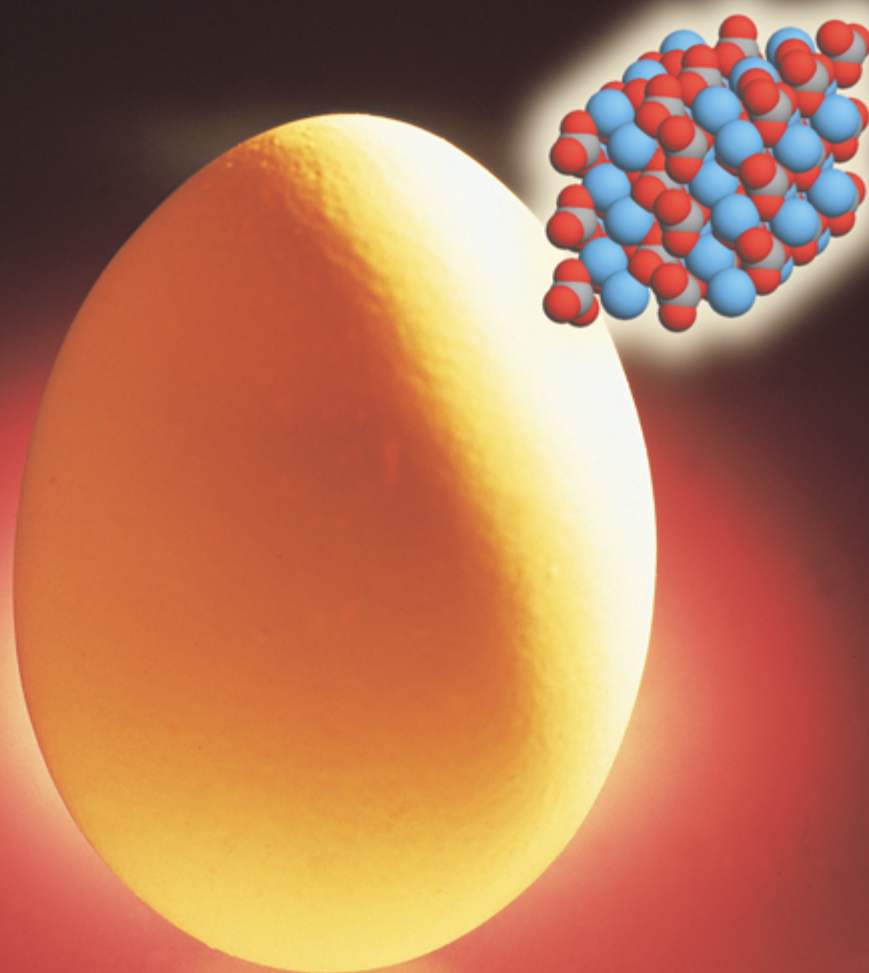


20

Ionic Equilibria III: The Solubility Product Principle



OUTLINE

- | | |
|--|---|
| 20-1 Solubility Product Constants | 20-4 Fractional Precipitation |
| 20-2 Determination of Solubility Product Constants | 20-5 Simultaneous Equilibria Involving Slightly Soluble Compounds |
| 20-3 Uses of Solubility Product Constants | 20-6 Dissolving Precipitates |

OBJECTIVES

After you have studied this chapter, you should be able to

- Write solubility product constant expressions
- Explain how K_{sp} 's are determined
- Use K_{sp} 's in chemical calculations
- Recognize some common, slightly soluble compounds
- Describe fractional precipitation and how it can be used to separate ions
- Explain how simultaneous equilibria can be used to control solubility
- Describe some methods for dissolving precipitates



In a process known as biom mineralization, some organisms produce solids that also occur naturally as minerals. The calcium carbonate, CaCO_3 , in an eggshell has the same crystal structure as in the mineral calcite.

So far we have discussed mainly compounds that are quite soluble in water. Although most compounds dissolve in water to some extent, many are so slightly soluble that they are called “insoluble compounds.” We shall now consider those that are only very slightly soluble. As a rough rule of thumb, compounds that dissolve in water to the extent of 0.020 mole/liter or more are classified as soluble. Refer to the solubility guidelines (Table 4-8) as necessary.

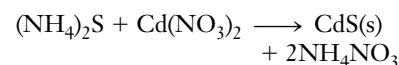
Slightly soluble compounds are important in many natural phenomena. Our bones and teeth are mostly calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, a slightly soluble compound. Also, many natural deposits of $\text{Ca}_3(\text{PO}_4)_2$ rock are mined and converted into agricultural fertilizer. Limestone caves have been formed by acidic water slowly dissolving away calcium carbonate, CaCO_3 . Sinkholes are created when acidic water dissolves away most of the underlying CaCO_3 . The remaining limestone can no longer support the weight above it, so it collapses, and a sinkhole is formed.

20-1 SOLUBILITY PRODUCT CONSTANTS

Suppose we add one gram of solid barium sulfate, BaSO_4 , to 1.0 liter of water at 25°C and stir until the solution is saturated. Very little BaSO_4 dissolves. Careful measurements of conductivity show that one liter of a saturated solution of barium sulfate contains only 0.0025 gram of BaSO_4 , no matter how much more BaSO_4 is added. The BaSO_4 that does dissolve is completely dissociated into its constituent ions.

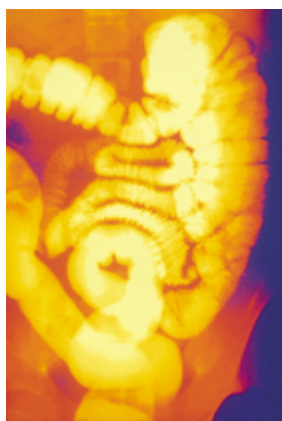


Pouring ammonium sulfide solution into a solution of cadmium nitrate gives a precipitate of cadmium sulfide.



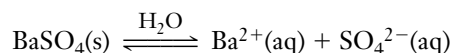
Cadmium sulfide is used as a pigment in artists' oil-based paints.

Barium sulfate is the “insoluble” substance taken orally before stomach X-rays are made because the barium atoms absorb X-rays well. Even though barium ions are quite toxic, barium sulfate can still be taken orally without danger. The compound is so insoluble that it passes through the digestive system essentially unchanged.



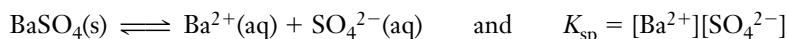
An X-ray photo of the gastrointestinal tract. The barium ions in BaSO_4 absorb X-radiation well.

The dissolving process of ions going into solution. During precipitation, ions are producing more solid as the ions leave the solution. For a saturated solution, the dissolving and precipitation rates are equal. For the very slightly soluble salts discussed in this chapter, the ion concentrations are very low compared with the concentration in this illustration.



(We usually omit H_2O over the arrows in equations like the preceding one.)

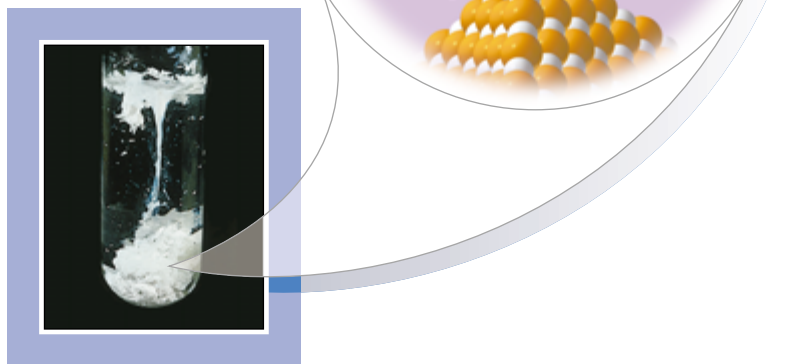
In equilibria that involve slightly soluble compounds in water, the equilibrium constant is called a **solubility product constant**, K_{sp} . The activity of the solid BaSO_4 is one (Section 17-11, Heterogeneous Equilibrium). Hence, the concentration of the solid is not included in the equilibrium constant expression. For a saturated solution of BaSO_4 in contact with solid BaSO_4 , we write



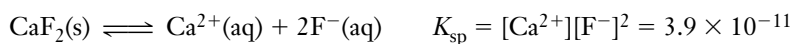
The solubility product constant for BaSO_4 is the product of the concentrations of its constituent ions in a saturated solution.

In general, the **solubility product expression** for a compound is the product of the concentrations of its constituent ions, each raised to the power that corresponds to the number of ions in one formula unit of the compound. The quantity is constant at constant temperature for a saturated solution of the compound. This statement is the **solubility product principle**.

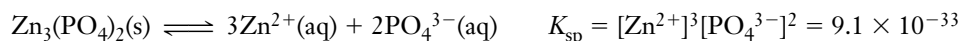
The existence of a substance in the solid state is indicated several ways. For example, $\text{BaSO}_4(\text{s})$, $\overline{\text{BaSO}_4}$, and $\text{BaSO}_4\downarrow$ are sometimes used to represent solid BaSO_4 . In this text we use the $\overline{(\text{s})}$ notation for formulas of solid substances in equilibrium with their saturated aqueous solutions.



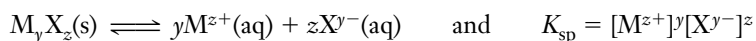
Consider dissolving slightly soluble calcium fluoride, CaF_2 , in H_2O .



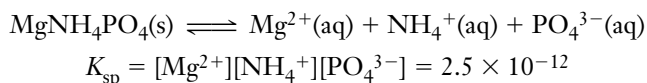
The very small amount of solid zinc phosphate, $\text{Zn}_3(\text{PO}_4)_2$, that dissolves in water gives three zinc ions and two phosphate ions per formula unit.



Generally, we may represent the dissolution of a slightly soluble compound and its K_{sp} expression as




In some cases a compound contains more than two kinds of ions. Dissolution of the slightly soluble compound magnesium ammonium phosphate, MgNH_4PO_4 , in water and its solubility product expression are represented as




We often shorten the term “solubility product constant” to “solubility product.” Thus, the solubility products for barium sulfate, BaSO_4 , and for calcium fluoride, CaF_2 , are written as



The **molar solubility** of a compound is the number of moles that dissolve to give one liter of saturated solution.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 19.4, Solubility Product Constant, and Screen 19.5, Determining K_{sp} .

 **Problem-Solving Tip:** *Names and Formulas of Several Ions Must Be Recognized*

To write the required equations for the dissolution and dissociation of salts, you must recognize the names and formulas of common, stable ions that are often present. Table 2-3 contains the names and formulas of several ions; since then you have learned others. Review these names and formulas carefully (formulas of ions must include their charges). Many of the ions you need to know are present in the salts listed in Appendix H.



(a)



(b)

Barium sulfate, BaSO_4 , occurs in the mineral barite (a). Calcium fluoride, CaF_2 , occurs in the mineral fluorite (b). Both are clear, colorless crystals. Minerals are often discolored by impurities.

20-2 DETERMINATION OF SOLUBILITY PRODUCT CONSTANTS

Unless otherwise indicated, solubility product constants and solubility data are given for 25°C (Appendix H).

We frequently use statements such as “The solution contains 0.0025 gram of BaSO₄.” What we mean is that 0.0025 gram of solid BaSO₄ *dissolves* to give a solution that contains equal concentrations of Ba²⁺ and SO₄²⁻ ions.

