15 Complex Ion and Precipitation Equilibria

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The limestone cliffs of Etretat are rocks of compressed calcium carbonate ($CaCO_3$). This compound is insoluble in water but can be dissolved by a strong acid. Acid rain can erode these cliffs.

Surrounded by beakers, by strange coils,
By ovens and flasks with twisted necks,
The chemist, fathoming the whims of attractions,
Artfully imposes on them their precise meetings.

—SULLY-PRUDHOMME
The Naked World (translated by William Dock)

Thus far, we have looked at the equilibrium established when acids, bases or both of these are added to water.

In this chapter we will discuss the equilibrium of complex ion formation (Section 15-1). Solubility (Section 15-2) and precipitation (Section 15-3), discussed in Chapter 4, are reexamined with a focus on an equilibrium constant K_{sp}. We will also learn how to dissolve precipitates (Section 15-4) by making them react with strong acids or complexing agents forming complex ions.

The equilibria involving complex ions and precipitates have applications in geology, medicine, and agriculture. In chemistry, you are more likely to meet up with these equilibria in the laboratory when you carry out experiments in qualitative analysis.

Chapter Outline

15-1 Complex Ion Equilibria; Formation Constant (K_f)

Recall from Chapter 13 the Lewis model for the definition of an acid and a base. Many of the electron acceptors for Lewis acids are transition metal ions (Lewis acids). These metal ions combine with molecules (e.g., H_2O, NH_3) or other ions (e.g., Cl^-, OH^-) that are good electron-pair donors (Lewis bases). The product of this combination is a **complex ion**. Chapter 19 will discuss the chemistry of these ions in greater detail.

The equilibrium constant for the formation of a complex ion is called a **formation constant** (or stability constant) and given the symbol K_f. A typical example is

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) \qquad K_f = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

Table 15.1 lists formation constants of complex ions. In each case, K_f applies to the formation of the complex by a reaction of the type just cited. Notice that

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Table 15.1 Formation Constants of Complex Ions

Complex Ion	K_f	Complex Ion	K_f
$AgCl_2^-$	1.8×10^5	$CuCl_2^-$	1×10^5
$Ag(CN)_2^-$	2×10^{20}	$Cu(NH_3)_4^{2+}$	2×10^{12}
$Ag(NH_3)_2^+$	1.7×10^7	$FeSCN^{2+}$	9.2×10^2
$Ag(S_2O_3)_2^{3-}$	1×10^{13}	$Fe(CN)_6^{3-}$	4×10^{52}
$Al(OH)_4^-$	1×10^{33}	$Fe(CN)_6^{4-}$	4×10^{45}
$Cd(CN)_4^{2-}$	2×10^{18}	$Hg(CN)_4^{2-}$	2×10^{41}
$Cd(NH_3)_4^{2+}$	2.8×10^7	$Ni(NH_3)_6^{2+}$	9×10^8
$Cd(OH)_4^{2-}$	1.2×10^9	$PtCl_4^{2-}$	1×10^{16}
$Co(NH_3)_6^{2+}$	1×10^5	*trans*-$Pt(NH_3)_2Cl_2$	3×10^{28}
$Co(NH_3)_6^{3+}$	1×10^{23}	*cis*-$Pt(NH_3)_2Cl_2$	3×10^{29}
$Co(NH_3)_5Cl^{2+}$	2×10^{28}	$Zn(CN)_4^{2-}$	6×10^{16}
$Co(NH_3)_5NO_2^{2+}$	1×10^{24}	$Zn(NH_3)_4^{2+}$	3.6×10^8
		$Zn(OH)_4^{2-}$	3×10^{14}

for most complex ions in Table 15.1, K_f is a large number: 10^5 or greater. This means that equilibrium considerations strongly favor complex formation. Consider, for example, the system

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

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

The large K_f value means that the forward reaction goes virtually to completion. Addition of ammonia to a solution of $AgNO_3$ will convert nearly all the Ag^+ ions to $Ag(NH_3)_2^+$ (see Example 15.1).

EXAMPLE 15.1

Consider the equilibrium

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_f = 1.7 \times 10^7$$

a What is the ratio $[Ag(NH_3)_2^+]/[Ag^+]$ in 0.10 *M* NH_3?

ANALYSIS

Information given:	reaction ($Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$) $K_f (1.7 \times 10^7)$ $[NH_3]$ (0.10 *M*)
Asked for:	$\dfrac{[Ag(NH_3)_2^+]}{[Ag^+]}$

STRATEGY

1. Write the K_f expression for the reaction.
2. Substitute the values for $[NH_3]$ and K_f into the expression to get the desired ratio.

continued

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SOLUTION

1. Equilibrium expression

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

2. $\dfrac{[Ag(NH_3)_2^+]}{[Ag^+]}$

$$1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+](0.10)^2} \longrightarrow \frac{[Ag(NH_3)_2^+]}{[Ag^+]} = 1.7 \times 10^7(0.10)^2 = 1.7 \times 10^5$$

b What concentration of NH_3 is required to convert 99% of Ag^+ to $Ag(NH_3)_2^+$?

ANALYSIS

Information given:	reaction ($Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$) $K_f(1.7 \times 10^7)$ 99% Ag^+ is converted to $Ag(NH_3)_2^+$
Asked for:	$[NH_3]$

STRATEGY

1. Converting 99% Ag^+ to $Ag(NH_3)_2^+$ means that for every 1 mol of Ag^+ there are 99 mol of $Ag(NH_3)_2^+$ or $\dfrac{[Ag(NH_3)_2^+]}{[Ag^+]} = \dfrac{99}{1}$.
2. Substitute the K_f value and the value for the ratio to find $[NH_3]$.

SOLUTION

$[NH_3]$

$$1.7 \times 10^7 = \left(\frac{99}{1}\right) \times \frac{1}{[NH_3]^2} \longrightarrow [NH_3] = 2.4 \times 10^{-3}\ M$$

c What is the equilibrium constant for the reaction:

$$Ag(NH_3)_2^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) + 2NH_3(aq)$$

(Take K_f $Ag(S_2O_3)_2^{3-}$ to be 1×10^{13}.)

ANALYSIS

Information given:	reaction ($Ag(NH_3)_2^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons 2NH_3(aq) + Ag(S_2O_3)_2^{3-}(aq)$) K_f for $Ag(NH_3)_2^+$ (1.7×10^7); K_f for $Ag(S_2O_3)_2^{3-}$(1×10^{13})
Asked for:	K for the reaction

STRATEGY AND SOLUTION

1. Focus on the reactant, $Ag(NH_3)_2^+$, in the desired equation. It contributes NH_3 as a product. Find an equation that "liberates" NH_3 from $Ag(NH_3)_2^+$. That equation is the reverse of the equation that forms $Ag(NH_3)_2^+$.

   (1) $Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+(aq) + 2NH_3(aq)$ $\qquad K_1 = 1/K_f = 1/(1.7 \times 10^7)$

2. Focus on the second reactant, $S_2O_3^{2-}$, in the desired equation. It is part of the reaction for the formation of $Ag(S_2O_3)_2^{3-}$. Write the equation for that reaction.

   (2) $Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$ $\qquad K_2 = K_f = 1 \times 10^{13}$

3. Combine both equations to get the final equation. Combine K_1 and K_2 to get K for the reaction using the rule of multiple equilibria.

$$\begin{array}{rl} (1)\ Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+(aq) + 2NH_3(aq) & K_1 = 1/K_f = 1/(1.7 \times 10^7) \\ (2)\ Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) & K_2 = K_f = 1 \times 10^{13} \\ \hline Ag(NH_3)_2^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) + 2NH_3(aq) & K = \dfrac{1 \times 10^{13}}{1.7 \times 10^7} = 6 \times 10^5 \end{array}$$

END POINT

Looking back at part (a), a ratio of 1.7×10^5 for $\dfrac{[Ag(NH_3)_2^+]}{[Ag^+]}$ means that in 0.10 M NH_3, there are 170,000 $Ag(NH_3)_2^+$ complex ions for every Ag^+ ion.

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Figure 15.1 Two coordination complexes are shown. Left is $Co(NH_3)_6^{3+}$. Right is $Co(NH_3)_5Cl^{2+}$.

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Figure 15.2 An aqueous solution of $SrCrO_4$ in equilibrium with solid $SrCrO_4$.

Although the solid doesn't appear in K_{sp}, it must be present for equilibrium.

From Example 15.1 we see that the reaction for the conversion of $Ag(NH_3)_2^+$ to $Ag(S_2O_3)_2^{3-}$ has a large equilibrium constant. Looking at it in a slightly different way, we can say that of these two complexes of Ag^+, the $Ag(S_2O_3)_2^{3-}$ ion is the more stable.

A similar situation applies to two complex ions of Co^{3+}:

$$Co(NH_3)_6^{3+}(aq) + Cl^-(aq) \rightleftharpoons Co(NH_3)_5Cl^{2+}(aq) + NH_3(aq)$$

$$K = \frac{K_f\, Co(NH_3)_5Cl^{2+}}{K_f\, Co(NH_3)_6^{3+}} = \frac{2 \times 10^{28}}{1 \times 10^{23}} = 2 \times 10^5$$

Addition of Cl^- ions to the complex $Co(NH_3)_6^{3+}$ converts it to the more stable complex $Co(NH_3)_5Cl^{2+}$, which has a pink color (Figure 15.1).

15-2 Solubility; Solubility Product Constant (K_{sp})

In Chapter 4, we considered a compound soluble if it dissolved in water and insoluble if it did not. In this section, we look at the dissolution process in the context of an equilibrium existing between the component ions of an ionic solid and the solid itself.

Consider $SrCrO_4$ in water (Figure 15.2). Much like the weak acid HF in water,

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

an equilibrium is established in solution between the compound ($SrCrO_4$) and its corresponding ions (Sr^{2+} and CrO_4^{2-}). The net ionic equation representing this equilibrium is

$$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

K_{sp} Expression

The rules in Chapters 12 and 13 make it possible to write the equilibrium constant expression for the dissolving of $SrCrO_4$. In particular, the solid does not appear in the expression; the concentration of each ion is raised to a power equal to its coefficient in the chemical equation.

$$K_{sp} = [Sr^{2+}][CrO_4^{2-}]$$

The symbol K_{sp} represents a particular type of equilibrium constant known as the **solubility product constant.** Like all equilibrium constants, K_{sp} has a fixed value for a given system at a particular temperature. At 25°C, K_{sp} for $SrCrO_4$ is about 3.6×10^{-5}; that is,

$$[Sr^{2+}][CrO_4^{2-}] = 3.6 \times 10^{-5}$$

This relation says that the product of the two ion concentrations at equilibrium must be 3.6×10^{-5}, regardless of how equilibrium is established.

EXAMPLE 15.2

Write expressions for K_{sp} for Ag_2CrO_4 and $Ca_3(PO_4)_2$.

STRATEGY

1. Start by writing the chemical equation for the solution process (solid on the left; ions on the right).
2. Write the K_{sp} expression. Recall that
   - solids do not appear.
   - concentrations ([ ]) are used.
   - the concentration of each ion is raised to a power equal to its coefficient in the chemical equation.

continued

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SOLUTION	
Ag_2CrO_4:	
1. Equation	$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$
2. K_{sp} expression	$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$
$Ca_3(PO_4)_2$:	
1. Equation	$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$
2. K_{sp}	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

K_{sp} and the Equilibrium Concentrations of Ions

The relation

$$K_{sp}\ SrCrO_4 = [Sr^{2+}][CrO_4^{2-}] = 3.6 \times 10^{-5}$$

can be used to calculate the equilibrium concentration of one ion if you know that of the other. Suppose, for example, the concentration of CrO_4^{2-} in a certain solution in equilibrium with $SrCrO_4$ is known to be $2.0 \times 10^{-3}\ M$. It follows that

$$[Sr^{2+}] = \frac{K_{sp}\ SrCrO_4}{[CrO_4^{2-}]} = \frac{3.6 \times 10^{-5}}{2.0 \times 10^{-3}} = 1.8 \times 10^{-2}\ M$$

If in another case, $[Sr^{2+}] = 1.0 \times 10^{-4}\ M$,

$$[CrO_4^{2-}] = \frac{K_{sp}\ SrCrO_4}{[Sr^{2+}]} = \frac{3.6 \times 10^{-5}}{1.0 \times 10^{-4}} = 3.6 \times 10^{-1}\ M$$

Example 15.3 illustrates the same kind of calculation for a different compound.

