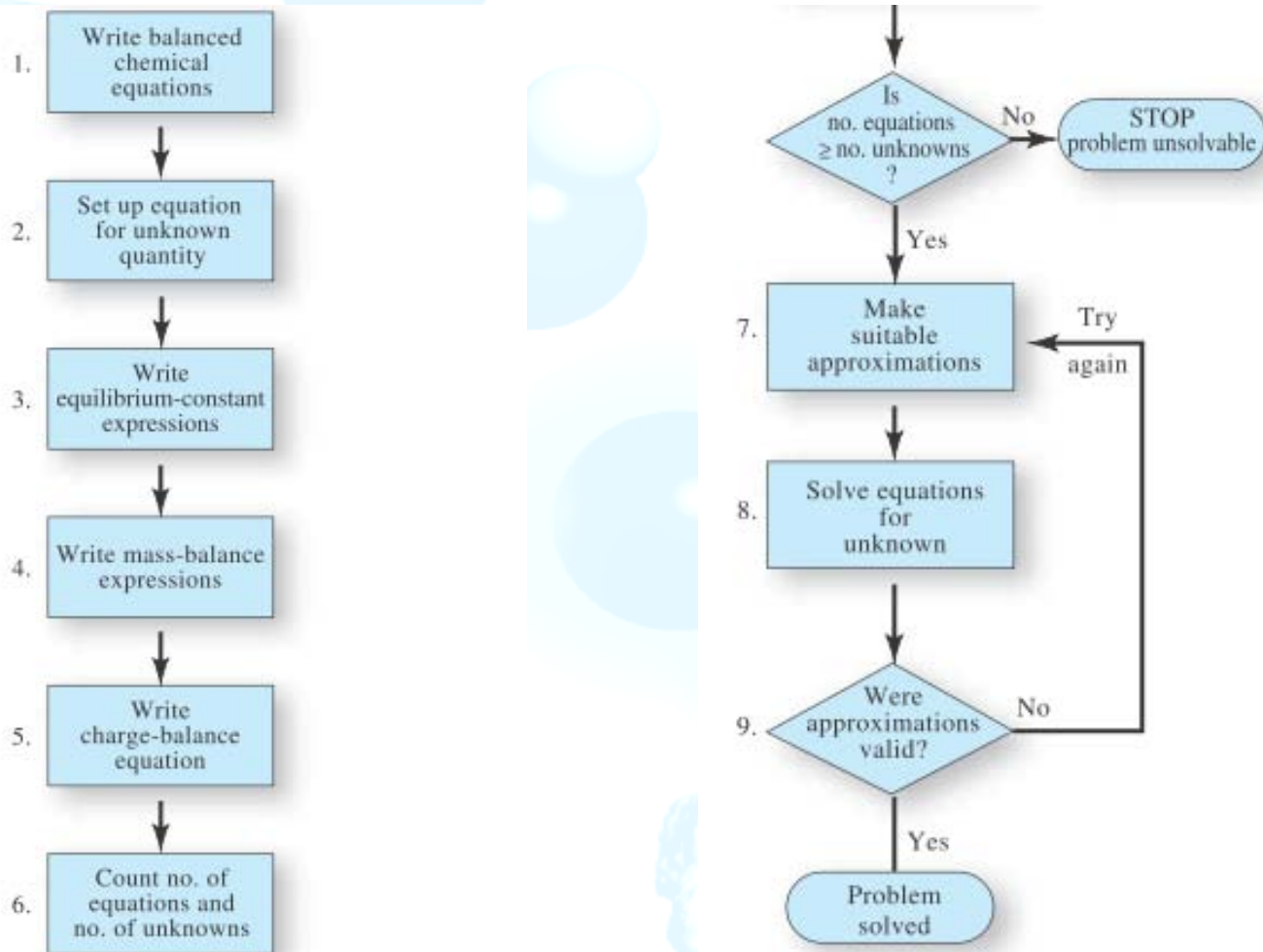(g) $2[Ca^{2+}] + [H_3O^+] = [OH^-] + [F^-]$

Figure 11-1   A systematic method for solving multiple-equilibrium problems.

Using Approximations to Solve Equilibrium Calculations

* Solving several nonlinear equations can be simplified by using suitable approximations.

* Approximations can be made only in charge-balance and mass-balance equations, never in equilibrium-constant expressions.

* If the assumption leads to an intolerable error, recalculate without the faulty approximation to arrive at a tentative answer.

Use of Computer Programs to Solve Multiple-Equilibrium Problems

*Several software packages are available for solving multiple nonlinear simultaneous equations rigorously. **Three such programs are Mathcad, Mathematica, Solver, MATLAB, TK, and** Excel.
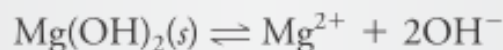
The Solubility of Metal Hydroxides

EXAMPLE 11-5

Calculate the molar solubility of $Mg(OH)_2$ in water.