1.1×10^{-5} mole of solid BaSO₄ dissolves to give a liter of saturated solution.

Calculated values may differ slightly from those found in tables due to data or rounding differences.

If the solubility of a compound is known, the value of its solubility product can be calculated.

EXAMPLE 20-1 Solubility Product Constants

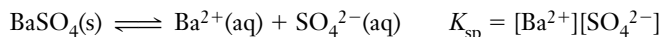
One (1.0) liter of saturated barium sulfate solution contains 0.0025 gram of dissolved BaSO₄. Calculate the solubility product constant for BaSO₄.

Plan

We write the equation for the dissolution of BaSO₄ and the expression for its solubility product constant, K_{sp} . From the solubility of BaSO₄ in H₂O, we calculate its molar solubility and the concentrations of the ions. This lets us calculate K_{sp} .

Solution

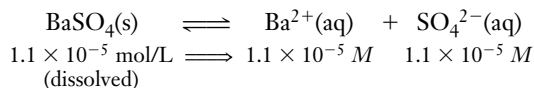
In saturated solutions, equilibrium exists between solid and dissolved solute. The equation for the dissolution of barium sulfate in water and its solubility product expression are



From the given solubility of BaSO₄ in H₂O we can calculate its *molar solubility*.

$$\frac{? \text{ mol BaSO}_4}{\text{L}} = \frac{2.5 \times 10^{-3} \text{ g BaSO}_4}{1.0 \text{ L}} \times \frac{1 \text{ mol BaSO}_4}{233 \text{ g BaSO}_4} = 1.1 \times 10^{-5} \text{ mol BaSO}_4/\text{L} \quad (\text{dissolved})$$

We know the molar solubility of BaSO₄. The dissolution equation shows that each formula unit of BaSO₄ that dissolves produces one Ba²⁺ ion and one SO₄²⁻ ion.



In a saturated solution $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 1.1 \times 10^{-5} \text{ M}$. Substituting these values into the K_{sp} expression for BaSO₄ gives the calculated value of K_{sp} .

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (1.1 \times 10^{-5})(1.1 \times 10^{-5}) = 1.2 \times 10^{-10}$$

You should now work Exercise 6.

EXAMPLE 20-2 Solubility Product Constant

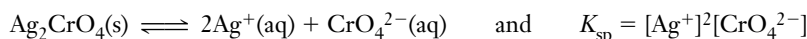
One (1.00) liter of a saturated solution of silver chromate at 25°C contains 0.0435 gram of Ag₂CrO₄. Calculate its solubility product constant.

Plan

We proceed as in Example 20-1.

Solution

The equation for the dissolution of silver chromate in water and its solubility product expression are

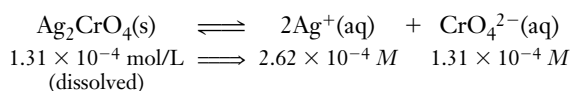


The molar solubility of silver chromate is calculated first.

$$\frac{? \text{ mol Ag}_2\text{CrO}_4}{\text{L}} = \frac{0.0435 \text{ g Ag}_2\text{CrO}_4}{1.00 \text{ L}} \times \frac{1 \text{ mol Ag}_2\text{CrO}_4}{332 \text{ g Ag}_2\text{CrO}_4} = 1.31 \times 10^{-4} \text{ mol/L (dissolved)}$$

1.31×10^{-4} mole of solid Ag_2CrO_4 dissolves to give a liter of saturated solution.

The equation for dissolution of Ag_2CrO_4 and its molar solubility give the concentrations of Ag^+ and CrO_4^{2-} ions in the saturated solution.



Substitution into the K_{sp} expression for Ag_2CrO_4 gives the value of K_{sp} .

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2.62 \times 10^{-4})^2(1.31 \times 10^{-4}) = 8.99 \times 10^{-12}$$

The calculated K_{sp} of Ag_2CrO_4 is 8.99×10^{-12} .

Values of solubility product constants are usually tabulated to only two significant figures.

You should now work Exercise 8.

The molar solubility and K_{sp} values for BaSO_4 and Ag_2CrO_4 are compared in Table 20-1. These data show that the molar solubility of Ag_2CrO_4 is greater than that of BaSO_4 . The K_{sp} for Ag_2CrO_4 , however, is less than the K_{sp} for BaSO_4 because the expression for Ag_2CrO_4 contains a *squared* term, $[\text{Ag}^+]^2$.

If we compare K_{sp} values for two 1:1 compounds, for example, AgCl and BaSO_4 , the compound with the larger K_{sp} value has the higher molar solubility. The same is true for any two compounds that have the same ion ratio, for example, the 1:2 compounds CaF_2 and $\text{Mg}(\text{OH})_2$ and the 2:1 compound Ag_2CO_3 .

$$K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$$

$$K_{\text{sp}}(\text{BaSO}_4) = 1.1 \times 10^{-10}$$

The molar solubility of AgCl is only slightly higher than that of BaSO_4 .

If two compounds have the *same ion ratio*, the one with the larger K_{sp} will have the higher *molar* solubility.

Appendix H lists some K_{sp} values. Refer to it as needed.

 **Problem-Solving Tip:** *It's Important to Know the Difference Between Solubility, Molar Solubility, and Solubility Product Expression*

Often it is necessary that you understand which of these is given or which is asked for. Recognition depends on a clear understanding of their definitions.


- The solubility of a compound is the amount of the compound that dissolves in a specified volume of solution. Solubility is usually expressed as either grams per liter or grams per 100. mL.
- The molar solubility of a compound is the number of moles that dissolve to give one liter of saturated solution.
- The solubility product expression for a compound is the product of the concentrations of its constituent ions, each raised to the power that corresponds to the number of ions in one formula unit of the compound.

TABLE 20-1 Comparison of Solubilities of BaSO_4 and Ag_2CrO_4

Compound	Molar Solubility	K_{sp}
BaSO_4	1.1×10^{-5} mol/L	$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$
Ag_2CrO_4	1.3×10^{-4} mol/L	$[\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 9.0 \times 10^{-12}$

20-3 USES OF SOLUBILITY PRODUCT CONSTANTS

When the solubility product for a compound is known, the solubility of the compound in H_2O at 25°C can be calculated as Example 20-3 illustrates.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 19.6, Estimating Salt Solubility.

The values of K_{sp} are obtained from Appendix H.

EXAMPLE 20-3 Molar Solubilities from K_{sp} Values

Calculate the molar solubilities, concentrations of the constituent ions, and solubilities in grams per liter for (a) silver chloride, AgCl ($K_{\text{sp}} = 1.8 \times 10^{-10}$), and (b) zinc hydroxide, $\text{Zn}(\text{OH})_2$ ($K_{\text{sp}} = 4.5 \times 10^{-17}$).

Plan

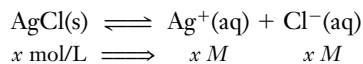
We are given the value for each solubility product constant. In each case we write the appropriate equation, represent the equilibrium concentrations, and then substitute into the K_{sp} expression.

Solution

(a) The equation for the dissolution of silver chloride and its solubility product expression are



Each formula unit of AgCl that dissolves produces one Ag^+ and one Cl^- . We let $x = \text{mol/L}$ of AgCl that dissolves, that is, the molar solubility.



Substitution into the solubility product expression gives

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = 1.8 \times 10^{-10} \quad x^2 = 1.8 \times 10^{-10} \quad x = 1.3 \times 10^{-5}$$

$$x = \text{molar solubility of AgCl} = 1.3 \times 10^{-5} \text{ mol/L}$$

One liter of saturated AgCl contains 1.3×10^{-5} mole of dissolved AgCl at 25°C . From the balanced equation we know the concentrations of the constituent ions.

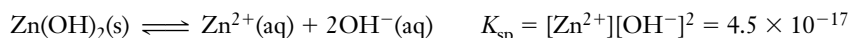
$$x = \text{molar solubility} = [\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ mol/L} = 1.3 \times 10^{-5} M$$

Now we can calculate the mass of dissolved AgCl in one liter of saturated solution.

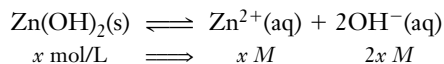
$$\frac{? \text{ g AgCl}}{\text{L}} = \frac{1.3 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143 \text{ g AgCl}}{1 \text{ mol AgCl}} = 1.9 \times 10^{-3} \text{ g AgCl/L}$$

A liter of saturated AgCl solution contains only 0.0019 g of dissolved AgCl .

(b) The equation for the dissolution of zinc hydroxide, $\text{Zn}(\text{OH})_2$, in water and its solubility product expression are



We let x = molar solubility, so $[\text{Zn}^{2+}] = x$ and $[\text{OH}^{-}] = 2x$, and we have



Substitution into the solubility product expression gives

$$\begin{aligned} [\text{Zn}^{2+}][\text{OH}^{-}]^2 &= (x)(2x)^2 = 4.5 \times 10^{-17} \\ 4x^3 &= 4.5 \times 10^{-17} \quad x^3 = 11 \times 10^{-18} \quad x = 2.2 \times 10^{-6} \end{aligned}$$

$$x = \text{molar solubility of Zn(OH)}_2 = 2.2 \times 10^{-6} \text{ mol Zn(OH)}_2/\text{L}$$

$$x = [\text{Zn}^{2+}] = 2.2 \times 10^{-6} \text{ M} \quad \text{and} \quad 2x = [\text{OH}^{-}] = 4.4 \times 10^{-6} \text{ M}$$

We can now calculate the mass of dissolved Zn(OH)_2 in one liter of saturated solution.

$$\frac{\text{g Zn(OH)}_2}{\text{L}} = \frac{2.2 \times 10^{-6} \text{ mol Zn(OH)}_2}{\text{L}} \times \frac{99 \text{ g Zn(OH)}_2}{1 \text{ mol Zn(OH)}_2} = 2.2 \times 10^{-4} \text{ g Zn(OH)}_2/\text{L}$$

A liter of saturated Zn(OH)_2 solution contains only 0.00022 g of dissolved Zn(OH)_2 .

You should now work Exercise 16.

Problem-Solving Tip: *The Dissolution of a Slightly Soluble Base Is not a K_b Problem*

The K_{sp} expression describes the equilibrium between a slightly soluble compound and its ions; in Example 20-3(b) one of those ions is OH^{-} . A K_b expression describes the equilibrium between a *soluble* basic species, for example, the ammonia molecule or the acetate ion, and the products it forms in solution, including OH^{-} . Do you see why the dissolution of Zn(OH)_2 is not a K_b problem? We found that $[\text{OH}^{-}] = 4.4 \times 10^{-6} \text{ M}$ in a *saturated* Zn(OH)_2 solution. From this we find $\text{pOH} = 5.36$ and $\text{pH} = 8.64$. A saturated Zn(OH)_2 solution is not very basic because Zn(OH)_2 is not very soluble in H_2O . The $[\text{OH}^{-}]$ is 44 times greater than it is in pure water.

The Common Ion Effect in Solubility Calculations

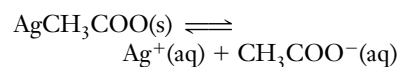
The common ion effect applies to solubility equilibria just as it does to other ionic equilibria. The solubility of a compound is less in a solution that contains an ion common to the compound than it is in pure water (as long as no other reaction is caused by the presence of the common ion).