EXAMPLE 15.3

Calcium phosphate, $Ca_3(PO_4)_2$, is a water-insoluble mineral, large quantities of which are used to make commercial fertilizers. Use the K_{sp} value for $Ca_3(PO_4)_2$ to determine the concentration of Ca^{2+} in equilibrium with the solid if $[PO_4^{3-}] = 5 \times 10^{-5}\ M$.

ANALYSIS	
Information given:	$[PO_4^{3-}]$ $(5 \times 10^{-5}\ M)$
Information implied:	K_{sp} for $Ca_3(PO_4)_2$
Asked for:	$[Ca^{2+}]$

STRATEGY

1. Write the chemical equation for the dissolution of $Ca_3(PO_4)_2$.
2. Write the K_{sp} expression.
3. Substitute into the K_{sp} expression to find $[Ca^{2+}]$.

SOLUTION	
1. Equation	$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$
2. K_{sp} expression	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$
3. $[Ca^{2+}]$	$1 \times 10^{-33} = [Ca^{2+}]^3(5 \times 10^{-5})^2 \longrightarrow [Ca^{2+}]^3 = 4 \times 10^{-25} \longrightarrow$ $[Ca^{2+}] = 7 \times 10^{-9}\ M$

END POINT

To check your answer, use the calculated $[Ca^{2+}]$ $(7 \times 10^{-9}\ M)$ and the given $[PO_4^{3-}]$ $(5 \times 10^{-5}\ M)$ to find K_{sp}.

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (7 \times 10^{-9})^3(5 \times 10^{-5})^2 = 9 \times 10^{-34}$$

The calculated K_{sp} is very close to the value listed in Table 15.2: 1×10^{-33}.

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Table 15.2 Solubility Product Constants at 25°C

		K_{sp}			K_{sp}
Acetates	$AgC_2H_3O_2$	1.9×10^{-3}	Hydroxides	$Al(OH)_3$	2×10^{-31}
Bromides	AgBr	5×10^{-13}		$Ca(OH)_2$	4.0×10^{-6}
	Hg_2Br_2	6×10^{-23}		$Fe(OH)_2$	5×10^{-17}
	$PbBr_2$	6.6×10^{-6}		$Fe(OH)_3$	3×10^{-39}
Carbonates	Ag_2CO_3	8×10^{-12}		$Mg(OH)_2$	6×10^{-12}
	$BaCO_3$	2.6×10^{-9}		$Tl(OH)_3$	2×10^{-44}
	$CaCO_3$	4.9×10^{-9}		$Zn(OH)_2$	4×10^{-17}
	$MgCO_3$	6.8×10^{-6}	Iodides	AgI	1×10^{-16}
	$PbCO_3$	1×10^{-13}		Hg_2I_2	5×10^{-29}
	$SrCO_3$	5.6×10^{-10}		PbI_2	8.4×10^{-9}
Chlorides	AgCl	1.8×10^{-10}	Phosphates	Ag_3PO_4	1×10^{-16}
	Hg_2Cl_2	1×10^{-18}		$AlPO_4$	1×10^{-20}
	$PbCl_2$	1.7×10^{-5}		$Ca_3(PO_4)_2$	1×10^{-33}
Chromates	Ag_2CrO_4	1×10^{-12}		$Mg_3(PO_4)_2$	1×10^{-24}
	$BaCrO_4$	1.2×10^{-10}	Sulfates	$BaSO_4$	1.1×10^{-10}
	$PbCrO_4$	2×10^{-14}		$CaSO_4$	7.1×10^{-5}
	$SrCrO_4$	3.6×10^{-5}		$PbSO_4$	1.8×10^{-8}
Fluorides	BaF_2	1.8×10^{-7}		$SrSO_4$	3.4×10^{-7}
	CaF_2	1.5×10^{-10}			
	MgF_2	7×10^{-11}			
	PbF_2	7.1×10^{-7}			

K_{sp} and Water Solubility

One way to establish equilibrium between a slightly soluble solid and its ions in solution is to stir the solid with water to form a saturated solution. As you might expect, the solubility of the solid, *s*, in moles per liter, is related to the solubility product constant, K_{sp}. In the case of barium sulfate dissolving in water we have

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

The solubility of $BaSO_4$ is exactly equal to the equilibrium concentration of either Ba^{2+} or SO_4^{2-}. In other words,

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

s is always the molar solubility.

and

$$K_{sp}\ BaSO_4 = [Ba^{2+}][SO_4^{2-}] = s^2$$

Solving,

$$s = (K_{sp})^{\frac{1}{2}} = (1.1 \times 10^{-10})^{\frac{1}{2}} = 1.0 \times 10^{-5}\ \text{mol/L}$$

When you hear the word "dissolve" imagine the solid breaking up into its component ions.

This means that a saturated solution can be prepared by dissolving 2.3 mg of $BaSO_4$ in enough water to make 1.0 L of solution. Putting it another way, dissolving *less* than 2.3 mg results in an unsaturated solution. If more than 2.3 mg are added, an equilibrium is established between the solution containing 1.0×10^{-5} *M* Ba^{2+} and SO_4^{2-} and the solid $BaSO_4$.

The relationship between K_{sp} and *s* depends on the type of solid.

When an ionic solid consists of anions and cations of different charges, the relation between K_{sp} and *s* takes a different form, but the principle is the same (Example 15.4).

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EXAMPLE 15.4 GRADED

Barium fluoride, BaF_2, is used in metallurgy as a welding and soldering agent. Its K_{sp} is 1.8×10^{-7}.

a What is its solubility in mol/L (molar solubility)?

ANALYSIS

Information given:	K_{sp} for BaF_2 (1.8×10^{-7})
Asked for:	molar solubility (solubility in mol/L)

STRATEGY

1. Write a net ionic equation to represent dissolving BaF_2.
2. Let s be the molar solubility of BaF_2; $s = [BaF_2]$ that dissolves.
3. Use stoichiometric ratios to relate BaF_2 to its ions.
4. Write the K_{sp} expression. Substitute into it and solve for s.

SOLUTION

1. Equation

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$$

2. Stoichiometric ratios

$$1 \text{ mol } BaF_2 \text{ dissolves/L} \longrightarrow 1 \text{ mol/L } Ba^{2+} \longrightarrow 2 \text{ mol/L } F^-$$
$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$
$$s \qquad\qquad s \qquad\qquad 2s$$

s

$$K_{sp} = [Ba^{2+}][F^-]^2 = (s)(2s)^2 = 4s^3$$

$$1.8 \times 10^{-7} = 4s^3; \; s = \left(\frac{1.8 \times 10^{-7}}{4}\right)^{\frac{1}{3}} = 3.6 \times 10^{-3} \, M$$

b What is its solubility in g/L?

ANALYSIS

Information given:	K_{sp} for BaF_2 (1.8×10^{-7}) from part (a): molar solubility of BaF_2 (3.6×10^{-3} M)
Information implied:	MM BaF_2
Asked for:	solubility of BaF_2 in g/L

STRATEGY

Use the molar mass of BaF_2 to change the molar solubility to the solubility in g/L.

SOLUTION

Solubility (g/L)	$3.6 \times 10^{-3} \dfrac{\text{mol}}{\text{L}} \times 175.3 \dfrac{\text{g}}{\text{mol}} = 0.63 \text{ g/L}$

c How many grams of BaF_2 are required to prepare 298 mL of a saturated solution of BaF_2?

ANALYSIS

Information given:	K_{sp} for BaF_2 (1.8×10^{-7}) from part (b): solubility of BaF_2 in g/L (0.63 g/L) volume of saturated solution (298 mL)
Asked for:	mass of BaF_2 to prepare a saturated solution.

STRATEGY

1. Recall the definition of a saturated solution. It has the maximum number of grams of a solute that can be dissolved (solubility).
2. Use the solubility in g/L as a conversion factor to find the mass needed to prepare 298 mL of a saturated solution.

continued

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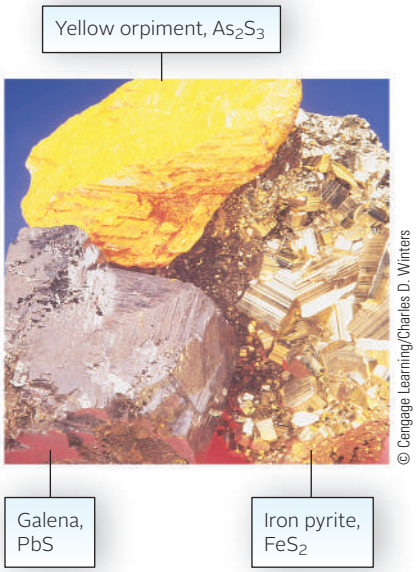
SOLUTION	
Mass BaF_2	$0.298\ \text{L} \times \dfrac{0.63\ \text{g}}{1\ \text{L}} = 0.19\ \text{g}$
END POINT	
You have to know either the molar solubility or the solubility in g/L to prepare a saturated solution.	



Sulfide minerals and K_{sp}. Sulfides are among the least soluble ionic compounds. Their K_{sp} values are often smaller than 10^{-25}. For this reason, many sulfides are found as minerals.

Frequently we find that the experimentally determined solubility of an ionic solid is larger than that predicted from K_{sp}. Consider, for example, $PbCl_2$, where the solubility calculated from the relation

$$4s^3 = K_{sp} = 1.7 \times 10^{-5}$$

is 0.016 mol/L. The measured solubility is considerably larger, 0.036 mol/L. The explanation for this is that some of the lead in $PbCl_2$ goes into solution in the form of species other than Pb^{2+}. In particular, we can detect the presence of the ions $Pb(OH)^+$ and $PbCl^+$.

The reverse of Example 15.4 involves finding K_{sp} of a compound given its solubility. The solubilities of many ionic compounds are determined experimentally and tabulated in chemical handbooks. Most solubility values are given in grams of solute dissolved in 100 grams of water. To obtain the molar solubility in moles/L, we have to assume that the density of the solution is equal to that of water. Then the number of grams of solute per 100 g water is equal to the number of grams of solute per 100 mL of solution. This assumption is valid because the mass of the compound in solution is small. To solve for K_{sp}, find the molar solubility of the solute and determine the concentration of its component ions. Substitute into the K_{sp} expression.

EXAMPLE 15.5

Consider the pesticide magnesium arsenate, $Mg_3(AsO_4)_2$. Its solubility is determined experimentally to be 1.6×10^{-3} g/100 g H_2O. What is the K_{sp} for $Mg_3(AsO_4)_2$? (Assume that the density of water is equal to the density of the solution.)

ANALYSIS	
Information given:	solubility (1.6×10^{-3} g/100 g H_2O)
Information implied:	density of the solution = density of water MM $Mg_3(AsO_4)_2$
Asked for:	K_{sp}

STRATEGY

1. Assume 1.6×10^{-3} g/100 g H_2O = 1.6×10^{-3} g/100 mL of solution. Convert this solubility data to molar solubility (mol/L). Use the molar mass of $Mg_3(AsO_4)_2$.
2. Write a net ionic equation to represent dissolving $Mg_3(AsO_4)_2$.
3. Use stoichiometric ratios to relate $[Mg_3(AsO_4)_2]$ to $[Mg^{2+}]$ and $[AsO_4^{3-}]$.
4. Substitute into the K_{sp} expression and find K_{sp}.

continued

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SOLUTION	
1. Molar solubility	$\frac{1.6 \times 10^{-3}\ \text{g}}{0.100\ \text{L}} \times \frac{1\ \text{mol}}{350.7\ \text{g}} = 4.6 \times 10^{-5}\ M$
2. Reaction	$Mg_3(AsO_4)_2(s) \rightleftharpoons 3Mg^{2+}(aq) + 2AsO_4^{3-}(aq)$
3. Stoichiometric ratios	1 mol $Mg_3(AsO_4)_2$ dissolved $\longrightarrow$ 3 mol Mg^{2+}; $[Mg^{2+}] = 3(4.6 \times 10^{-5}) = 1.4 \times 10^{-4}$
	1 mol $Mg_3(AsO_4)_2$ dissolved $\longrightarrow$ 2 mol AsO_4^{3-}; $[AsO_4^{3-}] = 2(4.6 \times 10^{-5}) = 9.2 \times 10^{-5}$
4. K_{sp}	$K_{sp} = [Mg^{2+}]^3[AsO_4^{3-}]^2 = (1.4 \times 10^{-4})^3(9.2 \times 10^{-5})^2 = 2.3 \times 10^{-20}$

K_{sp} and the Common Ion Effect

How would you expect the solubility of barium sulfate in water

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

to compare with that in a 0.10 *M* solution of Na_2SO_4, which contains the same *(common)* anion, SO_4^{2-}? A moment's reflection should convince you that the solubility in 0.10 *M* Na_2SO_4 must be *less* than that in pure water. Recall that when $BaSO_4$ is dissolved in pure water, $[SO_4^{2-}]$ is 1.0×10^{-5} *M*. Increasing the concentration of SO_4^{2-} to 0.10 *M* should, by Le Châtelier's principle, drive the above equilibrium to the *left,* repressing the solubility of barium sulfate. This is, indeed, the case (Example 15.6).