Solution

Step 1. **Write Equations for the Pertinent Equilibria** Two equilibria need to be considered:

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

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Step 2. **Define the Unknown** Since 1 mol of Mg^{2+} is formed for each mole of $Mg(OH)_2$ dissolved,

$$\text{solubility } Mg(OH)_2 = [Mg^{2+}]$$

Step 3. **Write All Equilibrium-Constant Expressions**

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12} \tag{11-5}$$

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \tag{11-6}$$

Step 4. **Write Mass-Balance Expressions** As shown by the two equilibrium equations, there are two sources of hydroxide ions: $Mg(OH)_2$ and H_2O. The hydroxide ion concentration resulting from dissociation of $Mg(OH)_2$ is twice the magnesium ion concentration, and the hydroxide ion concentration from the dissociation of water is equal to the hydronium ion concentration. Thus,

Step 5. Write the Charge-Balance Expression

$$[OH^-] = 2[Mg^{2+}] + [H_3O^+] \qquad (11\text{-}8)$$

Note that this equation is identical to Equation 11-7. Often, a mass-balance equation for a system is identical to the charge-balance equation.

Step 6. Count the Number of Independent Equations and Unknowns We have developed three independent algebraic equations (Equations 11-5, 11-6, and 11-7) and have three unknowns ($[Mg^{2+}]$, $[OH^-]$, and $[H_3O^+]$). Therefore, the problem can be solved rigorously.

Step 7a. Make Approximations We can make approximations only in Equation 11-7. Since the solubility-product constant for $Mg(OH)_2$ is relatively large, the solution will be somewhat basic. Therefore, it is reasonable to assume that $[H_3O^+] \ll [OH^-]$. Equation 11-7 then simplifies to

$$2[Mg^{2+}] \approx [OH^-]$$

Step 8. Solve the Equations Substitution of Equation 11-8 into Equation 11-5 gives

$$[Mg^{2+}](2[Mg^{2+}])^2 = 7.1 \times 10^{-12}$$

$$[Mg^{2+}]^3 = \frac{7.1 \times 10^{-12}}{4} = 1.78 \times 10^{-12}$$

$$[Mg^{2+}] = \text{solubility} = (1.78 \times 10^{-12})^{1/3} = 1.21 \times 10^{-4} \text{ or } 1.2 \times 10^{-4} \text{ M}$$

Step 9. Check the Assumptions Substitution into Equation 11-8 yields

$$[OH^-] = 2 \times 1.21 \times 10^{-4} = 2.42 \times 10^{-4} \text{ M}$$

and, from Equation 11-6,

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{2.42 \times 10^{-4}} = 4.1 \times 10^{-11} \text{ M}$$

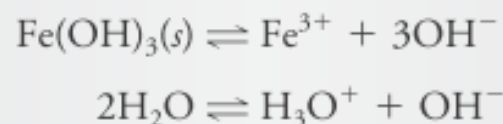Thus, our assumption that $[H_3O^+] \ll [OH^-]$ is certainly valid.

EXAMPLE 11-6

Calculate the solubility of $Fe(OH)_3$ in water.

Solution

Proceeding by the systematic approach used in Example 11-5, we write.

Step 1. Write the Equations for the Pertinent Equilibria

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3OH^-$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Step 2. Define the Unknown

$$solubility = [Fe^{3+}]$$

Step 3. Write All the Equilibrium-Constant Expressions

$$K_{sp} = [Fe^{3+}][OH^-]^3 = 2 \times 10^{-39}$$

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

Step 4 and 5. Write Mass-Balance and Charge-Balance Equations As in Example 11-5, the mass-balance equation and the charge-balance equations are identical, that is,

$$[OH^-] = 3[Fe^{3+}] + [H_3O^+]$$

Step 6. Count the Number of Independent Equations and Unknown We see that

Step 7a. Make Approximations As in Example 11-5, assume that $[H_3O^+]$ is very small so that $[H_3O^+] \ll 3[Fe^{3+}]$ and

$$3[Fe^{3+}] \approx [OH^-]$$

Step 8. Solve the Equations Substituting $[OH^-] = 3[Fe^{3+}]$ into the solubility-product expression gives

$$[Fe^{3+}](3[Fe^{3+}])^3 = 2 \times 10^{-39}$$

$$[Fe^{3+}] = \left(\frac{2 \times 10^{-39}}{27}\right)^{1/4} = 9 \times 10^{-11}$$

$$\text{solubility} = [Fe^{3+}] = 9 \times 10^{-11} \text{ M}$$

Step 9. Check the Assumption From the assumption made in Step 7, we can calculate a provisional value of $[OH^-]$:

$$[OH^-] \approx 3[Fe^{3+}] = 3 \times 9 \times 10^{-11} = 3 \times 10^{-10} \text{ M}$$

Using this value of $[OH^-]$ to compute a *provisional* value for $[H_3O^+]$, we have

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{3 \times 10^{-10}} = 3 \times 10^{-5} \text{ M}$$