EXAMPLE 20-4 Molar Solubilities and the Common Ion Effect

For magnesium fluoride, MgF_2 , $K_{\text{sp}} = 6.4 \times 10^{-9}$. (a) Calculate the molar solubility of magnesium fluoride in pure water. (b) Calculate the molar solubility of MgF_2 in 0.10 M sodium fluoride, NaF , solution. (c) Compare these molar solubilities.



The tube at the left contains a saturated solution of silver acetate, AgCH_3COO . When 1 M AgNO_3 is added to the tube, the equilibrium



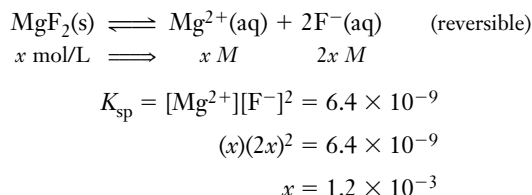
shifts to the left, demonstrating the common ion effect.

Plan

For part (a), we write the appropriate chemical equations and solubility product expression, designate the equilibrium concentrations, and then substitute into the solubility product expression. For part (b), we recognize that NaF is a soluble ionic compound that is completely dissociated into its ions. MgF_2 is a slightly soluble compound. Both compounds produce F^- ions so this is a common ion effect problem. We write the appropriate chemical equations and solubility product expression, represent the equilibrium concentrations, and substitute into the solubility product expression. For part (c), we compare the molar solubilities by calculating their ratio.

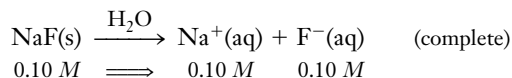
Solution

(a) We let x = molar solubility for MgF_2 , a slightly soluble salt.

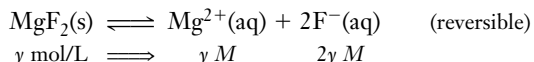


$1.2 \times 10^{-3} M$ = molar solubility of MgF_2 in pure water

(b) NaF is a soluble ionic salt and, therefore, $0.10 M \text{F}^-$ is produced by



We let y = molar solubility for MgF_2 , a slightly soluble salt.



The total $[\text{F}^-]$ is $0.10 M$ from NaF *plus* $2y M$ from MgF_2 , or $(0.10 + 2y) M$.

$$\begin{array}{l} K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^{-}]^2 = 6.4 \times 10^{-9} \\ (y)(0.10 + 2y)^2 = 6.4 \times 10^{-9} \end{array}$$

Very little MgF_2 dissolves, so y is small. This suggests that $2y \ll 0.10$, so $0.10 + 2y \approx 0.10$. Then

$$(y)(0.10)^2 = 6.4 \times 10^{-9} \quad \text{and} \quad y = 6.4 \times 10^{-7}$$

$6.4 \times 10^{-7} M$ = molar solubility of MgF_2 in $0.10 M$ NaF

(c) The ratio of molar solubility in water to molar solubility in $0.10 M$ NaF solution is:

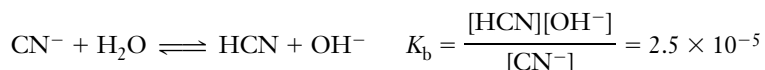
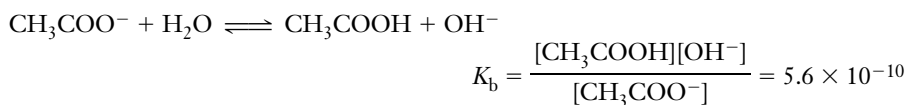
$$\frac{\text{molar solubility (in H}_2\text{O)}}{\text{molar solubility (in NaF solution)}} = \frac{1.2 \times 10^{-3} M}{6.4 \times 10^{-7} M} = \frac{1900}{1}$$

The molar solubility of MgF_2 in $0.10 M$ NaF ($6.4 \times 10^{-7} M$) is nearly 1900 times less than it is in pure water ($1.2 \times 10^{-3} M$).

You should now work Exercises 20 and 26.

THE EFFECTS OF HYDROLYSIS ON SOLUBILITY

In Section 18-8 we discussed the hydrolysis of anions of weak acids. For example, we found that for CH_3COO^- and CN^- ions,



We see that K_b for CN^- , the anion of a *very* weak acid, is much larger than K_b for CH_3COO^- , the anion of a much stronger acid. This tells us that in solutions of the same concentration, CN^- ions hydrolyze to a much greater extent than do CH_3COO^- ions. So we might expect that hydrolysis would have a much greater effect on the solubilities of cyanides such as AgCN than on the solubilities of acetates such as AgCH_3COO . It does.

Hydrolysis reduces the concentrations of anions of weak acids, such as F^- , CO_3^{2-} , CH_3COO^- , and CN^- , so its effect must be taken into account when we do very precise solubility calculations. Taking into account the effect of hydrolysis on solubilities of slightly soluble compounds is beyond the scope of this chapter, however.

The Reaction Quotient in Precipitation Reactions

Another application of the solubility product principle is the calculation of the maximum concentrations of ions that can coexist in solution. From these calculations we can determine whether a precipitate will form in a given solution. We compare Q_{sp} (Section 17-4) with K_{sp} .



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 19.7, Can a Precipitation Reaction Occur?

$Q_{\text{sp}} < K_{\text{sp}}$	Forward process is favored No precipitation occurs; if solid is present, more solid can dissolve
$Q_{\text{sp}} = K_{\text{sp}}$	Solution is <i>just</i> saturated Solid and solution are in equilibrium; neither forward nor reverse process is favored
$Q_{\text{sp}} > K_{\text{sp}}$	Reverse process is favored; precipitation occurs to form more solid

EXAMPLE 20-5 Predicting Precipitate Formation

If 100. mL of 0.00075 M sodium sulfate, Na_2SO_4 , is mixed with 50. mL of 0.015 M barium chloride, BaCl_2 , will a precipitate form?

Plan

We are mixing solutions of two soluble ionic salts. First we find the amount of each solute at the instant of mixing. Next we find the molarity of each solute *at the instant of mixing*. Then

we find the concentration of each ion in the *new* solution. Now we ask the question “*Could* any combination of the ions in this solution form a slightly soluble compound?” The answer is “Yes, Ba^{2+} and SO_4^{2-} *could* form BaSO_4 ,” so we calculate Q_{sp} and compare it with K_{sp} .

Solution

We find the *amount* of each solute at the instant of mixing.

$$\underline{?} \text{ mmol Na}_2\text{SO}_4 = 100. \text{ mL} \times \frac{0.00075 \text{ mmol Na}_2\text{SO}_4}{\text{mL}} = 0.075 \text{ mmol Na}_2\text{SO}_4$$

$$\underline{?} \text{ mmol BaCl}_2 = 50. \text{ mL} \times \frac{0.015 \text{ mmol BaCl}_2}{\text{mL}} = 0.75 \text{ mmol BaCl}_2$$

When *dilute* aqueous solutions are mixed, their volumes can be added to give the volume of the resulting solution.

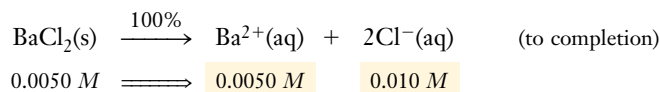
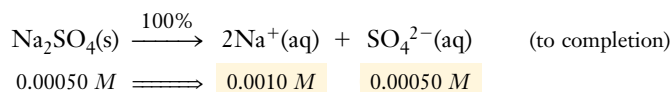
$$\text{volume of mixed solution} = 100. \text{ mL} + 50. \text{ mL} = 150. \text{ mL}$$

Then we find the *molarity of each solute at the instant of mixing*.

$$M_{\text{Na}_2\text{SO}_4} = \frac{0.075 \text{ mmol Na}_2\text{SO}_4}{150. \text{ mL}} = 0.00050 \text{ M Na}_2\text{SO}_4$$

$$M_{\text{BaCl}_2} = \frac{0.75 \text{ mmol BaCl}_2}{150. \text{ mL}} = 0.0050 \text{ M BaCl}_2$$

Now we find the *concentration of each ion* in the new solution.



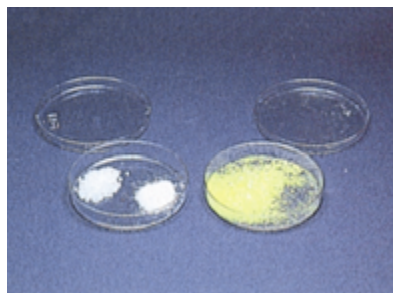
We consider the kinds of compounds mixed and determine whether a reaction could occur. Both Na_2SO_4 and BaCl_2 are soluble ionic salts. At the moment of mixing, the new solution contains a mixture of Na^+ , SO_4^{2-} , Ba^{2+} , and Cl^- ions. We must consider the possibility of forming two new compounds, NaCl and BaSO_4 . Sodium chloride is a soluble ionic compound so Na^+ and Cl^- do not combine in dilute aqueous solutions. BaSO_4 , however, is only very slightly soluble, and solid BaSO_4 will precipitate from the solution *if* $Q_{\text{sp}} > K_{\text{sp}}$ for BaSO_4 . K_{sp} for BaSO_4 is 1.1×10^{-10} . Substituting $[\text{Ba}^{2+}] = 0.0050 \text{ M}$ and $[\text{SO}_4^{2-}] = 0.00050 \text{ M}$ into the Q_{sp} expression for BaSO_4 , we get

$$Q_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (5.0 \times 10^{-3})(5.0 \times 10^{-4}) = 2.5 \times 10^{-6} \quad (Q_{\text{sp}} > K_{\text{sp}})$$

Because $Q_{\text{sp}} > K_{\text{sp}}$ solid BaSO_4 will precipitate until $[\text{Ba}^{2+}][\text{SO}_4^{2-}]$ just equals K_{sp} for BaSO_4 .

You should now work Exercises 28 and 30.

Recall that Q has the same form as the equilibrium constant, in this case K_{sp} , but the concentrations are not necessarily equilibrium concentrations.



When white solid potassium iodide, KI , and white solid lead(II) nitrate, $\text{Pb}(\text{NO}_3)_2$, are stirred together, some yellow lead(II) iodide, PbI_2 , forms. This reaction occurs in the small amount of water present in these solids.

 **Problem-Solving Tip: Detection of Precipitates**

The human eye is not a very sensitive detection device. As a rule of thumb, a precipitate can be seen with the naked eye if $Q_{\text{sp}} > K_{\text{sp}}$ by a factor of 1000. In Example 20-5, Q_{sp} exceeds K_{sp} by a factor of $\frac{2.5 \times 10^{-6}}{1.1 \times 10^{-10}} = 2.3 \times 10^4 = 23,000$. We expect to be able to see the BaSO_4 precipitate that is formed. Modern techniques enable us to detect smaller amounts of precipitates.

EXAMPLE 20-6 Initiation of Precipitation

What $[\text{Ba}^{2+}]$ is necessary to start the precipitation of BaSO_4 in a solution that is 0.0015 M in Na_2SO_4 ? Assume that the Ba^{2+} comes from addition of a solid soluble ionic compound such as BaCl_2 . For BaSO_4 , $K_{\text{sp}} = 1.1 \times 10^{-10}$.