A "common" ion comes from two sources such as $BaSO_4$ and Na_2SO_4.

EXAMPLE 15.6

Taking K_{sp} of $BaSO_4$ to be 1.1×10^{-10}, estimate its solubility (moles per liter) in 0.10 *M* Na_2SO_4 solution.

ANALYSIS	
Information given:	K_{sp} of $BaSO_4$ (1.1×10^{-10}) *M* for Na_2SO_4(0.10)
Asked for:	molar solubility

STRATEGY

1. Let s = mol $BaSO_4$ dissolved in a liter of solution and relate $[Ba^{2+}]$ and $[SO_4^{2-}]$ to $BaSO_4$ dissolved (s).
2. Set up the following table.

	$[Ba^{2+}]$	$[SO_4^{2-}]$
Original		
Change		
Equilibrium		

Show that at the start, there are no Ba^{2+} ions present and no SO_4^{2-} ions contributed by $BaSO_4$ but contributed by Na_2SO_4.

Let s be in the "change" row to show the amount of Ba^{2+} ions and SO_4^{2-} ions contributed by the dissolved $BaSO_4$.

3. Substitute your entries in the equilibrium row into the K_{sp} expression for $BaSO_4$.
4. Solve for s and assume that $s << SO_4^{2-}$ originally present.

continued

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SOLUTION

1. Ba^{2+}; SO_4^{2-}

amount of $BaSO_4$ dissolved = s = $[Ba^{2+}]$ = $[SO_4^{2-}]$

2. Table

	$[Ba^{2+}]$	$[SO_4^{2-}]$
Original	0	0.10
Change	$+s$	$+s$
Equilibrium	s	$0.10 + s$

3. K_{sp} expression

$$1.1 \times 10^{-10} = [Ba^{2+}][SO_4^{2-}] = (s)(0.10 + s)$$

4. s

Assume $s << 0.10$.

$$1.1 \times 10^{-10} = (s)(0.10) \longrightarrow s = 1.1 \times 10^{-9}\ M$$

s is indeed much smaller than 0.10, so the assumption is justified.

END POINT

The solubility in 0.10 M Na_2SO_4 is much less than that in pure water ($1.1 \times 10^{-9} << 1.0 \times 10^{-5}$), which is exactly what we predicted.

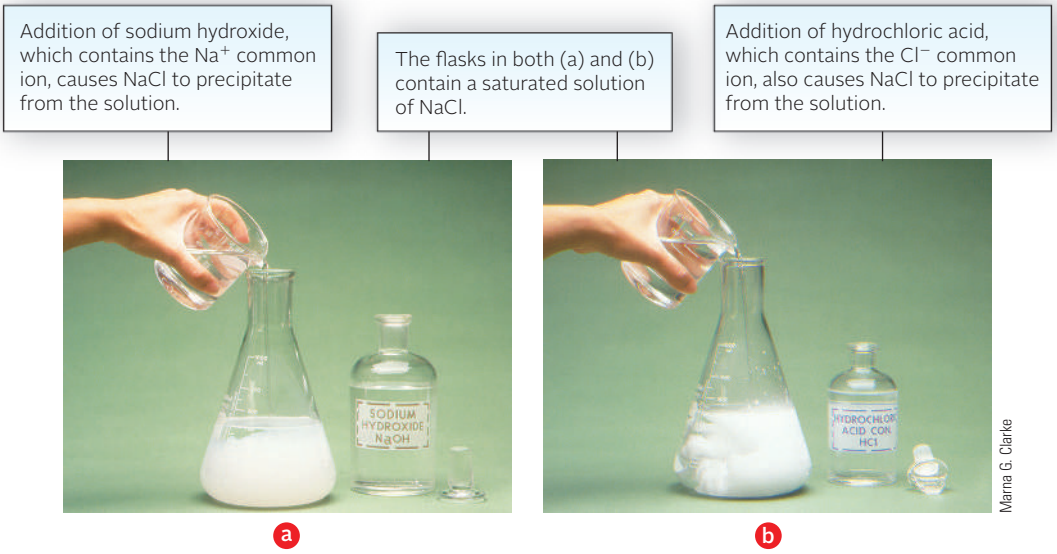

Figure 15.3 Sodium chloride and the common ion effect.

Figure 15.4 Precipitation of strontium chromate. A solution prepared by mixing solutions of $Sr(NO_3)_2$ and K_2CrO_4 is in equilibrium with yellow $SrCrO_4(s)$. In such a solution $[Sr^{2+}] \times [CrO_4^{2-}] = 3.6 \times 10^{-5}$.

The **common ion effect** illustrated in Example 15.6 is a general one. ***An ionic solid is less soluble in a solution containing a common ion than it is in water*** (Figure 15.3).

15-3 Precipitate Formation

As we saw in Chapter 4, a precipitate forms when a cation from one solution combines with an anion from another solution to form an insoluble ionic solid. We also considered how to predict whether such a reaction would occur and, if so, how to represent it by a net ionic equation.

Precipitation reactions, like all reactions, reach a position of equilibrium. Putting it another way, even the most "insoluble" electrolyte dissolves to at least a slight extent, thereby establishing equilibrium with its ions in solution. Suppose, for example, solutions of $Sr(NO_3)_2$ and K_2CrO_4 are mixed. In this case, Sr^{2+} ions combine with CrO_4^{2-} ions to form a yellow precipitate of strontium chromate, $SrCrO_4$ (Figure 15.4).

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Very quickly, an equilibrium is established between the solid and the corresponding ions in solution:

$$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

K_{sp} and Precipitate Formation

K_{sp} values can be used to make predictions as to whether or not a precipitate will form when two solutions are mixed. To do this, we follow an approach very similar to that used in Chapter 12, to determine the direction in which a system will move to reach equilibrium. We work with a quantity known as the **ion product constant**, Q, which has the same mathematical form as K_{sp}. The difference is that the concentrations that appear in Q are those that apply at a particular moment. Those that appear in K_{sp} are equilibrium concentrations. That is, the value of Q is expected to change as a precipitation reaction proceeds, approaching K_{sp} and eventually becoming equal to it.

Three cases can be distinguished (Figure 15.5):

1. If $Q > K_{sp}$, the solution contains a higher concentration of ions than it can hold at equilibrium. A ***precipitate forms,*** decreasing the concentrations until the ion product becomes equal to K_{sp} and equilibrium is established.
2. If $Q < K_{sp}$, the solution contains a lower concentration of ions than is required for equilibrium with the solid. The solution is unsaturated. ***No precipitate forms;*** equilibrium is not established.
3. If $Q = K_{sp}$, the solution is just saturated with ions and is at the point of precipitation.

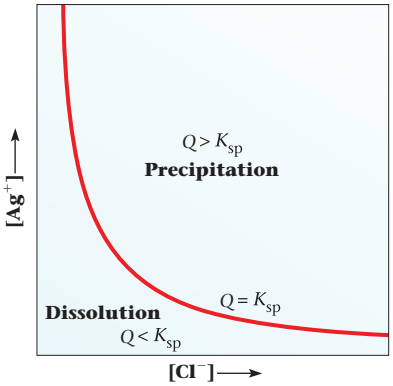

Figure 15.5 Equilibrium curve for silver chloride. Silver chloride (s) is in contact with Ag^+ and Cl^- ions in aqueous solution. The product Q of the concentration of ions $[Ag^+] \times [Cl^-]$ is equal to K_{sp} *(curved line)* when equilibrium exists. If $Q > K_{sp}$, $AgCl(s)$ tends to precipitate out until equilibrium is reached. If $Q < K_{sp}$, additional solid dissolves.

K_{sp} is a constant; Q can have any value.

EXAMPLE 15.7 GRADED

In the laboratory, strontium chromate ($K_{sp} = 3.6 \times 10^{-5}$) can be prepared by mixing solutions containing strontium ions and chromate ions, where the concentrations of these ions are high enough to form a precipitate.

a A solution has the following initial concentrations: $[Sr^{2+}] = 6.0 \times 10^{-3}\ M$, $[CrO_4^{2-}] = 3.0 \times 10^{-3}\ M$. Will a precipitate form?

ANALYSIS

Information given:	K_{sp} of $SrCrO_4$ (3.6×10^{-5}) $[Sr^{2+}]_{initial}$ ($6.0 \times 10^{-3}\ M$); $[CrO_4^{2-}]_{initial}$ ($3.0 \times 10^{-3}\ M$)
Asked for:	Will a precipitate form?

STRATEGY

1. Write the equation for the dissolution of $SrCrO_4$.
2. Substitute initial concentrations into the Q expression and find Q.
3. Compare the Q value to the K_{sp} value.

SOLUTION

1. Equation	$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$
2. Q	$Q = [Sr^{2+}]_{initial}[CrO_4^{2-}]_{initial} = (6.0 \times 10^{-3})(3.0 \times 10^{-3}) = 1.8 \times 10^{-5}$
3. Precipitate?	$K_{sp} = 3.6 \times 10^{-5} > Q = 1.8 \times 10^{-5}$; No precipitate forms.

b Is a precipitate obtained when 275 mL of $6.0 \times 10^{-3}\ M$ $Sr(NO_3)_2$ solution is mixed with 825 mL of $0.040\ M$ K_2CrO_4?

ANALYSIS

Information given:	K_{sp} of $SrCrO_4$ (3.6×10^{-5}) Sr^{2+} source is $Sr(NO_3)_2$: V (275 mL), M (6.0×10^{-3}) CrO_4^{2-} source is K_2CrO_4: V (825 mL), M (0.040)
Asked for:	Will a precipitate form?

continued

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STRATEGY

1. Find the initial number of moles n for Sr^{2+} and CrO_4^{2-} ions ($V \times M$).
2. Find $[Sr^{2+}]_{initial}$ and $[CrO_4^{2-}]_{initial}$ by taking n for each ion and dividing it by the total volume.
3. Substitute initial concentrations into the Q expression and find Q.
4. Compare the Q value to the K_{sp} value.

SOLUTION

1. $n_{initial}$ for Sr^{2+}	$n = (0.275\ L)(6.0 \times 10^{-3}\ mol/L) = 1.65 \times 10^{-3}\ mol$
$n_{initial}$ for CrO_4^{2-}	$n = (0.825\ L)(0.040\ mol/L) = 0.033\ mol$
2. $[Sr^{2+}]_{initial}$	$\dfrac{1.65 \times 10^{-3}\ mol}{(0.275 + 0.825)\ L} = 1.5 \times 10^{-3}\ M$
$[CrO_4^{2-}]_{initial}$	$\dfrac{0.033\ mol}{(0.275 + 0.825)\ L} = 0.030\ M$
3. Q	$Q = [Sr^{2+}]_{initial}[CrO_4^{2-}]_{initial} = (1.5 \times 10^{-3})(0.030) = 4.5 \times 10^{-5}$
4. Precipitate?	$K_{sp} = 3.6 \times 10^{-5} < Q = 4.5 \times 10^{-5}$; Yes, a precipitate forms (just barely!).