But 3×10^{-5} is not much smaller than three times our provisional value of $[Fe^{3+}]$. This discrepancy means that our assumption was invalid and the provisional values for $[Fe^{3+}]$, $[OH^-]$, and $[H_3O^+]$ are all significantly in error. Therefore, go back to Step 7a and assume that

$$3[Fe^{3+}] \ll [H_3O^+]$$

Now, the mass-balance expression becomes

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

Substituting this equality into the expression for K_w gives

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}\ M$$

Substituting this number into the solubility-product expression developed in Step 3 gives

$$[Fe^{3+}] = \frac{2 \times 10^{-39}}{(1.00 \times 10^{-7})^3} = 2 \times 10^{-18}\ M$$

Since $[H_3O^+] = [OH^-]$, our assumption is that $3[Fe^{3+}] \ll [OH^-]$ or $3 \times 2 \times 10^{-18} \ll 10^{-7}$. Thus, our assumption is valid, and we may write

$$solubility = 2 \times 10^{-18}\ M$$

Note the very large error (~8 orders of magnitude!) introduced by the invalid assumption.

The Effect of pH on Solubility

The solubility of precipitates containing an anion with basic properties, a cation with acidic properties, or both will depend on pH.
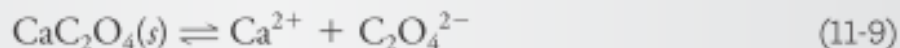
Solubility Calculations When the pH Is Constant
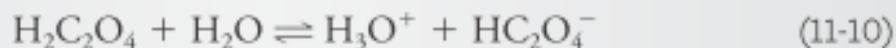
EXAMPLE 11-7

Calculate the molar solubility of calcium oxalate in a solution that has been buffered so that its pH is constant and equal to 4.00.

Solution

Step 1. Write Pertinent Equilibria

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \qquad (11\text{-}9)$$

Oxalate ions react with water to form $HC_2O_4^-$ and $H_2C_2O_4$. Thus, there are three other equilibria present in this solution:

$$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^- \qquad (11\text{-}10)$$

$$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-} \qquad (11\text{-}11)$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^- $$

Step 2. Define the Unknown Calcium oxalate is a strong electrolyte so that its molar analytical concentration is equal to the equilibrium calcium ion concentration, that is,

$$\text{solubility} = [Ca^{2+}] \qquad (11\text{-}12)$$

Step 2. Define the Unknown Calcium oxalate is a strong electrolyte so that its molar analytical concentration is equal to the equilibrium calcium ion concentration, that is,

$$\text{solubility} = [Ca^{2+}] \tag{11-12}$$

Step 3. Write All the Equilibrium-Constant Expressions

$$[Ca^{2+}][C_2O_4^{2-}] = K_{sp} = 1.7 \times 10^{-9} \tag{11-13}$$

$$\frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = K_1 = 5.60 \times 10^{-2} \tag{11-14}$$

$$\frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = K_2 = 5.42 \times 10^{-5} \tag{11-15}$$

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

Step 4. Mass-Balance Expressions Because CaC_2O_4 is the only source of Ca^{2+} and the three oxalate species.

$$[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] = \text{solubility} \tag{11-16}$$

Since the problem states that the pH is 4.00, we can also write that

$$[H_3O^+] = 1.00 \times 10^{-4} \text{ and } [OH^-] = K_w/[H_3O^+] = 1.00 \times 10^{-10}$$

Step 5. Write Charge-Balance Expression A **buffer** is required to maintain the pH at 4.00. The buffer most likely consists of some weak acid HA and its conjugate base, A^-. The nature of the three species and their concentrations have not been specified, however, so we do not have enough information to write a charge-balance equation.

Step 6. Count the Number of Independent Equations and Unknowns We have four unknowns ($[Ca^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$, and $[H_2C_2O_4]$) as well as four independent algebraic relationships (Equations 11-13, 11-14, 11-15, and 11-16). Therefore, an exact solution can be obtained, and the problem becomes one of algebra.

Step 7a. Make Approximations It is relatively easy to solve the system of equations exactly in this case, so we will not bother with approximations.

Step 8. Solve the Equations A convenient way to solve the problem is to substitute Equations 11-14 and 11-15 into 11-16 in such a way as to develop a relationship between $[Ca^{2+}]$, $[C_2O_4^{2-}]$, and $[H_3O^+]$. Thus, we rearrange Equation 11-15 to give

$$[HC_2O_4^-] = \frac{[H_3O^+][C_2O_4^{2-}]}{K_2}$$

Substituting numerical values for $[H_3O^+]$ and K_2 gives

$$[HC_2O_4^-] = \frac{1.00 \times 10^{-4}[C_2O_4^{2-}]}{5.42 \times 10^{-5}} = 1.85[C_2O_4^{2-}]$$

Substituting this relationship into Equation 11-14 and rearranging gives

$$[H_2C_2O_4] = \frac{[H_3O^+][C_2O_4^{2-}] \times 1.85}{K_1}$$

Substituting numerical values for $[H_3O^+]$ and K_1 yields

$$[H_2C_2O_4] = \frac{1.85 \times 10^{-4}[C_2O_4^{2-}]}{5.60 \times 10^{-2}} = 3.30 \times 10^{-3}[C_2O_4^{2-}]$$