Plan

These are the compounds in Example 20-5. We recognize that Na_2SO_4 is a soluble ionic compound and that the molarity of SO_4^{2-} is equal to the molarity of the Na_2SO_4 solution. We are given K_{sp} for BaSO_4 , so we solve for $[\text{Ba}^{2+}]$.

Solution

Because Na_2SO_4 is a soluble ionic compound, we know that $[\text{SO}_4^{2-}] = 0.0015\text{ M}$. We can use K_{sp} for BaSO_4 to calculate the $[\text{Ba}^{2+}]$ required for Q_{sp} to just equal K_{sp} .

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

$$[\text{Ba}^{2+}] = \frac{1.1 \times 10^{-10}}{[\text{SO}_4^{2-}]} = \frac{1.1 \times 10^{-10}}{1.5 \times 10^{-3}} = 7.3 \times 10^{-8}\text{ M}$$

Addition of enough BaCl_2 to give a barium ion concentration of $7.3 \times 10^{-8}\text{ M}$ just satisfies K_{sp} for BaSO_4 ; that is, $Q_{\text{sp}} = K_{\text{sp}}$. Ever so slightly more BaCl_2 would be required for Q_{sp} to exceed K_{sp} and for precipitation of BaSO_4 to occur. Therefore

$$[\text{Ba}^{2+}] > 7.3 \times 10^{-8}\text{ M} \quad (\text{to initiate precipitation of } \text{BaSO}_4)$$

You should now work Exercise 29.

Often we wish to remove an ion from solution by forming an insoluble compound (as in water purification). We use K_{sp} values to calculate the concentrations of ions remaining in solution *after* precipitation has occurred.

EXAMPLE 20-7 Concentration of Common Ion

Suppose we wish to recover silver from an aqueous solution that contains a soluble silver compound such as AgNO_3 by precipitating insoluble silver chloride, AgCl . A soluble ionic compound such as NaCl can be used as a source of Cl^- . What is the minimum concentration of chloride ion needed to reduce the dissolved silver ion concentration to a maximum of $1.0 \times 10^{-9}\text{ M}$? For AgCl , $K_{\text{sp}} = 1.8 \times 10^{-10}$.

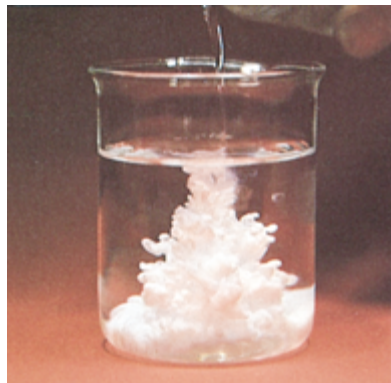
Plan

We are given K_{sp} for AgCl and the required equilibrium $[\text{Ag}^+]$, so we solve for $[\text{Cl}^-]$.



Sinkholes are formed when the underlying limestone, mostly CaCO_3 , is dissolved away by acidic water.

The recovery of silver from the solutions used in developing and fixing photographic film and prints presents just such a problem. Silver is an expensive metal, and the recovery is profitable. Moreover, if not recovered, the silver ions would constitute an undesirable pollutant in water supplies.



Silver chloride precipitates when chloride ions are added to a solution containing silver ions.

Clearly cations such as Na^+ or K^+ must also be present in this solution.

NaCl , NaBr , NaI , AgNO_3 , and NaNO_3 are soluble compounds that are completely dissociated in dilute aqueous solution.

We ignore the extremely small change in volume caused by addition of solid AgNO_3 .

Solution

The equation for the reaction of interest and the K_{sp} for AgCl are



To determine the $[\text{Cl}^{\text{-}}]$ required to reduce the $[\text{Ag}^{\text{+}}]$ to $1.0 \times 10^{-9} \text{ M}$, we solve the K_{sp} expression for $[\text{Cl}^{\text{-}}]$.

$$[\text{Cl}^{\text{-}}] = \frac{1.8 \times 10^{-10}}{[\text{Ag}^{\text{+}}]} = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-9}} = 0.18 \text{ M Cl}^{\text{-}}$$

To reduce the $[\text{Ag}^{\text{+}}]$ to $1.0 \times 10^{-9} \text{ M}$ ($0.00000011 \text{ g Ag}^{\text{+}}/\text{L}$), NaCl would be added until $[\text{Cl}^{\text{-}}] = 0.18 \text{ M}$ in the solution.

You should now work Exercise 32.

20-4 FRACTIONAL PRECIPITATION

We sometimes wish to remove some ions from solution while leaving others with similar properties in solution. This separation process is called **fractional precipitation**. Consider a solution that contains $\text{Cl}^{\text{-}}$, $\text{Br}^{\text{-}}$, and $\text{I}^{\text{-}}$ ions. These halide ions are anions of elements in the same family in the periodic table. We expect them to have similar properties. But we also expect some differences in properties, and that is what we find. Consider the solubility products for these silver halides.

Compound	Solubility Product
AgCl	1.8×10^{-10}
AgBr	3.3×10^{-13}
AgI	1.5×10^{-16}

These K_{sp} values show that AgI is less soluble than AgBr and that AgBr is less soluble than AgCl . Silver fluoride is quite soluble in water.

EXAMPLE 20-8 Concentration Required to Initiate Precipitation

Solid silver nitrate is slowly added to a solution that is 0.0010 M each in NaCl , NaBr , and NaI . Calculate the $[\text{Ag}^{\text{+}}]$ required to initiate the precipitation of each of the silver halides. For AgI , $K_{\text{sp}} = 1.5 \times 10^{-16}$; for AgBr , $K_{\text{sp}} = 3.3 \times 10^{-13}$; and for AgCl , $K_{\text{sp}} = 1.8 \times 10^{-10}$.

Plan

We are given a solution that contains equal concentrations of $\text{Cl}^{\text{-}}$, $\text{Br}^{\text{-}}$, and $\text{I}^{\text{-}}$ ions; all of which form insoluble silver salts. Then we slowly add $\text{Ag}^{\text{+}}$ ions. We use each K_{sp} to determine the $[\text{Ag}^{\text{+}}]$ that must be exceeded to initiate precipitation of each salt as we did in Example 20-6.

Solution

We calculate the $[\text{Ag}^{\text{+}}]$ necessary to begin to precipitate each of the silver halides. The solubility product for AgI is

$$[\text{Ag}^{\text{+}}][\text{I}^{\text{-}}] = 1.5 \times 10^{-16}$$

$[\text{I}^{\text{-}}] = 1.0 \times 10^{-3} \text{ M}$, so the $[\text{Ag}^{\text{+}}]$ that must be exceeded to start precipitation of AgI is

$$[\text{Ag}^+] = \frac{1.5 \times 10^{-16}}{[\text{I}^-]} = \frac{1.5 \times 10^{-16}}{1.0 \times 10^{-3}} = 1.5 \times 10^{-13} \text{ M}$$

Therefore, AgI will begin to precipitate when $[\text{Ag}^+] > 1.5 \times 10^{-13} \text{ M}$.

Repeating this kind of calculation for silver bromide gives

$$[\text{Ag}^+][\text{Br}^-] = 3.3 \times 10^{-13}$$

$$[\text{Ag}^+] = \frac{3.3 \times 10^{-13}}{[\text{Br}^-]} = \frac{3.3 \times 10^{-13}}{1.0 \times 10^{-3}} = 3.3 \times 10^{-10} \text{ M}$$

Thus, $[\text{Ag}^+] > 3.3 \times 10^{-10} \text{ M}$ is needed to start precipitation of AgBr.

For the precipitation of silver chloride to begin,

$$[\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-3}} = 1.8 \times 10^{-7} \text{ M}$$

To precipitate AgCl, we must have $[\text{Ag}^+] > 1.8 \times 10^{-7} \text{ M}$.

We have shown that

$$\begin{array}{ll} \text{to precipitate AgI,} & [\text{Ag}^+] > 1.5 \times 10^{-13} \text{ M} \\ \text{to precipitate AgBr,} & [\text{Ag}^+] > 3.3 \times 10^{-10} \text{ M} \\ \text{to precipitate AgCl,} & [\text{Ag}^+] > 1.8 \times 10^{-7} \text{ M} \end{array}$$

This calculation tells us that when AgNO_3 is added slowly to a solution that is 0.0010 M in each of NaI, NaBr, and NaCl, AgI precipitates first, AgBr precipitates second, and AgCl precipitates last. We can also calculate the amount of I^- precipitated before Br^- begins to precipitate and the amounts of I^- and Br^- precipitated before Cl^- begins to precipitate (Example 20-9).

EXAMPLE 20-9 Fractional Precipitation

Refer to Example 20-8. (a) Calculate the percentage of I^- precipitated before AgBr precipitates. (b) Calculate the percentages of I^- and Br^- precipitated before Cl^- precipitates.

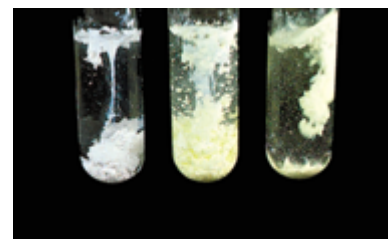
Plan

From Example 20-8 we know the $[\text{Ag}^+]$ that must be exceeded to initiate precipitation of each of three silver halides, AgI, AgBr, and AgCl. We use each of these values of $[\text{Ag}^+]$ with the appropriate K_{sp} expression, in turn, to find the concentration of each halide ion that remains in solution (unprecipitated). We express these halide ion concentrations as percent unprecipitated. Then we subtract each from exactly 100% to find the percentage of each halide that precipitates.

Freshly precipitated AgCl is white (*left*), AgBr is very pale yellow (*center*), and AgI is yellow (*right*). Polarizabilities of these halide ions increase in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$. Colors of the silver halides become more intense in the same direction. Solubilities of the silver halides increase in the opposite direction.

We are not suggesting that a $1.5 \times 10^{-13} \text{ M}$ solution of AgNO_3 be added. We are pointing out the fact that when sufficient AgNO_3 has been added to the solution to make $[\text{Ag}^+] > 1.5 \times 10^{-13} \text{ M}$, AgI begins to precipitate.

As AgNO_3 is added to the solution containing Cl^- , Br^- , and I^- ions, some AgBr and AgCl may precipitate *locally*. As the solution is stirred, AgBr and AgCl redissolve as long as $[\text{Ag}^+]$ is not large enough to exceed their K_{sp} values in the *bulk* of the solution.



In Example 20-7 we did a similar calculation, but we did not express the result in terms of the percentage of an ion precipitated.

We have subtracted 0.045% from *exactly* 100%. We have therefore *not* violated the rules for significant figures.