C Is a precipitate obtained when 12.0 g of Na_2CrO_4 are added to 333 mL of $4.5 \times 10^{-3}\ M\ Sr(NO_3)_2$? Assume no volume change after Na_2CrO_4 is added.

ANALYSIS

Information given:	K_{sp} of $SrCrO_4$ (3.6×10^{-5}) Sr^{2+} source is $Sr(NO_3)_2$: V (333 mL), M (4.5×10^{-3}) CrO_4^{2-} source is Na_2CrO_4: mass (12.0 g)
Information implied:	Molar mass of Na_2CrO_4
Asked for:	Will a precipitate form?

STRATEGY

1. Find initial number of moles n for CrO_4^{2-} ions. (mass/MM). Since the volume does not change, it is not necessary to find n for Sr^{2+}.
2. Find $[CrO_4^{2-}]_{initial}$ by taking n and dividing it by the volume. $[Sr^{2+}]_{initial}$ is given.
3. Substitute initial concentrations into the Q expression and find Q.
4. Compare the Q value to the K_{sp} value.

SOLUTION

1. $n_{initial}$ for CrO_4^{2-}	$n = \dfrac{12.0\ g}{162\ g/mol} = 0.0741\ mol$
2. $[Sr^{2+}]_{initial}$; $[CrO_4^{2-}]_{initial}$	$[Sr^{2+}]_{initial} = 4.5 \times 10^{-3}\ M$; $[CrO_4^{2-}]_{initial} = \dfrac{0.0741\ mol}{0.333\ L} = 0.222\ M$
3. Q	$Q = [Sr^{2+}]_{initial}[CrO_4^{2-}]_{initial} = (4.5 \times 10^{-3})(0.222) = 1.0 \times 10^{-3}$
4. Precipitate?	$K_{sp} = 3.6 \times 10^{-5} < Q = 1.0 \times 10^{-3}$; Yes, a precipitate forms.

Selective Precipitation

One way to separate two cations in water solution is to add an anion that precipitates only one of the cations. This approach is known as **selective precipitation.** To see how it works, consider a simple case, a solution containing Mg^{2+} and Na^+ ions. Referring to Table 15.2, you can see that Mg^{2+} forms a couple of insoluble compounds: $MgCO_3$ ($K_{sp} = 6.8 \times 10^{-6}$) and $Mg(OH)_2$ ($K_{sp} = 6 \times 10^{-12}$). In contrast, all of the common compounds of sodium are soluble, including the carbonate and hydroxide. It follows that you could readily separate Mg^{2+} from Na^+ by adding

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either CO_3^{2-} or OH^- ions to the solution. In either case, Mg^{2+} will precipitate while Na^+ remains in solution.

Now let us consider a somewhat more complex case. Suppose you have a solution containing Mg^{2+} and Ba^{2+}, both at 0.10 *M*, which you'd like to separate by adding CO_3^{2-} ions. From Table 15.2, it appears that $BaCO_3$ ($K_{sp} = 2.6 \times 10^{-9}$) is less soluble than $MgCO_3$ ($K_{sp} = 6.8 \times 10^{-6}$). Perhaps, by adding CO_3^{2-} ions carefully, you could precipitate Ba^{2+} selectively, leaving Mg^{2+} in solution.

This is indeed the case. To precipitate $BaCO_3$, add enough CO_3^{2-} ions to make their concentration 2.6×10^{-8} *M*:

$$[CO_3^{2-}] = \frac{K_{sp}\ BaCO_3}{[Ba^{2+}]} = \frac{2.6 \times 10^{-9}}{0.10} = 2.6 \times 10^{-8}\ M$$

At this very low concentration of CO_3^{2-}, $MgCO_3$ does not precipitate:

$$Q = [Mg^{2+}][CO_3^{2-}] = (0.10)(2.6 \times 10^{-8}) = 2.6 \times 10^{-9} < K_{sp}\ MgCO_3 = 6.8 \times 10^{-6}$$

To bring down $MgCO_3$, add more CO_3^{2-} until its concentration becomes 6.8×10^{-5} *M*:

$$[CO_3^{2-}] = \frac{K_{sp}\ MgCO_3}{[Mg^{2+}]} = \frac{6.8 \times 10^{-6}}{0.10} = 6.8 \times 10^{-5}\ M$$

At that point, virtually all of the Ba^{2+} ions have been precipitated:

$$[Ba^{2+}]\ \text{remaining} = \frac{K_{sp}\ BaCO_3}{[CO_3^{2-}]} = \frac{2.6 \times 10^{-9}}{6.8 \times 10^{-5}} = 3.8 \times 10^{-5}\ M$$

$$\%\ Ba^{2+}\ \text{remaining in solution} = \frac{3.8 \times 10^{-5}}{0.10} \times 100\% = 0.038\%$$

$$\%\ Ba^{2+}\ \text{precipitated} = 100.000 - 0.038 = 99.962$$

In other words it is possible to precipitate essentially all of the Ba^{2+} ions before Mg^{2+} starts to precipitate.

EXAMPLE 15.8 GRADED

A flask (Figure 15.6) contains a solution 0.10 *M* in Cl^- and 0.010 *M* in CrO_4^{2-}. $AgNO_3$ is added to the solution.

a Which anion, Cl^- or CrO_4^{2-}, precipitates first?

ANALYSIS

Information given:	$[Cl^-]$ (0.10 *M*); $[CrO_4^{2-}]$ (0.010 *M*)
Information implied:	K_{sp} of AgCl; K_{sp} of Ag_2CrO_4
Asked for:	Which anion will precipitate first?

STRATEGY

1. Substitute into the K_{sp} expression for AgCl and find $[Ag^+]$.
2. Substitute into the K_{sp} expression for Ag_2CrO_4 and find $[Ag^+]$.
3. The anion that requires the smaller amount of Ag^+ precipitates first.

SOLUTION

1. $[Ag^+]$ for AgCl	$K_{sp} = [Ag^+][Cl^-]$; $1.8 \times 10^{-10} = [Ag^+](0.10)$; $[Ag^+] = 1.8 \times 10^{-9}\ M$
2. $[Ag^+]$ for Ag_2CrO_4	$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$; $1 \times 10^{-12} = [Ag^+]^2(0.010)$; $[Ag^+] = 1 \times 10^{-5}\ M$
3. First anion to precipitate	$[Ag^+]$ required for AgCl precipitation (1.8×10^{-9} *M*) is *less* than $[Ag^+]$ required for Ag_2CrO_4 precipitation (1×10^{-5} *M*). AgCl precipitates first.

continued

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b What percentage of the first anion has been precipitated when the second anion starts to precipitate?

ANALYSIS

Information given:	$[Cl^-]$ (0.10 *M*); $[CrO_4^{2-}]$ (0.010 *M*) From part (a): $[Ag^+]$ when Ag_2CrO_4 starts to precipitate (1×10^{-5} *M*)
Asked for:	% Cl^- in solution when Ag_2CrO_4 starts to precipitate

STRATEGY

1. Find $[Cl^-]$ in solution when $[Ag^+] = 1 \times 10^{-5}$, the concentration of Ag^+ when Ag_2CrO_4 starts to precipitate.
2. Find % Cl^- remaining in solution

$$\frac{[Cl^-] \text{ remaining in solution}}{[Cl^-] \text{ initial}} \times 100\%$$

3. Find % Cl^- that precipitated

% Cl^- precipitated = 100.00% − % Cl^- still in solution

SOLUTION

1. $[Cl^-]$ remaining in solution

$$K_{sp} = [Ag^+][Cl^-]; \; 1.8 \times 10^{-10} = (1 \times 10^{-5})[Cl^-]; \; [Cl^-] = 2 \times 10^{-5} \; M$$

2. % Cl^- remaining in solution

$$\frac{[Cl^-] \text{ remaining in solution}}{[Cl^-] \text{ initial}} \times 100\% = \frac{2 \times 10^{-5}}{0.10} \times 100\% = 0.02\%$$

3. % Cl^- precipitated

100.00% − % Cl^- still in solution = 100.00% − 0.02% = 99.8%

END POINT

Look at Figure 15.6. *White* AgCl does indeed come down first, followed by *red* Ag_2CrO_4.

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Figure 15.6 Titration of Cl^- with Ag^+, using CrO_4^{2-} as an indicator. AgCl (cream color) comes down first, then Ag_2CrO_4 (red) precipitates.

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15-4 Dissolving Precipitates

Many different methods can be used to bring water-insoluble ionic solids into solution. Most commonly, this is done by adding a reagent to react with either the anion or the cation. The two most useful reagents for this purpose are

- a strong acid, H^+, used to react with basic anions (Figure 15.7).
- a complexing agent, most often NH_3 or OH^-, added to react with metal cations.

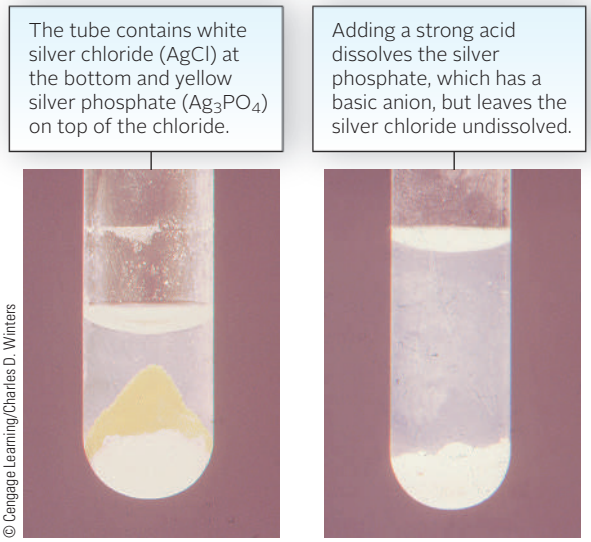

Figure 15.7 Dissolving a precipitate in acid.

Strong Acid

Water-insoluble metal hydroxides can be brought into solution with a strong acid such as HCl. The reaction with zinc hydroxide is typical:

$$Zn(OH)_2(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + 2H_2O$$

We can imagine that this reaction occurs in two (reversible) steps:

dissolving $Zn(OH)_2$ in water: $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + \cancel{2\,OH^-}(aq)$

neutralizing OH^- ions by H^+: $2H^+(aq) + \cancel{2\,OH^-}(aq) \rightleftharpoons 2H_2O$

$$Zn(OH)_2(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2H_2O$$

The equilibrium constant for the neutralization (Example 15.9) is so large that the overall reaction goes essentially to completion.

EXAMPLE 15.9 GRADED

Consider the following reaction:

$$Zn(OH)_2(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2H_2O$$

a Determine K for this system, applying the rule of multiple equilibria to the two-step process referred to above.

STRATEGY AND SOLUTION

1. Write the equation for the dissolution of $Zn(OH)_2$.

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq) \qquad K_1$$

$K_1 = K_{sp}$ for $Zn(OH)_2 = 4 \times 10^{-17}$

2. Note that H^+ must react with OH^- to get H_2O, a product of the reaction. There are 2 mol OH^- produced. Thus

$$2H^+(aq) + 2OH^-(aq) \rightleftharpoons 2H_2O \qquad K_2$$

Note that the equation for K_2 is the *reverse* of the equation for the ionization of water ($H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$). Thus,

$$K_2 = \frac{1}{K_w}$$

and since there are 2 mol water,

$$K_2 = \frac{1}{(K_w)^2} = \frac{1}{(1 \times 10^{-14})^2} = 1 \times 10^{28}$$

continued

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3. Adding the two equations and applying the rule of multiple equilibria, we obtain

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq) \qquad K_1 = 4 \times 10^{-17}$$
$$2H^+(aq) + 2OH^-(aq) \rightleftharpoons 2H_2O \qquad K_2 = 1 \times 10^{28}$$
$$Zn(OH)_2(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2H_2O \qquad K = (4 \times 10^{-17})(1 \times 10^{28}) = 4 \times 10^{11}$$

b Calculate the molar solubility, s, of $Zn(OH)_2$ in acid at pH 5.0.