Substituting these expressions for $[HC_2O_4^-]$ and $[H_2C_2O_4]$ into Equation 11-16 gives

$$[Ca^{2+}] = [C_2O_4^{2-}] + 1.85[C_2O_4^{2-}] + 3.30 \times 10^{-3}[C_2O_4^{2-}]$$

$$= 2.85[C_2O_4^{2-}]$$

or $\quad [C_2O_4^{2-}] = [Ca^{2+}]/2.85$

Substituting into Equation 11-13 gives

$$\frac{[Ca^{2+}][Ca^{2+}]}{2.85} = 1.7 \times 10^{-9}$$

$$[Ca^{2+}] = \text{solubility} = \sqrt{2.85 \times 1.7 \times 10^{-9}} = 7.0 \times 10^{-5} \, M$$

Solubility Calculations When the pH Is Variable

Computing the solubility of a precipitate such as calcium oxalate in a solution in which the pH is not fixed and know is considerably more complicated. Thus, to determine the solubility of CaC2O4 in pure water, we must take into account the change in OH2 and H3O1 that accompanies the solution process. In this example, there are four equilibria;

$$CaC_2O_4(s) \Leftrightarrow Ca^{+2} + C_2O_4^{-2}$$

$$C_2O_4^{-2} + H_2O \Leftrightarrow HC_2O_2^- + OH^-$$

$$HC_2O_4^- + H_2O \Leftrightarrow H_2C_2O_4 + OH^-$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

In contrast to Example 11-7, the hydroxide ion concentration now becomes an unknown, and an additional algebraic equation must therefore be developed to calculate the solubility of calcium oxalate. It is not difficult to write the six algebraic equations needed to calculate the solubility

of calcium oxalate (see Feature 11-1). Solving the six equations manually, however, is somewhat tedious and time consuming.

The Effect of Undissociated Solutes on Precipitation Calculations

A saturated solution of silver chloride contains significant amounts of undissociated silver chloride molecules as well as silver and chloride ions.

AgCl(s) $\Leftrightarrow$ AgCl(aq)
AgCl(aq) $\Leftrightarrow$ Ag+ + Cl-
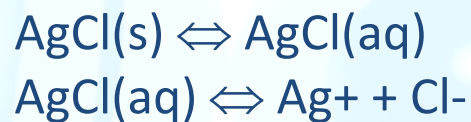
The equilibrium constant

K = [AgCl(aq)]/[AgCl(s)]

Where the numerator is the concentration of the undissocited species in the solution and the denominator is the concentration of silver chloride in the solid phase.

$$[AgCl(aq)] = K[AgCl(s)] = K_s = 3.6 \times 10^{-7}$$

The equilibrium constant K_d for the dissociation reaction is

$$\frac{[Ag+][Cl-]}{[AgCl(aq)]} = K_d = 5.0 \times 10^{-4}$$

The product of these two constants is equal to the solubility product:

$$[Ag^+][Cl^-] = K_d K_s = K_{sp}$$

EXAMPLE 11-8

Calculate the solubility of AgCl in distilled water.

Solution

$$\text{Solubility} = S = [\text{AgCl}(aq)] + [\text{Ag}^+]$$

$$[\text{Ag}^+] = [\text{Cl}^-]$$

$$[\text{Ag}^+][\text{Cl}^-] = K_{sp} = 1.82 \times 10^{-10}$$

$$[\text{Ag}^+] = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}$$

Substituting this value and K_s from Equation 11-25 gives

$$S = 1.35 \times 10^{-5} + 3.6 \times 10^{-7} = 1.38 \times 10^{-5}\ \text{M}$$

Note that neglecting [AgCl(aq)] leads to a 2% error in this example.

The Solubility of Precipitates in the Presence of Complexing Agents

The solubility of a precipitate may increase dramatically in the presence of reagents that form complexes with the anion or the cation of the precipitate.

Ex., fluoride ions prevent the quantitative precipitation of aluminum hydroxide although the solubility product of this precipitate is small
(2×10^{-32}).

$$[Al(OH)_3(s) \Leftrightarrow Al^{+3} + 3OH^-] + 6F^- \Leftrightarrow AlF_6^{-3}$$

The fluoride complex is sufficiently stable to permit fluoride ions to compete successfully with hydroxide ions for aluminum ions.

EXAMPLE 11-9

Derive an equation that describes the effect of the analytical concentration of KCl on the solubility of AgCl in an aqueous solution. Calculate the concentration of KCl at which the solubility is a minimum.

Solution

Step 1. Pertinent Equilibria Equations 11-27 through 11-30 describe the pertinent equilibria.