Solution

(a) In Example 20-8 we found that AgBr begins to precipitate when $[\text{Ag}^+] > 3.3 \times 10^{-10} \text{ M}$. This value for $[\text{Ag}^+]$ can be substituted into the K_{sp} expression for AgI to determine $[\text{I}^-]$ remaining *unprecipitated* when AgBr begins to precipitate.

$$[\text{Ag}^+][\text{I}^-] = 1.5 \times 10^{-16}$$

$$[\text{I}^-]_{\text{unppt'd}} = \frac{1.5 \times 10^{-16}}{[\text{Ag}^+]} = \frac{1.5 \times 10^{-16}}{3.3 \times 10^{-10}} = 4.5 \times 10^{-7} \text{ M}$$

The percentage of I^- unprecipitated is

$$\% \text{I}^-_{\text{unppt'd}} = \frac{[\text{I}^-]_{\text{unppt'd}}}{[\text{I}^-]_{\text{orig}}} \times 100\% = \frac{4.5 \times 10^{-7} \text{ M}}{1.0 \times 10^{-3} \text{ M}} \times 100\%$$

$$= 0.045\% \text{I}^- \text{ unprecipitated}$$

Therefore, 99.955% of the I^- precipitates *before* AgBr begins to precipitate.

(b) Similar calculations show that *just before* AgCl begins to precipitate, $[\text{Ag}^+] = 1.8 \times 10^{-7} \text{ M}$, and the $[\text{I}^-]$ unprecipitated is calculated as in part (a).

$$[\text{Ag}^+][\text{I}^-] = 1.5 \times 10^{-16}$$

$$[\text{I}^-]_{\text{unppt'd}} = \frac{1.5 \times 10^{-16}}{[\text{Ag}^+]} = \frac{1.5 \times 10^{-16}}{1.8 \times 10^{-7}} = 8.3 \times 10^{-10} \text{ M}$$

The percentage of I^- unprecipitated just before AgCl precipitates is

$$\% \text{I}^-_{\text{unppt'd}} = \frac{[\text{I}^-]_{\text{unppt'd}}}{[\text{I}^-]_{\text{orig}}} \times 100\% = \frac{8.3 \times 10^{-10} \text{ M}}{1.0 \times 10^{-3} \text{ M}} \times 100\%$$

$$= 0.000083\% \text{I}^- \text{ unprecipitated}$$

Therefore, 99.999917% of the I^- precipitates before AgCl begins to precipitate.

A similar calculation for the amount of Br^- precipitated just before AgCl begins to precipitate gives

$$[\text{Ag}^+][\text{Br}^-] = 3.3 \times 10^{-13}$$

$$[\text{Br}^-]_{\text{unppt'd}} = \frac{3.3 \times 10^{-13}}{[\text{Ag}^+]} = \frac{3.3 \times 10^{-13}}{1.8 \times 10^{-7}} = 1.8 \times 10^{-6} \text{ M}$$

$$\% \text{Br}^-_{\text{unppt'd}} = \frac{[\text{Br}^-]_{\text{unppt'd}}}{[\text{Br}^-]_{\text{orig}}} \times 100\% = \frac{1.8 \times 10^{-6} \text{ M}}{1.0 \times 10^{-3} \text{ M}} \times 100\%$$

$$= 0.18\% \text{Br}^- \text{ unprecipitated}$$

Thus, 99.82% of the Br^- precipitates before AgCl begins to precipitate.


You should now work Exercises 36 and 38.

We have described the series of reactions that occurs when solid AgNO_3 is added slowly to a solution that is 0.0010 M in Cl^- , Br^- , and I^- . Silver iodide begins to precipitate first; 99.955% of the I^- precipitates before any solid AgBr is formed. Silver bromide begins to

precipitate next; 99.82% of the Br^- and 99.999917% of the I^- precipitate before any solid AgCl forms. This shows that we can separate these ions very effectively by fractional precipitation.

20-5 SIMULTANEOUS EQUILIBRIA INVOLVING SLIGHTLY SOLUBLE COMPOUNDS

Many weak acids and bases react with many metal ions to form insoluble compounds. In such cases, we must take into account the weak acid or weak base equilibrium as well as the solubility equilibrium. The most common examples involve the reaction of metal ions with aqueous ammonia to form insoluble metal hydroxides.

 See the Saunders Interactive General Chemistry CD-ROM, Screen 19.10, Simultaneous Equilibria.

EXAMPLE 20-10 Simultaneous Equilibria

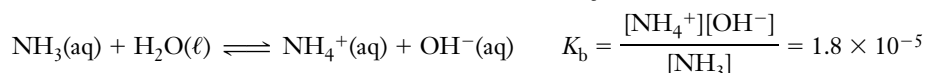
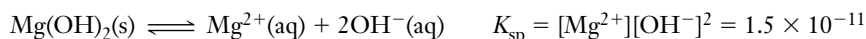
If a solution is made 0.10 M in magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, and 0.10 M in aqueous ammonia, a weak base, will magnesium hydroxide, $\text{Mg}(\text{OH})_2$, precipitate? K_{sp} for $\text{Mg}(\text{OH})_2$ is 1.5×10^{-11} , and K_{b} for aqueous NH_3 is 1.8×10^{-5} .

Plan

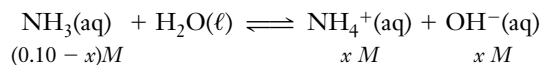
We first write equations for the two reversible reactions and their equilibrium constant expressions. We note that $[\text{OH}^-]$ appears in both equilibrium constant expressions. From the statement of the problem we know the concentration of Mg^{2+} . We use the K_{b} expression for aqueous NH_3 to find $[\text{OH}^-]$. Then we calculate Q_{sp} for $\text{Mg}(\text{OH})_2$ and compare it with its K_{sp} .

Solution

Two equilibria and their equilibrium constant expressions must be considered.



The $[\text{OH}^-]$ in 0.10 M aqueous NH_3 is calculated as in Example 18.14.



$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.10 - x)} \quad x = 1.3 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

Magnesium nitrate is a soluble ionic compound, so $[\text{Mg}^{2+}] = 0.10 \text{ M}$. Now that both $[\text{Mg}^{2+}]$ and $[\text{OH}^-]$ are known, we calculate Q_{sp} for $\text{Mg}(\text{OH})_2$.

$$\begin{aligned} [\text{Mg}^{2+}][\text{OH}^-]^2 &= Q_{\text{sp}} \\ (0.10)(1.3 \times 10^{-3})^2 &= 1.7 \times 10^{-7} = Q_{\text{sp}} \end{aligned}$$


$K_{\text{sp}} = 1.5 \times 10^{-11}$, so we see that $Q_{\text{sp}} > K_{\text{sp}}$.

Therefore, $\text{Mg}(\text{OH})_2$ would precipitate until $Q_{\text{sp}} = K_{\text{sp}}$.

You should now work Exercise 46.

We have calculated the $[\text{OH}^-]$ produced by the ionization of 0.10 M aqueous NH_3 . This is the equilibrium concentration of OH^- in this solution. There is no reason to double this value when we put it into the K_{sp} expression!

Example 20-11 shows how we can calculate the concentration of weak base that is required to initiate precipitation of an insoluble metal hydroxide.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 19.11, Solubility and pH.

EXAMPLE 20-11 *Simultaneous Equilibria*

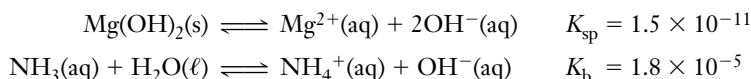
What concentration of aqueous ammonia is necessary to just start precipitation of $\text{Mg}(\text{OH})_2$ from a 0.10 M solution of $\text{Mg}(\text{NO}_3)_2$? Refer to Example 20-10.

Plan

We have the same reactions and equilibrium constant expressions as in Example 20-10. We are given $[\text{Mg}^{2+}]$, and so we use the K_{sp} expression of $\text{Mg}(\text{OH})_2$ to calculate the $[\text{OH}^-]$ necessary to initiate precipitation. Then we find the molarity of aqueous NH_3 solution that would furnish the desired $[\text{OH}^-]$.

Solution

Two equilibria and their equilibrium constant expressions must be considered.



We find the $[\text{OH}^-]$ necessary to initiate precipitation of $\text{Mg}(\text{OH})_2$ when $[\text{Mg}^{2+}] = 0.10 M$.

$$\begin{aligned}K_{\text{sp}} &= [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.5 \times 10^{-11} \\ [\text{OH}^-]^2 &= \frac{1.5 \times 10^{-11}}{[\text{Mg}^{2+}]} = \frac{1.5 \times 10^{-11}}{0.10} = 1.5 \times 10^{-10} & [\text{OH}^-] &= 1.2 \times 10^{-5} M\end{aligned}$$

$\therefore [\text{OH}^-] > 1.2 \times 10^{-5} M$ to initiate precipitation of $\text{Mg}(\text{OH})_2$.

Now we use the equilibrium of NH_3 as a weak base to find the $[\text{NH}_3]$ that will produce $1.2 \times 10^{-5} M \text{OH}^-$. Let x be the original $[\text{NH}_3]$.

$$\begin{aligned}\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell) &\rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \\ (x - 1.2 \times 10^{-5}) M & & 1.2 \times 10^{-5} M & 1.2 \times 10^{-5} M \\ K_{\text{b}} &= \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(1.2 \times 10^{-5})(1.2 \times 10^{-5})}{(x - 1.2 \times 10^{-5})} \\ 1.8 \times 10^{-5} x - 2.16 \times 10^{-10} &= 1.44 \times 10^{-10} \\ 1.8 \times 10^{-5} x &= 3.6 \times 10^{-10} \quad \text{so} \quad x = 2.0 \times 10^{-5} M = [\text{NH}_3]_{\text{orig}}\end{aligned}$$

Because 1.2×10^{-5} and x are of comparable magnitude, neither can be disregarded in the term $(x - 1.2 \times 10^{-5})$.

The solution must be ever so slightly greater than $2.0 \times 10^{-5} M$ in NH_3 to initiate precipitation of $\text{Mg}(\text{OH})_2$ in a 0.10 M solution of $\text{Mg}(\text{NO}_3)_2$.

A solution that contains a weak base can be buffered (by addition of a salt of the weak base) to decrease its basicity. Significant concentrations of some metal ions that form insoluble hydroxides can be kept in such solutions.

EXAMPLE 20-12 *Simultaneous Equilibria*

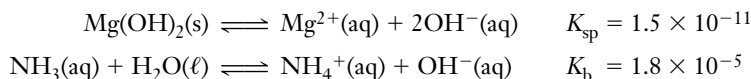
What minimum number of moles of NH_4Cl must be added to 1.0 liter of solution that is 0.10 M in $\text{Mg}(\text{NO}_3)_2$ and 0.10 M in NH_3 to prevent precipitation of $\text{Mg}(\text{OH})_2$?

Plan

These are the same compounds, in the same concentrations, that we used in Example 20-10. Because we know $[\text{Mg}^{2+}]$, we must find the maximum $[\text{OH}^-]$ that can exist in the solution *without exceeding* K_{sp} for $\text{Mg}(\text{OH})_2$. Then we find the minimum concentration of NH_4Cl that is necessary to buffer the NH_3 solution to keep the $[\text{OH}^-]$ below the calculated value.

Solution

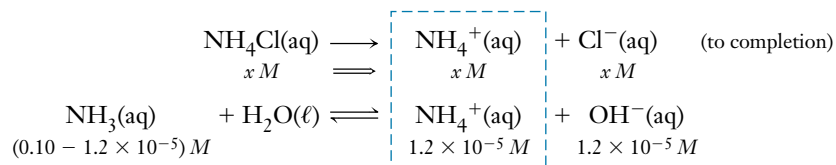
The buffering action of NH_4Cl in the presence of NH_3 decreases the concentration of OH^- . Again we have two equilibria.