ANALYSIS

Information given:	From part (a): equilibrium reaction ($Zn(OH)_2(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2H_2O$) From part (a): K for the reaction (4×10^{11}) pH (5.0)
Asked for:	molar solubility of $Zn(OH)_2$

STRATEGY

1. Find $[H^+]$.
2. Write the K expression.
3. Let $s = [Zn(OH)_2]$ that dissolves (molar solubility). Since $[Zn(OH)_2] = [Zn^{2+}]$, then $[Zn^{2+}] = s$. Substitute into the equilibrium expression.

SOLUTION

1. $[H^+]$	$5.0 = -\log_{10}[H^+]$; $[H^+] = 1.0 \times 10^{-5}$
2. K expression	$K = \dfrac{[Zn^{2+}]}{[H^+]^2}$
3. s	$4 \times 10^{11} = \dfrac{s}{(1.0 \times 10^{-5})^2} \longrightarrow s = 4 \times 10^1\ M$

END POINT

This extremely high concentration, 40 M, means that $Zn(OH)_2$ is completely soluble in acid at pH 5 (or any lower pH).

$BaSO_4$ cannot be dissolved by acid. Explain.

Strong acid can also be used to dissolve many water-insoluble salts in which the anion is a weak base. In particular, H^+ ions will dissolve

- *virtually all carbonates* (CO_3^{2-}). The product is the weak acid H_2CO_3, which then decomposes into CO_2 and H_2O. The equation for the reaction of H^+ ions with $ZnCO_3$ is typical:

$$ZnCO_3(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2CO_3(aq)$$

- *many sulfides* (S^{2-}). The driving force behind this reaction is the formation of the weak acid H_2S, much of which evolves as a gas. The reaction in the case of zinc sulfide is

$$ZnS(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2S(aq)$$

EXAMPLE 15.10

Write balanced equations to explain why each of the following precipitates dissolves in strong acid: $Al(OH)_3$, $CaCO_3$ and CoS

SOLUTION

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O$$
$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2CO_3(aq)$$
$$CoS(s) + 2H^+(aq) \longrightarrow Co^{2+}(aq) + H_2S(aq)$$

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Complex Formation

Ammonia and sodium hydroxide are commonly used to dissolve precipitates containing a cation that forms a stable complex with NH_3 or OH^- (Table 15.3). The reactions with zinc hydroxide are typical:

$$Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow Zn(NH_3)_4^{2+}(aq) + 2OH^-(aq)$$
$$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$$

The equilibrium constant for the solubility reaction is readily calculated. Consider, for example, the reaction by which zinc hydroxide dissolves in ammonia. Again, imagine that the reaction occurs in two steps:

$$Zn(OH)_2(s) \rightleftharpoons \cancel{Zn^{2+}}(aq) + 2OH^-(aq) \qquad K_{sp}\ Zn(OH)_2$$
$$\cancel{Zn^{2+}}(aq) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq) \qquad K_f\ Zn(NH_3)_4^{2+}$$
$$Zn(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq) + 2OH^-(aq)$$

Applying the rule of multiple equilibria,

$$K = K_{sp}\ Zn(OH)_2 \times K_f\ Zn(NH_3)_4^{2+} = (4 \times 10^{-17})(3.6 \times 10^8) = 1 \times 10^{-8}$$

In general, for any reaction of this type

$$K = K_{sp} \times K_f$$

where K_{sp} is the solubility product constant of the solid and K_f is the formation constant of the complex.

$Mg(OH)_2$ cannot be dissolved by NH_3 or NaOH. Explain.

Table 15.3 Complexes of Cations with NH_3 and OH^-

Cation	NH_3 Complex	OH^- Complex
Ag^+	$Ag(NH_3)_2^+$	—
Cu^{2+}	$Cu(NH_3)_4^{2+}$ (blue)	—
Cd^{2+}	$Cd(NH_3)_4^{2+}$	—
Sn^{4+}	—	$Sn(OH)_6^{2-}$
Sb^{3+}	—	$Sb(OH)_4^-$
Al^{3+}	—	$Al(OH)_4^-$
Ni^{2+}	$Ni(NH_3)_6^{2+}$ (blue)	—
Zn^{2+}	$Zn(NH_3)_4^{2+}$	$Zn(OH)_4^{2-}$

EXAMPLE 15.11

Consider the reaction by which silver chloride dissolves in ammonia (Figure 15.8):

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

a Taking $K_{sp}\ AgCl = 1.8 \times 10^{-10}$ and $K_f\ Ag(NH_3)_2^+ = 1.7 \times 10^7$, calculate K for this reaction.

STRATEGY AND SOLUTION

1. Write the equation for the dissolution of AgCl.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_1 = K_{sp}\ \text{for AgCl} = 1.8 \times 10^{-10}$$

2. Write the equation for the reaction between Ag^+ and NH_3.

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_2 = K_f = 1.7 \times 10^7$$

continued

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3. Adding the two equations and applying the rule of multiple equilibria, we obtain

$$AgCl(s) \rightleftharpoons \cancel{Ag^+(aq)} + Cl^-(aq) \qquad K_1 = 1.8 \times 10^{-10}$$
$$\cancel{Ag^+(aq)} + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_2 = 1.7 \times 10^7$$
$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad K = (1.8 \times 10^{-10})(1.7 \times 10^7) = 3.1 \times 10^{-3}$$

b Calculate the number of moles of AgCl that dissolve in one liter of 6.0 *M* NH_3.

ANALYSIS

Information given:	from part (a): equilibrium reaction ($AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$) from part (a): K for the reaction (3.1×10^{-3}) M for NH_3 (6.0)
Asked for:	molar solubility of AgCl in 6 *M* NH_3

STRATEGY

1. Write the K expression.
2. Set up an equilibrium table. Include only the ions. Note that for every mole/L of AgCl that dissolves (x), 2 mol of NH_3 are consumed ($-2x$), one mole of $Ag(NH_3)_2^+$ and one mole of Cl^-($+x$) are formed.
3. Substitute into the K expression and solve for x.

SOLUTION

1. K expression

$$K = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

2. table

	$[NH_3]$	$[Ag(NH_3)_2^+]$	$[Cl^-]$
Original	6.0	0	0
Change	$-2x$	$+x$	$+x$
Equilibrium	$6.0 - 2x$	x	x

3. x (molar solubility)

$$3.1 \times 10^{-3} = \frac{(x)(x)}{(6.0 - 2x)^2} = \frac{x^2}{(6.0 - 2x)^2}$$

Taking the square root of both sides: $0.056 = \dfrac{x}{6.0 - 2x} \longrightarrow x = 0.30\ M$

0.30 moles of AgCl dissolves in one liter of 6.0 *M* NH_3.

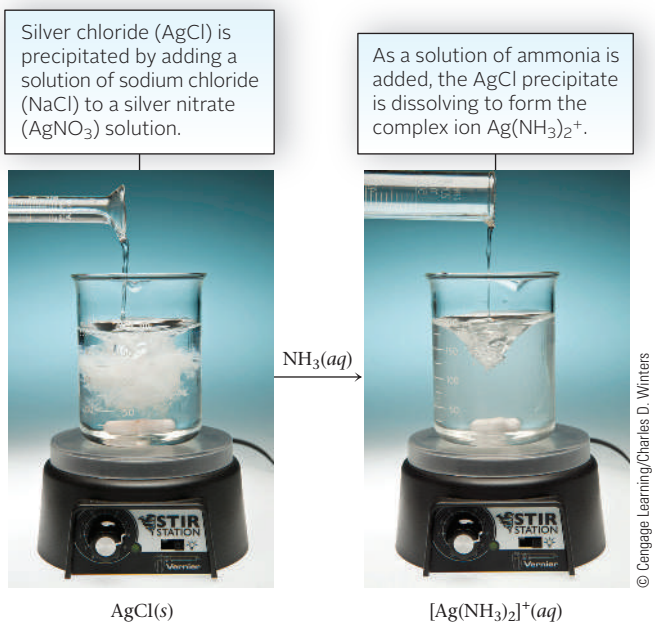

Figure 15.8 Dissolving a precipitate by complex formation.

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EXAMPLE 15.12 CONCEPTUAL

Column A lists a series of ionic solids, all of which are insoluble in water. Match each of these compounds with the appropriate description(s) listed in Column B. Note that more than one description can fit a particular compound.

A	B
$BaSO_4$	(a) $K_{sp} = s^2$
AgCl	(b) $K_{sp} = 4s^3$
$Zn(OH)_2$	(c) more soluble in water than in Na_2SO_4 solution
$CaSO_4$	(d) soluble in strong acid
	(e) soluble in strong base
	(f) soluble in ammonia

SOLUTION

$BaSO_4$ matches with (a) and (c)

AgCl matches with (a) and (f)

$Zn(OH)_2$ matches with (b), (d), (e), (f)

$CaSO_4$ matches with (a) and (c)

CHEMISTRY **BEYOND** THE CLASSROOM

Qualitative Analysis

In the laboratory you will most likely carry out one or more experiments involving the separation and identification of cations present in an "unknown" solution. A scheme of **qualitative analysis** for 21 different cations is shown in Table A. As you can see, the general approach is to take out each group (I, II, III, IV) in succession, using *selective precipitation*.

Group I consists of the only three common cations that form insoluble chlorides: Ag^+, Pb^{2+}, and Hg_2^{2+}. Addition of hydrochloric acid precipitates AgCl, $PbCl_2$, and Hg_2Cl_2. Cations in Groups II, III, and IV remain in solution, since their chlorides are soluble.

Group II consists of six different cations, all of which form very insoluble sulfides (Figure A). These compounds are precipitated selectively by adding hydrogen sulfide, a toxic, foul-smelling gas, at a pH of 0.5. At this rather high H^+ ion concentration, 0.3 *M*, the equilibrium

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

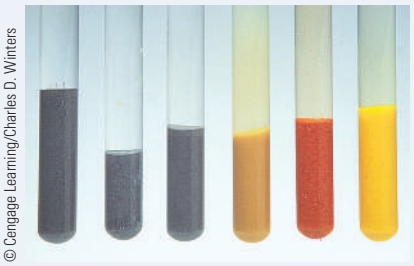
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Figure A Group II sulfides. *(From left to right)* CuS, Bi_2S_3, and HgS are black; CdS is orange-yellow; Sb_2S_3 is brilliant red-orange; and SnS_2 is yellow.

Table A Cation Groups of Qualitative Analysis

Group	Cations	Precipitating Reagent/Conditions
I	Ag^+, Pb^{2+}, Hg_2^{2+}	6 *M* HCl
II	Cu^{2+}, Bi^{3+}, Hg^{2+}, Cd^{2+}, Sn^{4+}, Sb^{3+}	0.1 *M* H_2S at a pH of 0.5
III	Al^{3+}, Cr^{3+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}	0.1 *M* H_2S at a pH of 9
IV	Ba^{2+}, Ca^{2+}, Mg^{2+}; Na^+, K^+	0.2 *M* $(NH_4)_2CO_3$ at a pH of 9.5. No precipitate with Na^+, K^+

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lies far to the left. The concentration of S^{2-} is extremely low, but sufficient to precipitate all the cations in this group, including Cu^{2+}.

$$Cu^{2+}(aq) + H_2S(aq) \longrightarrow CuS(s) + 2H^+(aq) \quad K = 1 \times 10^{16}$$

Group III sulfides are much more difficult to precipitate than those of Group II. Compare, for example, the equilibrium constant for the reaction

$$Mn^{2+}(aq) + H_2S(aq) \rightleftharpoons MnS(s) + 2H^+(aq) \quad K = 2 \times 10^{-7}$$

with that given above for the precipitation of CuS. However, when the solution is made basic (pH = 9), the situation changes. The concentration of H^+ ion drops sharply and, as you would expect from Le Châtelier's principle, the reaction just cited becomes much more spontaneous. Five of the Group III cations precipitate as sulfides. The other two come down as hydroxides, e.g.,

$$Al^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$$

The colors of these precipitates are shown in Figure B.

Group IV cations have soluble chlorides and sulfides, so they are still in solution at this point. The alkaline earth cations (Mg^{2+}, Ca^{2+}, Ba^{2+}) are precipitated as carbonates

$$M^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MCO_3(s) \quad M = Mg, Ca, Ba$$

The alkali metal cations are identified by flame tests (Figure C).