Step 2. Definition of Unknown The molar solubility S of AgCl is equal to the sum of the concentrations of the silver-containing species:

$$\text{solubility} = S = [\text{AgCl}(aq)] + [\text{Ag}^+] + [\text{AgCl}_2^-] + [\text{AgCl}_3^{2-}] \tag{11-31}$$

Step 3. Equilibrium-Constant Expressions Equilibrium constants available in the literature include

$$[\text{Ag}^+][\text{Cl}^-] = K_{sp} = 1.82 \times 10^{-10} \tag{11-32}$$

$$\frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}(aq)]} = K_d = 3.9 \times 10^{-4} \tag{11-33}$$

$$\frac{[\text{AgCl}_2^-]}{[\text{AgCl}(aq)][\text{Cl}^-]} = K_2 = 2.0 \times 10^{-5} \tag{11-34}$$

$$\frac{[\text{AgCl}_3^{2-}]}{[\text{AgCl}_2^-][\text{Cl}^-]} = K_3 = 1 \tag{11-35}$$

Step 4. Mass-Balance Equation

$$[\text{Cl}^-] = c_{\text{KCl}} + [\text{Ag}^+] - [\text{AgCl}_2^-] - 2[\text{AgCl}_3^{2-}] \tag{11-36}$$

The second term on the right-hand side of this equation gives the chloride ion concentration produced by the dissolution of the precipitate, and the next two terms correspond to the *decrease* in chloride ion concentration resulting from the formation of the two chloro complexes from AgCl.

Step 5. Charge-Balance Equation As in some of the earlier examples, the charge-balance equation is identical to the mass-balance equation. We begin with the basic charge balance equation,

$$[K^+] + [Ag^+] = [Cl^-] + [AgCl_2^-] + 2[AgCl_3^{2-}]$$

If we substitute $c_{KCl} = [K^+]$ into this equation, we find that

$$c_{KCl} + [Ag^+] = [Cl^-] + [AgCl_2^-] + 2[AgCl_3^{2-}]$$

and

$$[Cl^-] = c_{KCl} + [Ag^+] - [AgCl_2^-] - 2[AgCl_3^{2-}]$$

This last expression is identical to the mass balance expression in Step 4.

Step 6. Number of Equations and Unknowns We have five equations (11-32 through 11-36) and five unknowns ($[Ag^+]$, $[AgCl(aq)]$, $[AgCl_2^-]$, $[AgCl_3^{2-}]$, and $[Cl^-]$).

Step 7a. Assumptions We assume that, over a considerable range of chloride ion concentrations, the solubility of AgCl is so small that Equation 11-36 can be greatly simplified by the assumption that

$$[Ag^+] - [AgCl_2^-] - 2[AgCl_3^{2-}] \ll c_{KCl}$$

It is not certain that this is a valid assumption, but it is worth trying because it greatly simplifies the problem. With this assumption, then, Equation 11-36 reduces to

$$[Cl^-] = c_{KCl} \tag{11-37}$$

Step 8. Solution of Equations For convenience, we multiply Equations 11-34 and 11-35 to give

$$\frac{[AgCl_3^{2-}]}{[Cl^-]^2} = K_2K_3 = 2.0 \times 10^{-5} \times 1 = 2.0 \times 10^{-5} \tag{11-38}$$

To calculate $[AgCl(aq)]$, we divide Equation 11-32 by Equation 11-33 and rearrange:

$$[AgCl(aq)] = \frac{K_{sp}}{K_d} = \frac{1.82 \times 10^{-10}}{3.9 \times 10^{-4}} = 4.7 \times 10^{-7} \qquad (11\text{-}39)$$

Note that the concentration of this species is *constant and independent of the chloride concentration.*

Substitution of Equations 11-39, 11-32, 11-33, and 11-38 into Equation 11-31 permits us to express the solubility in terms of the chloride ion concentration and the several constants.

$$S = \frac{K_{sp}}{K_d} + \frac{K_{sp}}{[Cl^-]} + K_2[Cl^-] + K_2K_3[Cl^-]^2 \qquad (11\text{-}40)$$

By substituting Equation 11-37 into Equation 11-40, we find the desired relationship between the solubility and the analytical concentration of KCl:

$$S = \frac{K_{sp}}{K_d} + \frac{K_{sp}}{c_{KCl}} + K_2c_{KCl} + K_2K_3c_{KCl}^2 \qquad (11\text{-}41)$$

To find the minimum in S, we set the derivative of S with respect to c_{KCl} equal to zero:

$$\frac{dS}{dc_{KCl}} = 0 = \frac{K_{sp}}{c_{KCl}^2} + K_2 + 2K_2K_3c_{KCl}$$

$$2K_2K_3c_{KCl}^3 + c_{KCl}^2K_2 - K_{sp} = 0$$

Substituting numerical values gives

$$(4.0 \times 10^{-5})c_{KCl}^3 + (2.0 \times 10^{-5})c_{KCl}^2 - 1.82 \times 10^{-10} = 0$$