To find the *maximum* $[\text{OH}^-]$ that can exist in solution *without causing precipitation*, we substitute $[\text{Mg}^{2+}]$ into the K_{sp} for $\text{Mg}(\text{OH})_2$.

$$\begin{aligned}[\text{Mg}^{2+}][\text{OH}^-]^2 &= 1.5 \times 10^{-11} \\ [\text{OH}^-]^2 &= \frac{1.5 \times 10^{-11}}{[\text{Mg}^{2+}]} = \frac{1.5 \times 10^{-11}}{0.10} = 1.5 \times 10^{-10} \\ [\text{OH}^-] &= 1.2 \times 10^{-5} \text{ M} \quad (\text{maximum } [\text{OH}^-] \text{ possible})\end{aligned}$$

To prevent precipitation of $\text{Mg}(\text{OH})_2$ in *this* solution, $[\text{OH}^-]$ must be equal to or less than $1.2 \times 10^{-5} \text{ M}$. K_{b} for aqueous NH_3 is used to calculate the number of moles of NH_4Cl necessary to buffer 1.0 L of 0.10 M aqueous NH_3 so that $[\text{OH}^-] = 1.2 \times 10^{-5} \text{ M}$. Let x = number of mol/L of NH_4Cl required.



We can assume that $(x + 1.2 \times 10^{-5}) \approx x$ and $(0.10 - 1.2 \times 10^{-5}) \approx 0.10$.

$$\frac{(x)(1.2 \times 10^{-5})}{0.10} = 1.8 \times 10^{-5}$$

$$x = 0.15 \text{ mol of } \text{NH}_4^+ \text{ per liter of solution}$$

Addition of 0.15 mol of NH_4Cl to 1.0 L of 0.10 M aqueous NH_3 decreases $[\text{OH}^-]$ to $1.2 \times 10^{-5} \text{ M}$. Then K_{sp} for $\text{Mg}(\text{OH})_2$ is not exceeded in this solution, and so no precipitate would form.

You should now work Exercises 42 and 44.

Examples 20-10, 20-11, and 20-12 illustrate a very important point.

All relevant equilibria must be satisfied when more than one equilibrium is required to describe a solution.

In Example 20-10 we found that $\text{Mg}(\text{OH})_2$ will precipitate from a solution that is 0.10 M in $\text{Mg}(\text{NO}_3)_2$ and 0.10 M in NH_3 .

You may wish to refer to Example 19-6 to refresh your understanding of buffer solutions.

20-6 DISSOLVING PRECIPITATES

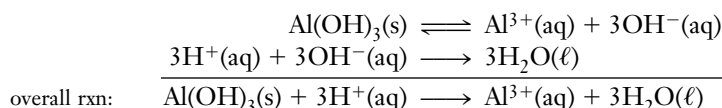
A precipitate dissolves when the concentrations of its ions are reduced so that K_{sp} is no longer exceeded, that is, when $Q_{sp} < K_{sp}$. The precipitate then dissolves until $Q_{sp} = K_{sp}$. The precipitates can be dissolved by several types of reactions. All involve removing ions from solution.

Converting an Ion to a Weak Electrolyte

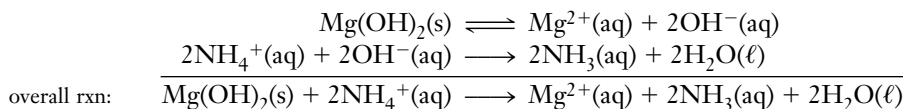
Three specific illustrations follow.

Solubility products, like other equilibrium constants, are thermodynamic quantities. They tell us nothing about how fast a given reaction occurs, only whether it can occur under specified conditions.

1. *Converting OH^- to H_2O .* Insoluble $\text{Al}(\text{OH})_3$ dissolves in acids. H^+ ions react with OH^- ions [from the saturated $\text{Al}(\text{OH})_3$ solution] to form the weak electrolyte H_2O . This makes $[\text{Al}^{3+}][\text{OH}^-]^3 < K_{sp}$, so that the dissolution equilibrium shifts to the right and $\text{Al}(\text{OH})_3$ dissolves.

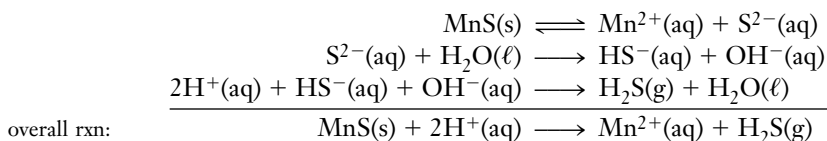


2. *Converting NH_4^+ to NH_3 .* Ammonium ions, from a salt such as NH_4Cl , dissolve insoluble $\text{Mg}(\text{OH})_2$. The NH_4^+ ions combine with OH^- ions in the saturated $\text{Mg}(\text{OH})_2$ solution. This forms the weak electrolytes NH_3 and H_2O . The result is $[\text{Mg}^{2+}][\text{OH}^-]^2 < K_{sp}$, and so the $\text{Mg}(\text{OH})_2$ dissolves.



This process, dissolution of $\text{Mg}(\text{OH})_2$ in an NH_4Cl solution, is the reverse of the reaction we considered in Example 20-10. There, $\text{Mg}(\text{OH})_2$ precipitated from a solution of aqueous NH_3 .

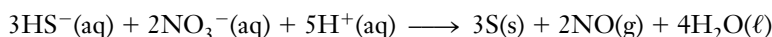
3. *Converting S^{2-} to H_2S .* Nonoxidizing acids dissolve most insoluble metal sulfides. For example, 6 M HCl dissolves MnS. The H^+ ions combine with S^{2-} ions to form H_2S , a gas that bubbles out of the solution. The result is $[\text{Mn}^{2+}][\text{S}^{2-}] < K_{sp}$, and so the MnS dissolves.

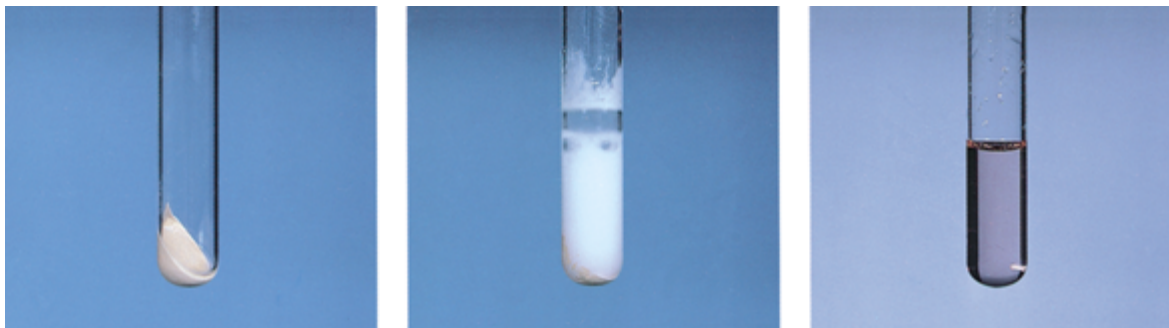


S^{2-} like O^{2-} does not exist in appreciable amounts in aqueous solutions.

Converting an Ion to Another Species by a Redox Reaction

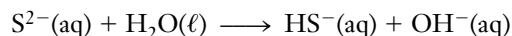
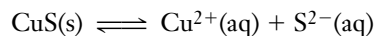
Most insoluble metal sulfides dissolve in hot dilute HNO_3 because NO_3^- ions oxidize S^{2-} ions, or actually their hydrolysis product (HS^-), to elemental sulfur. This removes HS^- (and thus S^{2-}) ions from the solution and promotes the dissolving of more of the metal sulfide.



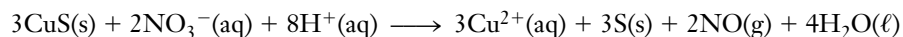


Manganese(II) sulfide, MnS , is salmon-colored. MnS dissolves in 6 M HCl . The resulting solution of MnCl_2 is pale pink.

Consider copper(II) sulfide, CuS , in equilibrium with its ions. This equilibrium lies far to the left. Removal of the S^{2-} or HS^- ions by oxidation to elemental sulfur favors the reaction to the right, and so $\text{CuS}(s)$ dissolves in hot dilute HNO_3 .



We multiply the first two equations by 3, add the three equations, and cancel like terms. This gives the net ionic equation for dissolving $\text{CuS}(s)$ in hot dilute HNO_3 .

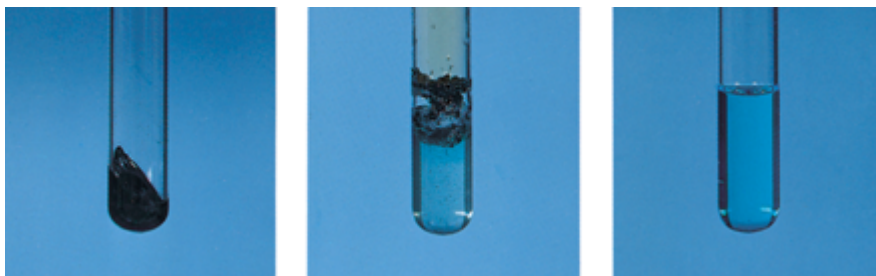


It is sometimes convenient to ignore hydrolysis of S^{2-} ions in aqueous solutions. Leaving out the hydrolysis step may give the false impression that S^{2-} ions exist in solution. The overall net ionic equation for this redox reaction will be the same, however, with or without consideration of hydrolysis of the S^{2-} ions.

Complex Ion Formation

The cations in many slightly soluble compounds can form complex ions. This often results in dissolution of the slightly soluble compound. Some metal ions share electron pairs donated by molecules and ions such as NH_3 , CN^- , OH^- , F^- , Cl^- , Br^- , and I^- form coordinate covalent bonds to metal ions. Coordinate covalent bonds are formed as these electron-donating groups (ligands) replace H_2O molecules from hydrated metal ions. The

“Ligand” is the name given to an atom or a group of atoms bonded to the central element in complex ions. Ligands are Lewis bases.



Copper(II) sulfide, CuS , is black. As CuS dissolves in 6 M HNO_3 , some NO is oxidized to brown NO_2 by O_2 in the air. The resulting solution of $\text{Cu}(\text{NO}_3)_2$ is blue.

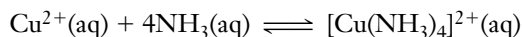
See the *Saunders Interactive General Chemistry CD-ROM*, Screen 19.12, Complex Ion Formation and Solubility.

As before, the outer brackets mean molar concentrations. The inner brackets are part of the formula of the complex ion.

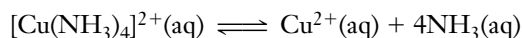
For brevity we shall omit H_2O from formulas of hydrated ions. For example, we write $[\text{Cu}(\text{OH}_2)_6]^{2+}$ as Cu^{2+} .

decrease in the concentration of the hydrated metal ion shifts the solubility equilibrium to the right.