Once the groups are separated from one another, the individual cations in each group must, of course, be separated and identified. This is where things get complicated. A process that might be referred to as "selective dissolving" is often involved. Consider, for example, the precipitate obtained in Group I: $PbCl_2$, AgCl, and Hg_2Cl_2. Of the three solids, lead chloride is by far the most soluble in water. Stirring it with hot water brings it into solution

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

leaving the other two compounds behind. Further treatment with ammonia dissolves silver chloride

$$AgCl(s) + 2NH_3(aq) \longrightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

but not Hg_2Cl_2.

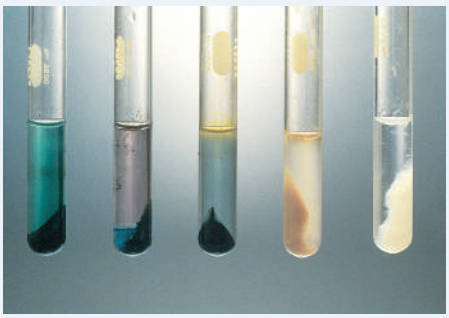

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Figure B Group III sulfides and hydroxides. *(Left)* Five Group III cations precipitate as sulfides. These are NiS, CoS, and FeS (all of which are black), MnS (salmon), and ZnS (white). *(Right)* Two cations precipitate as hydroxides, $Al(OH)_3$ (white) and $Cr(OH)_3$ (gray-green).

James Morganthaler

Ray Boyington/S. Ruven Smith

Figure C Flame tests for Na^+ (yellow) and K^+ (violet). A drop of solution is picked up on a platinum loop and immersed in the flame. The test for K^+ is best done with a filter that hides the strong Na^+ color.

Key Concepts

1. Relate K_f for a complex ion to the ratio of concentration of complex ion to metal ion.
   (Example 15.1, Problems 1–4)
2. Write the K_{sp} expression for any ionic solid.
   (Example 15.2, Problems 5–8)
3. Use the value of K_{sp} to
   - calculate the concentration of one ion knowing that of the other.
     (Example 15.3, Problems 9–14)
   - calculate molar solubility or use molar solubility to calculate the value of K_{sp}.
     (Examples 15.4, 15.5, Problems 15–26)
   - calculate solubility in a solution containing a common ion.
     (Example 15.6, Problems 19, 20)
   - determine whether a precipitate forms.
     (Example 15.7, Problems 27–32)
   - determine which ion will precipitate first in a solution.
     (Example 15.8, Problems 33–38)
4. Calculate K for
   - dissolving a metal oxide in strong acid.
     (Example 15.9, Problem 46)
   - dissolving a precipitate in a complexing agent.
     (Example 15.11, Problems 45, 47–54)
5. Write a balanced net ionic equation to explain why a precipitate dissolves in
   - a strong acid.
     (Example 15.10, Problems 39, 40)
   - NH_3 or OH^-.
     (Example 15.12, Problems 41–44)

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Key Terms

common ion effect
complex ion
formation constant
ion product constant
selective precipitation
solubility product constant

Summary Problem

Consider zinc hydroxide ($K_{sp} = 4 \times 10^{-17}$), commonly used as a protective coating on metals. It can be formed when solutions of zinc nitrate and sodium hydroxide are combined. (Assume volumes are additive in all cases.)

(a) Write the K_{sp} expression for zinc hydroxide.

(b) How many milligrams of NaOH must be added to 125 mL of 0.0120 *M* $Zn(NO_3)_2$ to just start the precipitation of $Zn(OH)_2$? (Ignore OH^- ions from water.)

(c) Will a precipitate form if 10.00 mL of 0.0200 *M* NaOH are added to 250.0 mL of 0.098 *M* $Zn(NO_3)_2$?

(d) How many milligrams of zinc hydroxide are required to prepare 700.0 mL of a saturated $Zn(OH)_2$ solution?

(e) What is the pH of a saturated solution of $Zn(OH)_2$?

(f) Which would precipitate first, $Zn(OH)_2$ or $Al(OH)_3$, when 0.075 mol of NaOH are added to a 0.500-L solution containing 0.0100 mol Zn^{2+} and 0.0100 mol Al^{3+} ions? (K_{sp} of $Al(OH)_3$ is 2×10^{-31}.)

(g) Write equations and calculate *K* for the following reactions:

1. Dissolving $Zn(OH)_2$ in strong acid.
2. Dissolving $Zn(OH)_2$ in strong base.
3. Dissolving $Zn(OH)_2$ in aqueous NH_3 forming $Zn(NH_3)_4^{2+}$.

(h) How many grams of $Zn(OH)_2$ can be dissolved in 2.50 L of 0.166 *M* NaOH? (The complex ion $Zn(OH)_4^{2-}$ is formed.)

Answers

(a) $K_{sp} = [Zn^{2+}][OH^-]^2$
(b) 3×10^{-4} mg
(c) Yes
(d) 0.2 mg
(e) 8.6
(f) $Al(OH)_3$
(g) 1. $Zn(OH)_2(s) + 2H^+(aq) \rightleftharpoons 2H_2O + Zn^{2+}(aq)$ $K = 4 \times 10^{11}$
2. $Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$ $K = 0.01$
3. $Zn(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq) + 2OH^-(aq)$ $K = 1 \times 10^{-8}$
(h) 0.07 g

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

15-1 Complex Ion Equilibria; Formation Constant (K_f)

1. At what concentration of ammonia is
(a) $[Cd^{2+}] = [Cd(NH_3)_4^{2+}]$?
(b) $[Co^{2+}] = [Co(NH_3)_6^{2+}]$?

2. At what concentration of cyanide ion is
(a) $[Cd^{2+}] = 10^{-8} \times [Cd(CN)_4^{2-}]$?
(b) $[Fe^{2+}] = 10^{-20} \times [Fe(CN)_6^{4-}]$?

3. Consider the complex ion $[Ni(en)_3]^{2+}$. Its K_f is 2.1×10^{18}. At what concentration of *en* is 67% of the Ni^{2+} converted to $[Ni(en)_3]^{2+}$?

4. Consider the complex ion $Hg(Cl)_4^{2-}$. Its K_f value is 1.2×10^{15}. At what concentration of Cl^- is 58% of the Hg^{2+} converted to $Hg(Cl)_4^{2-}$?

15-2 Solubility; Solubility Product Constant (K_{sp})

Expression for K_{sp}

5. Write the equilibrium equation and the K_{sp} expression for each of the following:
(a) AgBr (b) $Ca(OH)_2$
(c) Co_2S_3 (d) $Fe_3(PO_4)_2$

6. Write the equilibrium equation and the K_{sp} expression for each of the following.
(a) AgCl (b) $Al_2(CO_3)_3$
(c) MnS_2 (d) $Mg(OH)_2$

7. Write the equilibrium equations on which the following K_{sp} expressions are based.
(a) $[Hg_2^{2+}]\,[Cl^-]^2$ (b) $[Pb^{2+}]\,[CrO_4^{2-}]$
(c) $[Mn^{4+}]\,[O^{2-}]^2$ (d) $[Al^{3+}]^2\,[S^{2-}]^3$

8. Write the equilibrium equations on which the following K_{sp} expressions are based.
(a) $[Pb^{4+}]\,[O^{2-}]^2$ (b) $[Hg^{2+}]^3\,[PO_4^{3-}]^2$
(c) $[Ni^{3+}]\,[OH^-]^3$ (d) $[Ag^+]^2\,[SO_4^{2-}]$

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K_{sp} and the Equilibrium Concentration of Ions

9. Given K_{sp} and the equilibrium concentration of one ion, calculate the equilibrium concentration of the other ion.
(a) barium bromate: $K_{sp} = 2.4 \times 10^{-4}$; $[Ba^{2+}] = 1.9 \times 10^{-2}$
(b) cadmium(II) phosphate: $K_{sp} = 2.5 \times 10^{-33}$; $[Cd^{2+}] = 8.2 \times 10^{-6}$
(c) iron(II) fluoride: $K_{sp} = 2.4 \times 10^{-6}$; $[F^-] = 3.7 \times 10^{-3}$

10. Follow the directions for Question 9 for the following compounds:
(a) lithium phosphate: $K_{sp} = 3.2 \times 10^{-9}$; $[PO_4^{3-}] = 7.5 \times 10^{-4}\ M$
(b) silver nitrite: $K_{sp} = 6.0 \times 10^{-4}$; $[Ag^+] = 0.025\ M$
(c) tin(II) hydroxide: $K_{sp} = 1.4 \times 10^{-28}$; pH = 9.35

11. Calculate the concentration of the following ions in equilibrium with $1.63 \times 10^{-3}\ M\ Ba^{2+}$.
(a) SO_4^{2-} (b) F^- (c) CO_3^{2-}

12. Calculate the concentration of the following ions in equilibrium with $1.24 \times 10^{-4}\ M\ Ca^{2+}$.
(a) CO_3^{2-} (b) OH^- (c) PO_4^{3-}

13. Fill in the blanks in the following table.

	Compound	[cation]	[anion]	K_{sp}
(a)	$CoCO_3$	_____	_____	1×10^{-10}
(b)	LaF_3	_____	7×10^{-6}	2×10^{-19}
(c)	$Ba_3(PO_4)_2$	4.2×10^{-8}	_____	6×10^{-39}

14. Fill in the blanks in the following table.

	Compound	[cation]	[anion]	K_{sp}
(a)	BaC_2O_4	_____	_____	1.6×10^{-6}
(b)	$Cr(OH)_3$	2.7×10^{-8}	_____	6.3×10^{-31}
(c)	$Pb_3(PO_4)_2$	_____	8×10^{-6}	1×10^{-54}

K_{sp} and Solubility

15. Calculate the molar solubility of the following compounds:
(a) calcium iodate: $K_{sp} = 6.5 \times 10^{-6}$
(b) cadmium(III) phosphate: $K_{sp} = 2.5 \times 10^{-33}$
(c) silver oxalate: $K_{sp} = 5.4 \times 10^{-12}$

16. Calculate the molar solubility of the following compounds.
(a) MgF_2 (b) $Fe(OH)_3$ (c) $Mg_3(PO_4)_2$

17. Calculate the K_{sp} of the following compounds, given their molar solubilities.
(a) TlBr: 1.9×10^{-3}
(b) $Ni(OH)_2$: 5.2×10^{-6}
(c) $Cu_3(AsO_4)_2$: 3.7×10^{-8}

18. Calculate the K_{sp} of the following compounds, given their molar solubilities.
(a) MgC_2O_4, $9.2 \times 10^{-3}\ M$
(b) $Mn(OH)_2$, $3.5 \times 10^{-5}\ M$
(c) $Cd_3(PO_4)_2$, $1.5 \times 10^{-7}\ M$

19. Calculate the solubility (in grams per liter) of silver chloride in the following.
(a) pure water
(b) $0.025\ M\ BaCl_2$
(c) $0.17\ M\ AgNO_3$

20. Calculate the solubility (in grams per liter) of magnesium hydroxide in the following.
(a) pure water
(b) $0.041\ M\ Ba(OH)_2$
(c) $0.0050\ M\ MgCl_2$

21. Copper(I) chloride, CuCl, is the starting material for the fungicide copper oxychloride. At 25°C, a saturated solution of CuCl is prepared by dissolving 10.1 mg of CuCl in 0.250 L of water. What is the K_{sp} for copper(I) chloride?

22. A saturated solution of $Ni(OH)_2$ can be prepared by dissolving 0.239 mg of $Ni(OH)_2$ in water to make 500.0 mL of solution. What is the K_{sp} for $Ni(OH)_2$?

23. One gram of $PbCl_2$ is dissolved in 1.0 L of hot water. When the solution is cooled to 25°C, will some of the $PbCl_2$ crystallize out? If so, how much?

24. K_{sp} for $CaSO_4$ at 100°C is estimated to be 1.6×10^{-5}. At 25°C, 0.915 g of $CaSO_4$ is added to one liter of water.
(a) Will all the $CaSO_4$ dissolve?
(b) If the solution is heated to 100°C, will all the $CaSO_4$ dissolve?