Following the procedure shown in Feature 9-4, we can solve this equation by successive approximations to obtain

$$c_{KCl} = 0.0030 = [Cl^-]$$

To check the assumption made earlier, we calculate the concentrations of the various species. Substitutions into Equations 11-32, 11-34, and 11-36 yield

$$[Ag^+] = (1.82 \times 10^{-10})/0.0030 = 6.1 \times 10^{-8} \text{ M}$$

$$[AgCl_2^-] = 2.0 \times 10^{-5} \times 0.0030 = 6.0 \times 10^{-8} \text{ M}$$

$$[AgCl_3^{2-}] = 2.0 \times 10^{-5} \times (0.0030)^2 = 1.8 \times 10^{-10} \text{ M}$$

Thus, our assumption that c_{KCl} is much larger than the concentrations of the silver-containing ions is reasonable. The minimum solubility is obtained by substitution of these concentrations and $[AgCl(aq)]$ into Equation 11-31:

$$S = 4.7 \times 10^{-7} + 6.1 \times 10^{-8} + 6.0 \times 10^{-8} + 1.8 \times 10^{-10}$$

$$= 5.9 \times 10^{-7} \text{ M}$$

Figure 11-2 The effect of chloride ion concentration on the solubility of AgCl. The solid curve sows the total concentration of dissolved AgCl.

The broken lines show the concentrations of the various silver-containing species.
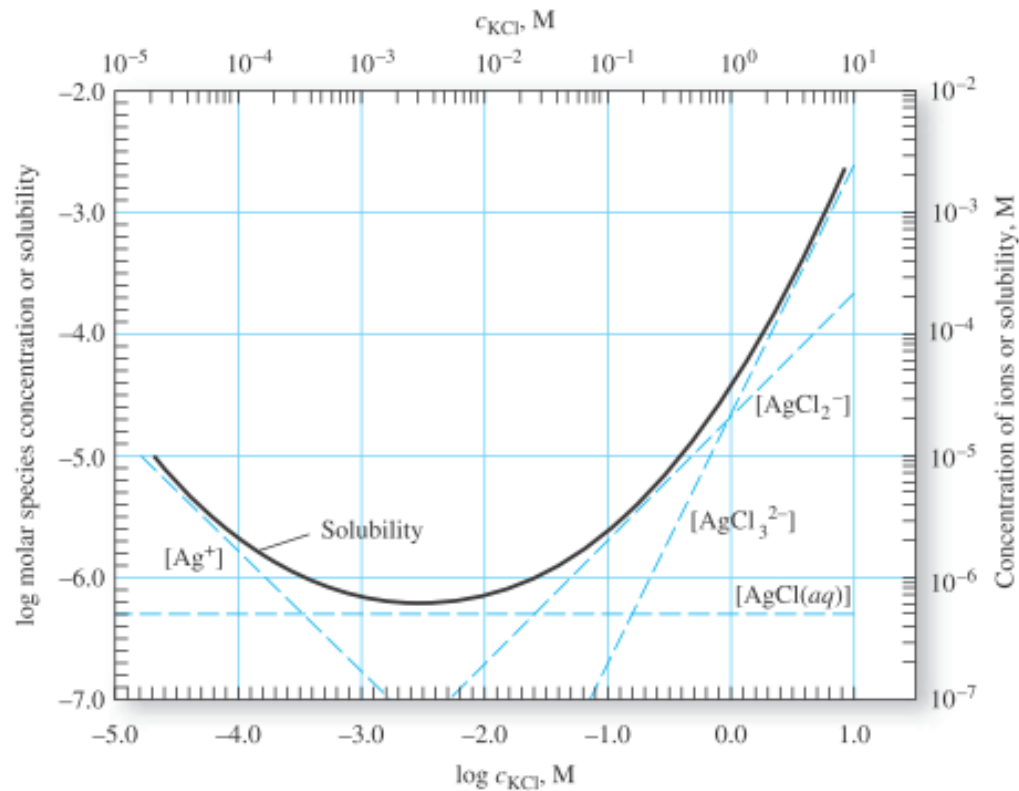
11C Separation of ions by control of the concentration of the precipitating agent

Several precipitating reagents permit separation of ions on solubility differences.

Such separations require close control of the active reagent concentration at a suitable and predetermined level., and is usually achieved by controlling the pH of the solution with suitable buffers.

This is applicable to anionic reagents in which the anion is the conjugate base of a weak acid.

EXAMPLE 11-10

Can Fe^{3+} and Mg^{2+} be separated quantitatively as hydroxides from a solution that is 0.10 M in each cation? If the separation is possible, what range of OH^- concentrations is permissible?

Solution

Solubility-product constants for the two precipitates are

$$K_{sp} = [Fe^{3+}][OH^-]^3 = 2 \times 10^{-39}$$

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12}$$

The K_{sp} for $Fe(OH)_3$ is so much smaller than that for $Mg(OH)_2$ that it appears likely that the former will precipitate at a lower OH^- concentration. We can answer the questions posed in this problem by (1) calculating the OH^- concentration required to achieve quantitative precipitation of Fe^{3+} and (2) computing the OH^- concentration at which $Mg(OH)_2$ just begins to precipitate. If (1) is smaller than (2), a separation is feasible in principle, and the range of permissible OH^- concentrations is defined by the two values.