Many copper(II) compounds react with excess aqueous NH_3 to form the deep-blue complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

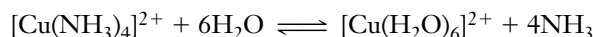


The dissociation of this complex ion is represented as



$$K_d = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[[\text{Cu}(\text{NH}_3)_4]^{2+}]} = 8.5 \times 10^{-13}$$

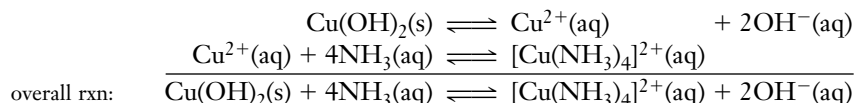
Recall that $\text{Cu}^{2+}(\text{aq})$ is really a hydrated ion, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. The preceding reaction and its K_d expression are represented more accurately as



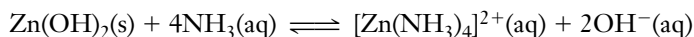
$$K_d = \frac{[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]^4}{[[\text{Cu}(\text{NH}_3)_4]^{2+}]} = 8.5 \times 10^{-13}$$

The more effectively a ligand competes with H_2O for a coordination site on the metal ions, the smaller K_d is. This tells us that in a comparison of complexes with the same number of ligands, the smaller the K_d value, the more stable the complex ion. Some complex ions and their dissociation constants, K_d , are listed in Appendix I.

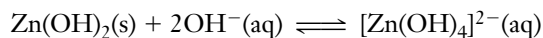
Copper(II) hydroxide dissolves in an excess of aqueous NH_3 to form the deep-blue complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$. This decreases the $[\text{Cu}^{2+}]$ so that $[\text{Cu}^{2+}][\text{OH}^-]^2 < K_{sp}$, and so the $\text{Cu}(\text{OH})_2$ dissolves.



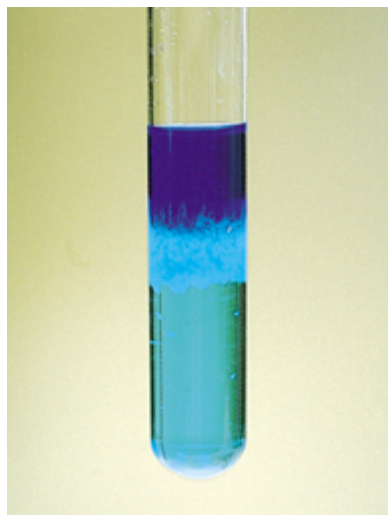
Similarly, $\text{Zn}(\text{OH})_2$ dissolves in excess NH_3 to form $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions.



Amphoteric hydroxides such as $\text{Zn}(\text{OH})_2$ also dissolve in excess strong base by forming complex ions (Section 10-6).



We see that we are able to shift equilibria (in this case, dissolve $\text{Zn}(\text{OH})_2$) by taking advantage of complex ion formation.



Concentrated aqueous NH_3 was added *slowly* to a solution of copper(II) sulfate, CuSO_4 . Unreacted blue copper(II) sulfate solution remains in the bottom part of the test tube. The light-blue precipitate in the middle is copper(II) hydroxide, $\text{Cu}(\text{OH})_2$. The top layer contains deep-blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions that were formed as some $\text{Cu}(\text{OH})_2$ dissolved in excess aqueous NH_3 .

Key Terms

Complex ions Ions resulting from the formation of coordinate covalent bonds between simple cations and other ions or molecules.

Dissociation constant The equilibrium constant that applies to the dissociation of a complex ion into a simple ion and coordinating species (ligands).

Fractional precipitation Removal of some ions from solution by precipitation while leaving other ions, with similar properties, in solution.

Molar solubility The number of moles of a solute that dissolve to produce a liter of saturated solution.

Precipitate A solid formed by mixing in solution the constituent ions of a slightly soluble compound.

Solubility product constant, K_{sp} The equilibrium constant that applies to the dissolution of a slightly soluble compound.

Solubility product principle The solubility product constant expression for a slightly soluble compound is the product of the concentrations of the constituent ions, each raised to the power that corresponds to the number of ions in one formula unit.

Exercises

Consult Appendix H for solubility product constant values and Appendix I for complex ion dissociation constants, as needed.

Solubility Product

- The solubility product constant values listed in Appendix H were determined at 25°C. How would those K_{sp} values change, if at all, with a change in temperature?
- State the solubility product principle. What is its significance?
- Why do we not include a term for the solid in a solubility product expression?
- What do we mean when we refer to the molar solubility of a compound?
- Write the solubility product expression for each of the following salts. (a) SnI_2 ; (b) $\text{Bi}_2(\text{SO}_4)_3$; (c) CuBr ; (d) Ag_3PO_4 .
- Write the solubility product expression for each of the following salts. (a) $\text{Co}_3(\text{AsO}_4)_2$; (b) Hg_2I_2 [contains mercury(I) ions, Hg_2^{2+}]; (c) MgF_2 ; (d) $(\text{Ag})_2\text{CO}_3$.
- The K_{sp} value for BaSO_4 is calculated from the expression $K_{sp} = [\text{Ba}^{+2}][\text{SO}_4^{-2}]$, whereas the K_{sp} value for $\text{Mg}(\text{OH})_2$ is calculated from the expression, $K_{sp} = [\text{Mg}^{+2}][\text{OH}^-]^2$. Explain why the hydroxide ion concentration is squared, but none of the other concentrations is squared.

Experimental Determination of K_{sp}

Values of K_{sp} calculated from the solubility data in these exercises may not agree exactly with the solubility products given in Appendix H because of rounding differences.

- From the solubility data given for the following compounds, calculate their solubility product constants.
 - SrCrO_4 , strontium chromate, 1.2 mg/mL
 - BiI_3 , bismuth iodide, 7.7×10^{-3} g/L
 - $\text{Fe}(\text{OH})_2$, iron(II) hydroxide, 1.1×10^{-3} g/L
 - SnI_2 , tin(II) iodide, 10.9 g/L
- From the solubility data given for the following compounds, calculate their solubility product constants.

- CuBr , copper(I) bromide, 1.0×10^{-3} g/L
- AgI , silver iodide, 2.8×10^{-8} g/10 mL
- $\text{Pb}_3(\text{PO}_4)_2$, lead(II) phosphate, 6.2×10^{-7} g/L
- Ag_2SO_4 , silver sulfate, 5.0 mg/mL

- Construct a table like Table 20-1 for the compounds listed in Exercise 8. Which compound has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the largest K_{sp} ; (d) the smallest K_{sp} ?
- Construct a table like Table 20-1 for the compounds listed in Exercise 9. Which compound has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the largest K_{sp} ; (d) the smallest K_{sp} ?
- A solution is produced by stirring 1 gram of calcium fluoride in one liter of water at 25°C. Careful analysis shows that 0.0163 grams of calcium fluoride has dissolved. Calculate the K_{sp} for calcium fluoride based on these data.
- Calculate the K_{sp} for zinc phosphate if 1.18×10^{-4} grams of zinc phosphate dissolved to make 2.0 liters of a saturated solution.

Uses of Solubility Product Constants

- The solubility product for calcium carbonate is 4.8×10^{-9} . What is the solubility of calcium carbonate in grams per liter of solution?
- Calculate molar solubilities, concentrations of constituent ions, and solubilities in grams per liter for the following compounds at 25°C: (a) $\text{Zn}(\text{CN})_2$, zinc cyanide; (b) PbI_2 , lead iodide; (c) $\text{Pb}_3(\text{AsO}_4)_2$, lead(II) arsenate; (d) Hg_2CO_3 , mercury(I) carbonate [the formula for the mercury(I) ion is Hg_2^{2+}].
- Calculate molar solubilities, concentrations of constituent ions, and solubilities in grams per liter for the following compounds at 25°C: (a) CuI , copper(I) iodide; (b) $\text{Ba}_3(\text{PO}_4)_2$, barium phosphate; (c) MgF_2 , magnesium fluoride; (d) $\text{Pb}_3(\text{PO}_4)_2$, lead(II) phosphate.
- What is the concentration of lead ions in one liter of saturated PbCrO_4 solution?

18. Barium sulfate is used to produce distinct X-rays of the gastrointestinal tract. What is the maximum mass of barium sulfate that can dissolve in 10.0 liters of water, a volume much greater than the volume of the average gastrointestinal tract?
19. Calculate the molar solubility of AgBr in 0.015 *M* KBr solution.
20. Calculate the molar solubility of Ag₂SO₄ in 0.15 *M* K₂SO₄ solution.
21. Construct a table similar to Table 20-1 for the compounds listed in Exercise 15. Which compound has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the highest solubility, expressed in grams per liter; (d) the lowest solubility, expressed in grams per liter?
22. Construct a table similar to Table 20-1 for the compounds listed in Exercise 16. Which compound has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the highest solubility, expressed in grams per liter; (d) the lowest solubility, expressed in grams per liter?
23. Of the three compounds BaCO₃, Fe(OH)₂, and Ag₂CrO₄, which has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the highest solubility, expressed in grams per liter; and (d) the lowest solubility, expressed in grams per liter?
24. Of the three compounds, Ag₃PO₄, AgI, and PbCO₃, which has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the highest solubility, expressed in grams per liter; and (d) the lowest solubility, expressed in grams per liter?
25. What volume of water is required to dissolve 10. grams of copper(II) carbonate, CuCO₃?
26. Which has the greater molar solubility in 0.20 *M* K₂CrO₄ solution: BaCrO₄ or Ag₂CrO₄?
27. Will a precipitate form when 1.00 g of AgNO₃ is added to 50.0 mL of 0.050 *M* NaCl? If so, would you expect the precipitate to be visible?
28. Will a precipitate of PbCl₂ form when 5.0 g of solid Pb(NO₃)₂ is added to 1.00 L of 0.010 *M* NaCl? Assume that volume change is negligible.
29. Sodium bromide and lead nitrate are soluble in water. Will lead bromide precipitate when 1.03 g of NaBr and 0.332 g of Pb(NO₃)₂ are dissolved in sufficient water to make 1.00 L of solution?
30. Will a precipitate of Cu(OH)₂ form when 10.0 mL of 0.010 *M* NaOH is added to 1.00 L of 0.010 *M* CuCl₂?
31. A solution is 0.0100 *M* in Pb²⁺ ions. If 0.103 mol of solid Na₂SO₄ is added to 1.00 L of this solution (with negligible volume change), what percentage of the Pb²⁺ ions remain in solution?
32. A solution is 0.0100 *M* in Pb²⁺ ions. If 0.103 mol of solid NaI is added to 1.00 L of this solution (with negligible volume change), what percentage of the Pb²⁺ ions remain in solution?
- *33. A solution is 0.0100 *M* in Ba(NO₃)₂. If 0.103 mol of solid Na₃PO₄ is added to 1.00 L of this solution (with negligible volume change), what percentage of the Ba²⁺ ions remain in solution?