25. At 25°C, 100.0 mL of a $Ba(OH)_2$ solution is prepared by dissolving $Ba(OH)_2$ in an alkaline solution. At equilibrium, the saturated solution has $0.138\ M\ Ba^{2+}$ and a pH of 13.28. Estimate K_{sp} for $Ba(OH)_2$.

26. At 25°C, 10.24 mg of $Cr(OH)_2$ are dissolved in enough water to make 125 mL of solution. When equilibrium is established, the solution has a pH of 8.49. Estimate K_{sp} for $Cr(OH)_2$.

15-3 Precipitate Formation

K_{sp} and Precipitation

27. Calcium nitrate is added to a sodium sulfate solution that is $0.0150\ M$.
(a) At what concentration of Ca^{2+} does a precipitate first start to form?
(b) Enough $Ca(NO_3)_2$ is added to make $[Ca^{2+}] = 0.0075\ M$. What percentage of the original sulfate ion has precipitated?

28. Cadmium(II) chloride is added to a solution of potassium hydroxide with a pH of 9.62. (K_{sp} $Cd(OH)_2 = 2.5 \times 10^{-14}$)
(a) At what concentration of Cd^{2+} does a precipitate first start to form?
(b) Enough cadmium(II) chloride is added to make $[Cd^{2+}] = 0.0013\ M$. What is the pH of the resulting solution?
(c) What percentage of the original hydroxide ion is left in solution?

29. Water from a well is found to contain 3.0 mg of calcium ion per liter. If 0.50 mg of sodium sulfate is added to one liter of the well water without changing its volume, will a precipitate form? What should $[SO_4^{2-}]$ be to just start precipitation?

30. Silver(I) sulfate ($K_{sp} = 1.2 \times 10^{-5}$) is used in the electroplating of silver. A 1.0-L solution is prepared by mixing 15 g of silver nitrate with 20 g (2 significant figures) of potassium sulfate. Will a precipitate form? At what $[Ag^+]$ concentration will precipitation (if any) start?

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31. A solution is prepared by mixing 13.00 mL of 0.0021 *M* aqueous $Hg_2(NO_3)_2$ with 25.0 mL of 0.015 *M* HCl. Assume that volumes are additive.
(**a**) Will precipitation occur?
(**b**) Calculate $[Hg_2^{2+}]$, $[Cl^-]$, and $[NO_3^-]$ after equilibrium is established.

32. A solution is prepared by mixing 45.00 mL of 0.022 *M* $AgNO_3$ with 13.00 mL of 0.0014 *M* Na_2CO_3. Assume that volumes are additive.
(**a**) Will precipitation occur?
(**b**) Calculate $[Ag^+]$, $[CO_3^{2-}]$, $[Na^+]$, and $[NO_3^-]$ after equilibrium is established.

Selective Precipitation

33. A solution is 0.047 *M* in both NaF and Na_2CO_3. Solid strontium nitrate, $Sr(NO_3)_2$, is added without changing the volume of the solution.
(**a**) Which salt, $SrCO_3$ or SrF_2 ($K_{sp} = 4.3 \times 10^{-9}$), will precipitate first?
(**b**) What is $[Sr^{2+}]$ when the salt in (a) first begins to precipitate?

34. Solid lead nitrate is added to a solution that is 0.020 *M* in OH^- and SO_4^{2-}. Addition of the lead nitrate does not change the volume of the solution.
(**a**) Which compound, $PbSO_4$ or $Pb(OH)_2$ ($K_{sp} = 2.8 \times 10^{-16}$), will precipitate first?
(**b**) What is the pH of the solution when $PbSO_4$ first starts to precipitate?

35. A solution is made up by adding 0.632 g of barium nitrate and 0.920 g of lanthanum nitrate, $La(NO_3)_3$, to enough water to make 0.500 L of solution. Solid sodium iodate, $NaIO_3$, is added (without volume change) to the solution.
(**a**) Which salt will precipitate first? $La(IO_3)_3$ ($K_{sp} = 7.50 \times 10^{-12}$) or $BaIO_3$ ($K_{sp} = 4.0 \times 10^{-9}$)?
(**b**) What is $[IO_3^-]$ when the salt in (a) first begins to precipitate?

36. A solution is made up by adding 0.839 g of silver(I) nitrate and 1.024 g of lead(II) nitrate to enough water to make 492 mL of solution. Solid sodium chromate, Na_2CrO_4, is added without changing the volume of the solution.
(**a**) Which salt will precipitate first, Ag_2CrO_4 or $PbCrO_4$?
(**b**) What is the concentration of the chromate ion when the first salt starts to precipitate?

37. A solution is made up by mixing 125 mL of 0.100 *M* $AuNO_3$ and 225 mL of 0.049 *M* $AgNO_3$. Twenty-five mL of a 0.0100 *M* solution of HCl is then added. K_{sp} of AuCl = 2.0×10^{-13}. When equilibrium is established, will there be
- no precipitate?
- a precipitate of AuCl only?
- a precipitate of AgCl only?
- a precipitate of both AgCl and AuCl?

38. To a beaker with 500.0 mL of water are added 95 mg of $Ba(NO_3)_2$, 95 mg of $Ca(NO_3)_2$, and 100.0 mg of Na_2CO_3. After equilibrium is established, will there be
- no precipitate?
- a precipitate of $BaCO_3$ only?
- a precipitate of $CaCO_3$ only?
- a precipitate of both $CaCO_3$ and $BaCO_3$?

Assume that the volume of the solution is still 500.0 mL after the addition of the salts.

15-4 Dissolving Precipitates

39. Write net ionic equations for the reaction of H^+ with
(**a**) Fe_2S_3
(**b**) $Mg(OH)_2$
(**c**) $MgCO_3$
(**d**) $Pt(NH_3)_4^{2+}$
(**e**) Hg_2I_2

40. Write net ionic equations for the reactions of each of the following compounds with a strong acid.
(**a**) CaF_2
(**b**) $CuCO_3$
(**c**) $Ti(OH)_3$
(**d**) $Sn(OH)_6^{2-}$
(**e**) $Cd(NH_3)_4^{2+}$

41. Write a net ionic equation for the reaction with aqueous NH_3 in which
(**a**) Pt^{2+} forms a complex ion.
(**b**) Ag^+ forms a precipitate.
(**c**) $Ni(OH)_3$ dissolves.

42. Write a net ionic equation for the reaction with ammonia by which
(**a**) $Cu(OH)_2$ dissolves.
(**b**) Cd^{2+} forms a complex ion.
(**c**) Pb^{2+} forms a precipitate.

43. Write a net ionic equation for the reaction with OH^- by which
(**a**) Sb^{3+} forms a precipitate.
(**b**) antimony(III) hydroxide dissolves when more OH^- is added.
(**c**) Sb^{3+} forms a complex ion.

44. Write a net ionic equation for the reaction with Al^{3+} by which
(**a**) a complex ion forms when it reacts with OH^-.
(**b**) a precipitate forms when it reacts with the phosphate ion.
(**c**) the precipitate formed with OH^- is dissolved by a strong acid.

Solution Equilibria

45. Write an overall net ionic equation and calculate *K* for the reaction where $CoCO_3$ ($K_{sp} = 1.0 \times 10^{-10}$) is dissolved by $Na_2C_2O_4$ (Na_2ox) to form $[Coox_3]^{4-}$ ($K_f = 5 \times 10^9$).

46. Write an overall net ionic equation and calculate *K* for the reaction where $Co(OH)_2$ ($K_{sp} = 2 \times 10^{-16}$) is dissolved by HCl.

47. Consider the reaction

$$AgC_2H_3O_2(s) + Cl^-(aq) \longrightarrow AgCl(s) + C_2H_3O_2^-(aq)$$

(**a**) Calculate *K* for the reaction.
(**b**) Will more AgCl precipitate if H^+ ions are added?

48. Consider the reaction

$$BaF_2(s) + SO_4^{2-}(aq) \rightleftharpoons BaSO_4(s) + 2F^-(aq)$$

(**a**) Calculate *K* for the reaction.
(**b**) Will $BaSO_4$ precipitate if Na_2SO_4 is added to a saturated solution of BaF_2?

49. Aluminum hydroxide reacts with an excess of hydroxide ions to form the complex ion $Al(OH)_4^-$.
(**a**) Write an equation for this reaction.
(**b**) Calculate *K*.
(**c**) Determine the solubility of $Al(OH)_3$ (in mol/L) at pH 12.0.

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50. Consider the reaction

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) + 2OH^-(aq)$$

(a) Calculate K given that for $Cu(OH)_2$ $K_{sp} = 2 \times 10^{-19}$ and for $Cu(NH_3)_4^{2+}$ $K_f = 2 \times 10^{12}$.
(b) Determine the solubility of $Cu(OH)_2$ (in mol/L) in 4.5 M NH_3.

51. Calculate the molar solubility of gold(I) chloride ($K_{sp} = 2.0 \times 10^{-13}$) in 0.10 M NaCN. The complex ion formed is $[Au(CN)_2]^-$ with $K_f = 2 \times 10^{38}$. Ignore any other competing equilibra.

52. Calculate the molar solubility of $PbCl_2$ in 0.2 M NaOH. The complex formed is $Pb(OH)_3^-$ ($K_f = 3.8 \times 10^{14}$). Ignore any other competing equilibria.

53. For the reaction

$$CdC_2O_4(s) + 4NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq) + C_2O_4^{2-}(aq)$$

(a) calculate K. (K_{sp} for CdC_2O_4 is 1.5×10^{-8}.)
(b) calculate $[NH_3]$ at equilibrium when 2.00 g of CdC_2O_4 are dissolved in 1.00 L of solution.

54. For the reaction

$$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$$

(a) Calculate K for the reaction.
(b) Find $[OH^-]$ when 10.0 g of $Zn(OH)_2$ are dissolved in 1.0 L of solution.

Unclassified

55. What are the concentrations of Cu^{2+}, NH_3, and $Cu(NH_3)_4^{2+}$ at equilibrium when 18.8 g of $Cu(NO_3)_2$ are added to 1.0 L of a 0.400 M solution of aqueous ammonia? Assume that the reaction goes to completion and forms $Cu(NH_3)_4^{2+}$.

56. For the system

$$\text{hemoglobin}\cdot O_2(aq) + CO(g) \rightleftharpoons \text{hemoglobin}\cdot CO(aq) + O_2(g)$$

$K = 2.0 \times 10^2$. What must be the ratio of P_{CO}/P_{O_2} if 12.0% of the hemoglobin in the bloodstream is converted to the CO complex?

57. Calcium ions in blood trigger clotting. To prevent that in donated blood, sodium oxalate, $Na_2C_2O_4$, is added to remove calcium ions according to the following equation.

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

Blood contains about 0.10 mg Ca^{2+}/mL. If a 250.0-mL sample of donated blood is treated with an equal volume of 0.160 M $Na_2C_2O_4$, estimate $[Ca^{2+}]$ after precipitation. (K_{sp} $CaC_2O_4 = 4 \times 10^{-9}$)

58. A saturated solution of lithium carbonate (Li_2CO_3) freezes at −0.33°C. Estimate K_{sp} for Li_2CO_3. Assume complete dissociation and a density for the solution of 1.0 g/mL.

59. A town adds 2.0 ppm of F^- ion to fluoridate its water supply. (Fluoridation of water reduces the incidence of dental caries). If the concentration of Ca^{2+} in the water is 3.5×10^{-4} M, will a precipitate of CaF_2 form when the water is fluoridated?

60. Consider the following hypothetical dissociation:

$$AB_3(s) \rightleftharpoons A^{3+}(aq) + 3B^-(aq) \qquad \Delta H < 0$$

What effect will each of the following have on the position of equilibrium?
(a) addition of $A(NO_3)_3$
(b) increase in temperature
(c) adding Na^+, forming NaB

61. When 25.0 mL of 0.500 M iron(II) sulfate is combined with 35.0 mL of 0.332 M barium hydroxide, two different precipitates are formed.
(a) Write a net ionic equation for the reaction that takes place.
(b) Estimate the mass of the precipitates formed.
(c) What are the equilibrium concentrations of the ions in solution?