To determine (1), we must first specify what constitutes a quantitative removal of Fe^{3+} from the solution. The decision here is arbitrary and depends on the purpose of the separation. In this example and the next, we consider a precipitation to be quantitative when all but 1 part in 1000 of the ion has been removed from the solution, that is, when $[Fe^{3+}] < 1 \times 10^{-4}$ M.

We can calculate the OH^- concentration in equilibrium with 1×10^{-1} M Fe^{3+} by substituting directly into the solubility-product expression:

$$K_{sp} = (1.0 \times 10^{-4})[OH^-]^3 = 2 \times 10^{-39}$$

$$[OH^-] = [(2 \times 10^{-39})/(1.0 \times 10^{-4})]^{1/3} = 3 \times 10^{-12} \text{ M}$$

Thus, if we maintain the OH^- concentration at about 3×10^{-12} M, the Fe^{3+} concentration will be lowered to 1×10^{-4} M. Note that quantitative precipitation of $Fe(OH)_3$ is achieved in a distinctly acidic medium (pH ≈ 2.5).

To determine what maximum OH^- concentration can exist in the solution without causing formation of $Mg(OH)_2$, we note that precipitation cannot occur until the product $[Mg^{2+}] [OH^-]^2$ exceeds the solubility product, 7.1×10^{-12}. Substitution of 0.1 (the molar Mg^{2+} concentration of the solution) into the solubility-product expression permits the calculation of the maximum OH^- concentration that can be tolerated:

$$K_{sp} = 0.10[OH^-]^2 = 7.1 \times 10^{-12}$$

$$[OH^-] = 8.4 \times 10^{-6} \text{ M}$$

When the OH^- concentration exceeds this level, the solution will be supersaturated with respect to $Mg(OH)_2$, and precipitation should begin.

From these calculations, we conclude that quantitative separation of $Fe(OH)_3$ can be achieved if the OH^- concentration is greater than 3×10^{-12} M and that $Mg(OH)_2$ will not precipitate until an OH^- concentration of 8.4×10^{-6} M is reached. Therefore, it is possible, in principle, to separate Fe^{3+} from Mg^{2+} by maintaining the OH^- concentration between these levels. In practice, the concentration of OH^- is kept as low as practical—often about 10^{-10} M. Note that these calculations neglect activity effects.

Sulfide Separations

Sulfide ion forms precipitates with heavy metal cations that have solubility products that vary from 10^{-10} to 10^{-90} or smaller.

The concentration of S^{-2} can be varied over a range of about 0.1 M to 10^{-22} M by controlling the pH of a saturated solution of hydrogen sulfide.

These properties make possible a number of useful cation separations.

Consider the precipitation of the divalent cation M^{+2}

$$MS(s) \Longleftrightarrow M^{+2} + S^{-2} \qquad K_{sp} = [M^{+2}][S^{-2}]$$

$$H_2S + H_2O \Longleftrightarrow H_3O^+ + HS^- \qquad K_1 = \frac{[H_3O^+][HS^-]}{[H_2S]} = 9.6 \times 10^{-8}$$

$$HS^- + H_2O \Longleftrightarrow H_3O^+ + S^{-2} \qquad K_2 = \frac{[H_3O^+][S^{-2}]}{[HS^-]} = 1.3 \times 10^{-14}$$

Solubility = $[M^{+2}]$

Thus, we may write as a mass-balance expression:

$$[S^{-2}] + [HS^-] + [H_2S] = 0.1$$

Calculation can be simplified by assuming that $([S^{-2}] + [HS^-]) \ll [H_2S]$

$$[H_2S] \approx 0.10 \text{ M}$$

The two dissociation-constant expressions for hydrogen sulfide can be multiplied to given an expression for the overall dissociation of hydrgen sulfide to sulfide ion:

$$H_2S + 2H_2O \Longleftrightarrow 2H_2O^+ + S^{-2} \quad K_1K_2 = \frac{[H_3O^+]^2[S^{-2}]}{[H_2S]} = 1.2 \times 10^{-21}$$
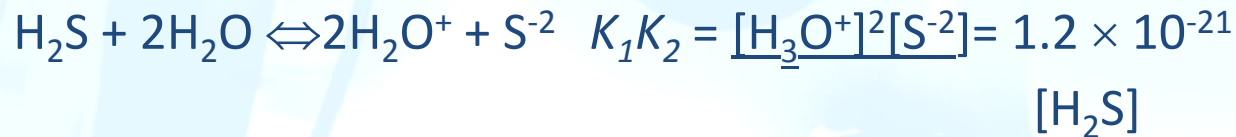
Substituting the value for [H2S] and re-arranging, we get:

$$[S^{-2}] = \frac{1.2 \times 10^{-22}}{[H_3O^+]^2}$$

Figure 11-3 The sulfide ion concentration of a saturated hydrogen sulfide solution varies inversely with the square of the hydrogen ion concentration.
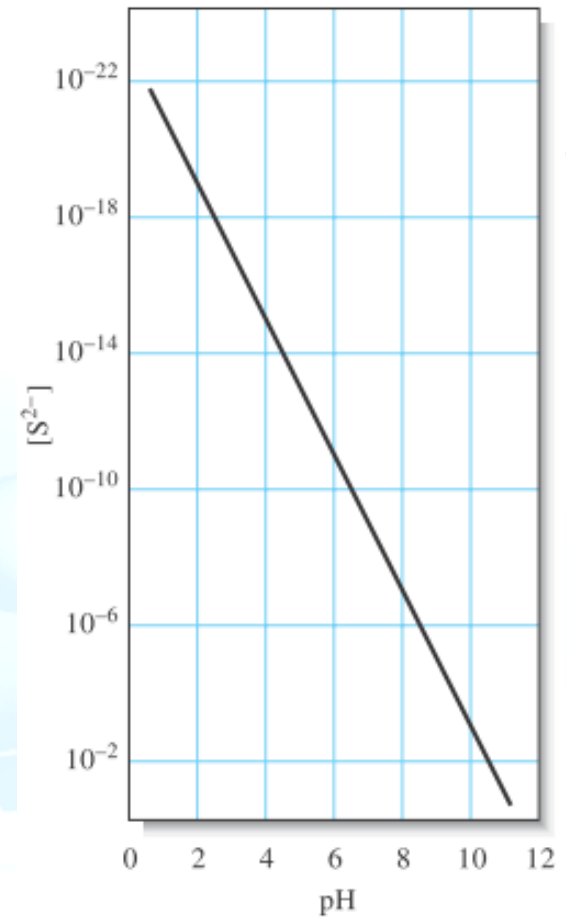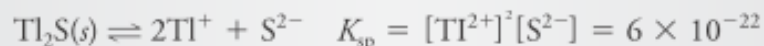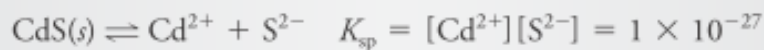
EXAMPLE 11-11

Cadmium sulfide is less soluble than thallium(I) sulfide. Find the conditions under which Cd^{2+} and Tl^+ can, in theory, be separated quantitatively with H_2S from a solution that is 0.1 M in each cation.

Solution

The constants for the two solubility equilibria are:

$$CdS(s) \rightleftharpoons Cd^{2+} + S^{2-} \quad K_{sp} = [Cd^{2+}][S^{2-}] = 1 \times 10^{-27}$$

$$Tl_2S(s) \rightleftharpoons 2Tl^+ + S^{2-} \quad K_{sp} = [Tl^{2+}]^2[S^{2-}] = 6 \times 10^{-22}$$

Since CdS precipitates at a lower $[S^{2-}]$ than does Tl_2S, we first compute the sulfide ion concentration necessary for quantitative removal of Cd^{2+} from solution. As in Example 11-10, we arbitrarily specify that separation is quantitative when all but 1 part in 1000 of the Cd^{2+} has been removed, that is, the concentration of the cation has been lowered to 1.00×10^{-4} M. Substituting this value into the solubility-product expression gives

$$K_{sp} = 10^{-4}[S^{2-}] = 1 \times 10^{-27}$$

$$[S^{2-}] = 1 \times 10^{-23} \text{ M}$$

If we maintain the sulfide concentration at this level or greater, we may assume that quantitative removal of the cadmium will take place. Next, we compute the $[S^{2-}]$ needed to initiate precipitation of Tl_2S from a 0.1 M solution. Precipitation will begin when the solubility product is just exceeded. Since the solution is 0.1 M in Tl^+,

$$(0.1)^2[S^{2-}] = 6 \times 10^{-22}$$

$$[S^{2-}] = 6 \times 10^{-20} \text{ M}$$

These two calculations show that quantitative precipitation of Cd^{2+} takes place if $[S^{2-}]$ is made greater than 1×10^{-23} M. No precipitation of Tl^+ occurs, however, until $[S^{2-}]$ becomes greater than 6×10^{-20} M.

Substituting these two values for $[S^{2-}]$ into Equation 11-42 permits us to calculate the $[H_3O^+]$ range required for the separation.

$$[H_3O^+]^2 = \frac{1.2 \times 10^{-22}}{1 \times 10^{-23}} = 12$$

$$[H_3O^+] = 3.5 \text{ M}$$

and

$$[H_3O^+]^2 = \frac{1.2 \times 10^{-22}}{6 \times 10^{-20}} = 2.0 \times 10^{-3}$$

$$[H_3O^+] = 0.045 \text{ M}$$

By maintaining $[H_3O^+]$ between approximately 0.045 and 3.5 M, we should be able to separate Cd^{2+} quantitatively from Tl^+. Because of the high ionic strength of such acidic solutions, it may be necessary to correct for activity effects.