Fractional Precipitation

34. What is fractional precipitation?
35. Solid Na₂SO₄ is added slowly to a solution that is 0.10 *M* in Pb(NO₃)₂ and 0.10 *M* in Ba(NO₃)₂. In what order will solid PbSO₄ and BaSO₄ form? Calculate the percentage of Ba²⁺ that precipitates just before PbSO₄ begins to precipitate.
36. To a solution that is 0.10 *M* in Cu⁺, 0.10 *M* in Ag⁺, and 0.10 *M* in Au⁺, solid NaCl is added slowly. Assume that there is no volume change due to the addition of solid NaCl. (a) Which compound will begin to precipitate first? (b) Calculate [Au⁺] when AgCl just begins to precipitate. What percentage of the Au⁺ has precipitated at this point? (c) Calculate [Au⁺] and [Ag⁺] when CuCl just begins to precipitate.
37. A solution is 0.015 *M* in Pb²⁺ and 0.015 *M* in Ag⁺. As Cl⁻ is introduced to the solution by the addition of solid NaCl, determine (a) which substance will precipitate first, AgCl or PbCl₂, and (b) the fraction of the metal ion in the first precipitate that remains in solution at the moment the precipitation of the second compound begins.
38. A solution is 0.050 *M* in K₂SO₄ and 0.050 *M* in K₂CrO₄. A solution of Pb(NO₃)₂ is added slowly without changing the volume appreciably. (a) Which salt, PbSO₄ or PbCrO₄, will precipitate first? (b) What is [Pb²⁺] when the salt in part (a) begins to precipitate? (c) What is [Pb²⁺] when the other lead salt begins to precipitate? (d) What are [SO₄²⁻] and [CrO₄²⁻] when the lead salt in part (c) begins to precipitate?
39. Solid Pb(NO₃)₂ is added slowly to a solution that is 0.015 *M* each in NaOH, K₂CO₃, and Na₂SO₄. (a) In what order will solid Pb(OH)₂, PbCO₃, and PbSO₄ begin to precipitate? (b) Calculate the percentages of OH⁻ and CO₃²⁻ that have precipitated when PbSO₄ begins to precipitate.
40. Suppose you have three beakers that contain, respectively, 100 mL of each of the following solutions: (i) 0.0015 *M* KOH; (ii) 0.0015 *M* K₂CO₃; (iii) 0.0015 *M* KCN. (a) If solid zinc nitrate, Zn(NO₃)₂, were added slowly to each beaker, what concentration of Zn²⁺ would be required to initiate precipitation? (b) If solid zinc nitrate were added to each beaker until [Zn²⁺] = 0.0015 *M*, what concentrations of OH⁻, CO₃²⁻, and CN⁻ would remain in solution, that is, unprecipitated? Neglect any volume change when solid is added.
41. Suppose you have three beakers that contain, respectively, 100 mL each of the following solutions: (i) 0.0015 *M* KOH; (ii) 0.0015 *M* K₂CO₃; (iii) 0.0015 *M* KI. (a) If solid lead nitrate, Pb(NO₃)₂, were added slowly to each beaker, what

concentration of Pb^{2+} would be required to initiate precipitation? (b) If solid lead nitrate were added to each beaker until $[\text{Pb}^{2+}] = 0.0015 \text{ M}$, what concentrations of OH^- , CO_3^{2-} , and I^- would remain in solution, that is, unprecipitated? Neglect any volume change when solute is added.

Simultaneous Equilibria

42. If a solution is made 0.080 *M* in $\text{Mg}(\text{NO}_3)_2$, 0.075 *M* in aqueous ammonia, and 3.5 *M* in NH_4NO_3 , will $\text{Mg}(\text{OH})_2$ precipitate? What is the pH of this solution?
43. If a solution is made 0.090 *M* in $\text{Mg}(\text{NO}_3)_2$, 0.090 *M* in aqueous ammonia, and 0.080 *M* in NH_4NO_3 , will $\text{Mg}(\text{OH})_2$ precipitate? What is the pH of this solution?
- *44. Calculate the solubility of CaF_2 in a solution that is buffered at $[\text{H}^+] = 0.0050 \text{ M}$ with $[\text{HF}] = 0.10 \text{ M}$.
- *45. Calculate the solubility of AgCN in a solution that is buffered at $[\text{H}^+] = 0.000200 \text{ M}$, with $[\text{HCN}] = 0.01 \text{ M}$.
46. If a solution is $2.0 \times 10^{-5} \text{ M}$ in $\text{Mn}(\text{NO}_3)_2$ and $1.0 \times 10^{-3} \text{ M}$ in aqueous ammonia, will $\text{Mn}(\text{OH})_2$ precipitate?
47. If a solution is 0.040 *M* in manganese(II) nitrate, $\text{Mn}(\text{NO}_3)_2$, and 0.080 *M* in aqueous ammonia, will manganese(II) hydroxide, $\text{Mn}(\text{OH})_2$, precipitate?
48. Milk of magnesia is a suspension of the slightly soluble compound $\text{Mg}(\text{OH})_2$ in water. (a) What is the molar solubility of $\text{Mg}(\text{OH})_2$ in a 0.015 *M* NaOH solution? (b) What is the molar solubility of $\text{Mg}(\text{OH})_2$ in a 0.015 *M* MgCl_2 solution?
49. How many moles of $\text{Cr}(\text{OH})_3$ will dissolve in 1.00 L of a solution with a pH of 5.00?
50. Determine whether a precipitate forms when a 0.00050 *M* solution of magnesium nitrate is brought to a pH of 8.75.
- *51. What concentration of NH_4NO_3 is necessary to prevent precipitation of $\text{Mn}(\text{OH})_2$ in the solution of Exercise 47?
52. (a) What is the pH of a saturated solution of $\text{Mn}(\text{OH})_2$? (b) What is the solubility in g $\text{Mn}(\text{OH})_2/100 \text{ mL}$ of solution?
53. (a) What is the pH of a saturated solution of $\text{Mg}(\text{OH})_2$? (b) What is the solubility in g $\text{Mg}(\text{OH})_2/100 \text{ mL}$ of solution?

Dissolution of Precipitates and Complex Ion Formation

54. Explain, by writing appropriate equations, how the following insoluble compounds can be dissolved by the addition of a solution of nitric acid. (Carbonates dissolve in strong acids to form carbon dioxide, which is evolved as a gas, and water.) What is the “driving force” for each reaction? (a) $\text{Cu}(\text{OH})_2$; (b) $\text{Al}(\text{OH})_3$; (c) MnCO_3 ; (d) $\text{Pb}(\text{OH})_2\text{CO}_3$.
55. Explain, by writing equations, how the following insoluble compounds can be dissolved by the addition of a

solution of ammonium nitrate or ammonium chloride. (a) $\text{Mg}(\text{OH})_2$; (b) $\text{Mn}(\text{OH})_2$; (c) $\text{Ni}(\text{OH})_2$.

56. The following insoluble sulfides can be dissolved in 3 *M* hydrochloric acid. Explain how this is possible, and write the appropriate equations. (a) MnS ; (b) CuS .
57. The following sulfides are less soluble than those listed in Exercise 56 and can be dissolved in hot 6 *M* nitric acid, an oxidizing acid. Explain how, and write the appropriate balanced equations. (a) PbS ; (b) CuS ; (c) Bi_2S_3 .
58. Why would MnS be expected to be more soluble in 0.10 *M* HCl solution than in water? Would the same be true for $\text{Mn}(\text{NO}_3)_2$?
- *59. For each pair, choose the salt that would be expected to be more soluble in acidic solution than in pure water, and justify your choice: (a) $\text{Hg}_2(\text{CH}_3\text{COO})_2$ or Hg_2Br_2 ; (b) $\text{Pb}(\text{OH})_2$ or PbI_2 ; (c) AgI or AgNO_2 .

Mixed Exercises

60. We mix 25.0 mL of a 0.0030 *M* solution of BaCl_2 and 50.0 mL of a 0.050 *M* solution of NaF . (a) Find $[\text{Ba}^{2+}]$ and $[\text{F}^-]$ in the mixed solution at the instant of mixing (before any possible reaction occurs). (b) Would BaF_2 precipitate?
- *61. A concentrated, strong acid is added to a solid mixture of 0.015-mol samples of $\text{Fe}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ placed in 1.0 L of water. At what values of pH will the dissolution of each hydroxide be complete? (Assume negligible volume change.)
62. A solution is 0.015 *M* in I^- ions and 0.015 *M* in Br^- ions. Ag^+ ions are introduced to the solution by the addition of solid AgNO_3 . Determine (a) which compound will precipitate first, AgI or AgBr , and (b) the percentage of the halide ion in the first precipitate that is removed from solution before the precipitation of the second compound begins.
63. Calculate the molar solubility of Ag_2SO_4 (a) in pure water, (b) in 0.015 *M* AgNO_3 , and (c) in 0.015 *M* K_2SO_4 .

CONCEPTUAL EXERCISES

64. Suppose there was a deposit of gold(I) chloride in a river bed. What minimum volume of water, at 25°C, would be required to dissolve 1.0 gram of gold ions?
65. (a) Are “insoluble” substances really insoluble? (b) What do we mean when we refer to insoluble substances?
66. Solubility product calculations are actually based on heterogeneous equilibria. Why are pure solids and liquids exempted from these calculations?
67. Draw a picture of a portion of a saturated silver chloride solution at the molecular level. Show a small amount of solid plus some dissociated ions. You need not show water or waters of hydration. Prepare a second drawing that

includes the same volume of solution but twice as much solid. Should your drawing include more, less, or the same number of silver ions?

68. The solubility product constants of silver chloride, AgCl , and silver chromate, Ag_2CrO_4 , are 1.8×10^{-10} and 9.0×10^{-12} , respectively. Suppose that the chloride, Cl^- (aq), and chromate, CrO_4^{2-} (aq), ions are both present in the same solution at concentrations of 0.010 M each. A standard solution of silver ions, Ag^+ (aq), is dispensed slowly from a buret into this solution while it is stirred vigorously. Solid silver chloride is white, and silver chromate is red. What will be the concentration of Cl^- (aq) ions in the mixture when the first tint of red color appears in the mixture?

BUILDING YOUR KNOWLEDGE

69. How many moles of CO_3^{2-} must be added to 0.50 liter of a 0.10 M Sr^{2+} solution to produce a solution that is $1.0 \times 10^{-6} \text{ M}$ Sr^{2+} ? How many moles of CO_3^{2-} are in the final solution and how many moles of CO_3^{2-} are in the precipitate formed? Assume no volume change for the solution.
70. A fluoridated water supply contains 1 mg/L of F^- . What is the maximum amount of Ca^{2+} , expressed in grams per liter, that can exist in this water supply?
71. Many industrial operations require very large amounts of water as a coolant in heat exchange processes. Muddy or cloudy water is usually unsatisfactory because the dispersed solids may clog filters or deposit sediment in pipes and pumps. Murky water can be clarified on a large scale by adding agents to coagulate colloidal material, and then allowing the precipitate to settle out in holding tanks or ponds before the clarified water is sent to plant intakes. Recent methods employ the addition of both calcium hydroxide and magnesium carbonate. If 56 g of $\text{Ca}(\text{OH})_2$ and 45 g of MgCO_3 were added to 520 liters of water, would these compounds form a precipitate?
72. Magnesium carbonate is used in the manufacture of a high-density *magnesite* brick. This material is not well suited to general exterior use because the magnesium carbonate easily erodes. What percentage of 28 grams of surface-exposed MgCO_3 would be lost through the solvent action of 15 liters of water? Assume sufficient contact time for the water to become saturated with MgCO_3 .