62. Consider a 2.0-L aqueous solution of 4.17 M NH_3, where 21.0 g of NH_4Cl are dissolved. To this solution, 4.8 g of $CaCl_2$ are added.
(a) What is $[OH^-]$ before $CaCl_2$ is added?
(b) Will a precipitate form?
(c) What is $[Ca^{2+}]$ after equilibrium is established?

63. Marble is almost pure $CaCO_3$. Acid rain has a devastating effect on marble statuary left outdoors. Assume that the reaction which occurs is

$$CaCO_3(s) + H^+(aq) \longrightarrow Ca^{2+}(aq) + HCO_3^-(aq)$$

Neglecting all other competing equilibria and using Tables 15.1 and 13.2, calculate
(a) K for the reaction.
(b) the molar solubility of $CaCO_3$ in pure water.
(c) the molar solubility of $CaCO_3$ in acid rainwater with a pH of 4.00.

64. Consider the following solubility data for calcium oxalate (CaC_2O_4):

$$K_{sp} \text{ at } 25°C = 4 \times 10^{-9}$$
$$K_{sp} \text{ at } 95°C = 1 \times 10^{-8}$$

Five hundred mL of a saturated solution are prepared at 95°C. How many milligrams of CaC_2O_4 will precipitate when the solution is cooled to 25°C? (Assume that supersaturation does not take place.)

Conceptual Problems

65. Consider three complexes of Ag^+ and their formation constants, K_f.

Complex Ion	K_f
$Ag(NH_3)_2^+$	1.6×10^7
$Ag(CN)_2^-$	5.6×10^{18}
$AgBr_2^-$	1.3×10^7

Which statements are true?
(a) $Ag(NH_3)_2^+$ is more stable than $Ag(CN)_2^-$.
(b) Adding a strong acid (HNO_3) to a solution that is 0.010 M in $Ag(NH_3)_2^+$ will tend to dissociate the complex ion into Ag^+ and NH_4^+.
(c) Adding a strong acid (HNO_3) to a solution that is 0.010 M in $AgBr_2^-$ will tend to dissociate the complex ion into Ag^+ and Br^-.
(d) To dissolve AgI, one can add either NaCN or HCN as a source of the cyanide ion. Fewer moles of NaCN would be required.
(e) Solution A is 0.10 M in Br^- and contains the complex ion $AgBr_2^-$. Solution B is 0.10 M in CN^- and contains the complex ion $Ag(CN)_2^-$. Solution B will have more particles of complex ion per particle of Ag^+ than solution A.

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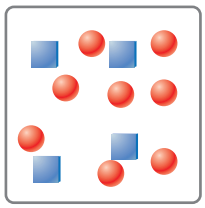
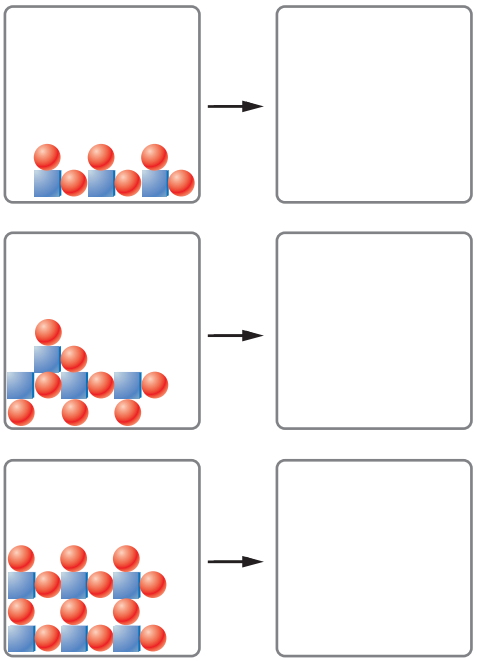
66. The box below represents one liter of a saturated solution of the species  , where squares represent the cation and circles represent the anion. Water molecules, though present, are not shown.



Complete the next three figures below by filling one-liter boxes to the right of the arrow, showing the state of the ions after water is added to form saturated solutions. The species represented to the left of the arrow is the solid form of the ions represented above. Do not show the water molecules.



67. Consider a saturated solution of $BaCO_3$ at 75°C. Answer the following questions using **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or write **MI** if *more information* is required.

(**a**) At equilibrium $[Ba^{2+}]$ _____ $[CO_3^{2-}]$.

(**b**) The temperature is increased to 200°C. The K_{sp} at 75°C _____ K_{sp} at 200°C.

(**c**) A solution of $NaNO_3$ is added. $[Ba^{2+}]$ before $NaNO_3$ is added _____ $[Ba^{2+}]$ after $NaNO_3$ is added.

(**d**) Solid Na_2CO_3 is added. After equilibrium is reestablished, $[Ba^{2+}]$ _____ $[CO_3^{2-}]$.

68. Which of the following statements are true?

(**a**) For an insoluble metallic salt, K_{sp} is always less than 1.

(**b**) More $PbCl_2$ can be dissolved at 100°C than at 25°C. One can conclude that dissolving $PbCl_2$ is an exothermic process.

(**c**) When strips of copper metal are added to a saturated solution of $Cu(OH)_2$, a precipitate of $Cu(OH)_2$ can be expected to form because of the common ion effect.

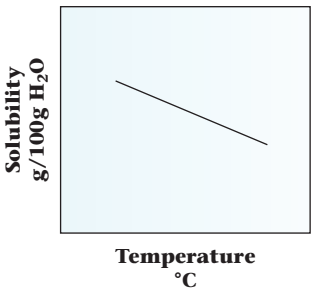
69. Consider the insoluble salts JQ, K_2R, L_2S_3, MT_2, and NU_3. They are formed from the metal ions J^+, K^+, L^{3+}, M^{2+}, and N^{3+} and the nonmetal ions Q^-, R^{2-}, S^{2-}, T^-, and U^-. All the salts have the same K_{sp}, 1×10^{-10}, at 25°C.

(**a**) Which salt has the highest molar solubility?

(**b**) Does the salt with the highest molar solubility have the highest solubility in g salt/100 g water?

(**c**) Can the solubility of each salt in g/100 g water be determined from the information given? If yes, calculate the solubility of each salt in g/100 g water. If no, why not?

70. Consider the following graph of the solubility of a compound X versus temperature.



Is dissolving X an exothermic process?

71. Consider the equilibrium curve for AgCl shown below. Which of the following statements about a solution at point A on the curve are true?

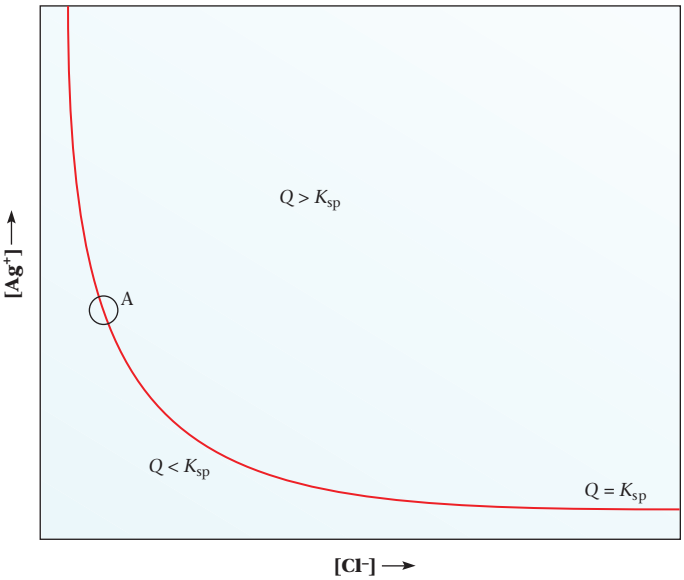
(**a**) The solution is saturated and at equilibrium.

(**b**) Addition of NaCl increases the concentration of Cl^- in solution.

(**c**) Addition of NaCl increases the concentration of Ag^+ in solution.

(**d**) Addition of Ag^+ results in the precipitation of AgCl.

(**e**) Addition of solid $NaNO_3$ to the solution without change in volume does not change $[Ag^+]$ or $[Cl^-]$.



72. Dissolving $CaCO_3$ is an endothermic reaction. The following five graphs represent an experiment done on $CaCO_3$. Match the experiment to the graph.

(**a**) HCl is added.

(**b**) The temperature is increased.

(**c**) $CaCl_2$ is added.

(**d**) NaCl is added.

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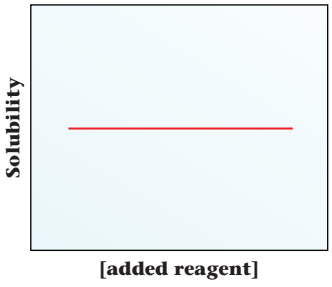

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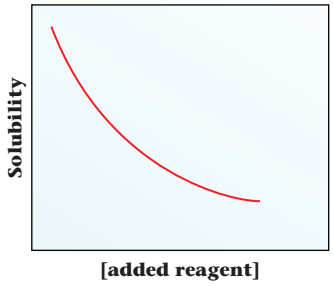

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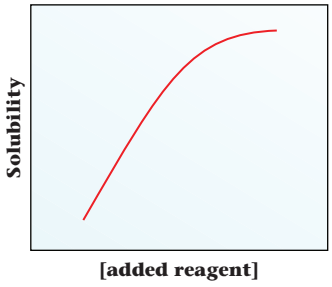

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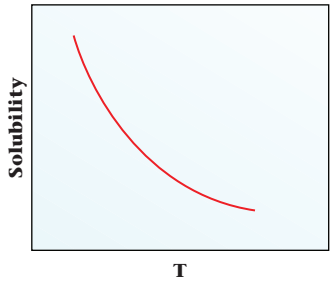

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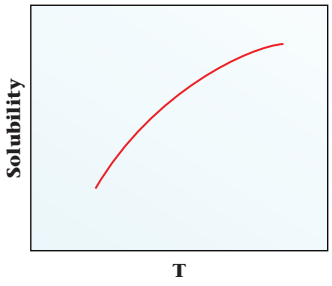

Challenge Problems

73. Insoluble hydroxides such as $Zn(OH)_2$ are better dissolved in solutions that are slightly acidic, such as aqueous HCN. Find the molar solubility of $Ca(OH)_2$ in 0.15 *M* HCN and compare it with the solubility in water: (*Hint:* Find *K* for the following reaction.)

$$Zn(OH)_2(s) + 2HCN(aq) \rightleftharpoons Zn^{2+}(aq) + 2CN^-(aq) + 2H_2O$$

74. What is the solubility of CaF_2 in a buffer solution containing 0.30 *M* $HCHO_2$ and 0.20 *M* $NaCHO_2$? *Hint:* Consider the equation

$$CaF_2(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + 2HF(aq)$$

and solve the equilibrium problem.

75. What is $[Br^-]$ just as AgCl begins to precipitate when 1.5 *M* $AgNO_3$ is slowly added to a solution containing 0.050 *M* Cl^- and 0.050 *M* Br^-?

76. The concentrations of various cations in seawater, in moles per liter, are

Ion	Na^+	Mg^{2+}	Ca^{2+}	Al^{3+}	Fe^{3+}
Molarity (*M*)	0.46	0.056	0.01	4×10^{-7}	2×10^{-7}

(a) At what $[OH^-]$ does $Mg(OH)_2$ start to precipitate?
(b) At this concentration, will any of the other ions precipitate?
(c) If enough OH^- is added to precipitate 50% of the Mg^{2+}, what percentage of each of the other ions will precipitate?
(d) Under the conditions in (c), what mass of precipitate will be obtained from one liter of seawater?

77. Consider the equilibrium

$$Zn(NH_3)_4^{2+}(aq) + 4OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq) + 4NH_3(aq)$$

(a) Calculate *K* for this reaction.
(b) What is the ratio $[Zn(NH_3)_4^{2+}]/[Zn(OH)_4^{2-}]$ in a solution 1.0 *M* in NH_3?

78. Calculate *K* for the following reaction:

$$Cd(NH_3)_4^{2+}(aq) + 4H^+(aq) + 2F^-(aq) \rightleftharpoons CdF_2(s) + 4NH_4^+(aq)$$

K_{sp} for CdF_2 is 6.4×10^{-3}.

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