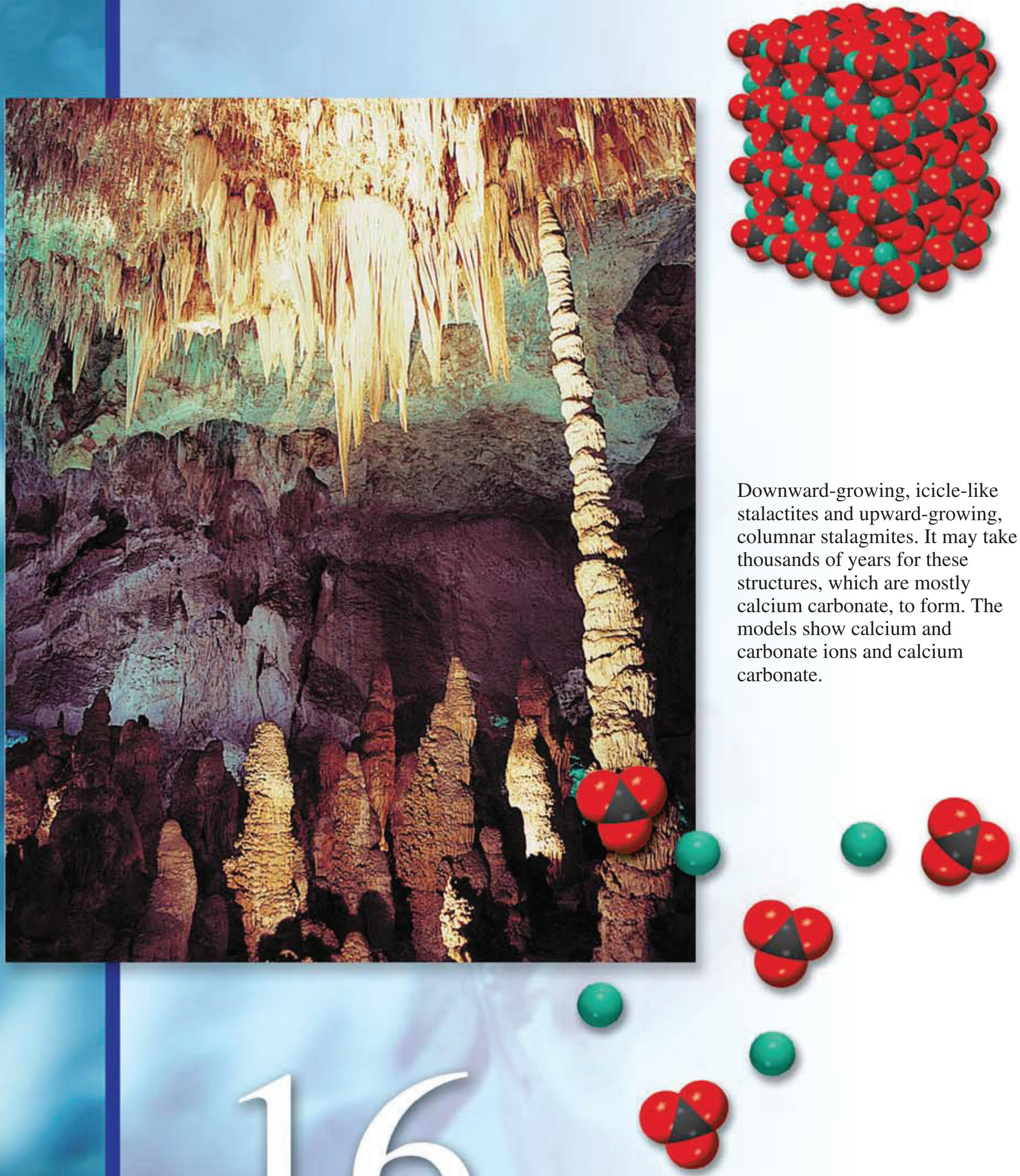
Acid-Base Equilibria and Solubility Equilibria



Downward-growing, icicle-like stalactites and upward-growing, columnar stalagmites. It may take thousands of years for these structures, which are mostly calcium carbonate, to form. The models show calcium and carbonate ions and calcium carbonate.

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16.6 Solubility Equilibria

Precipitation reactions are important in industry, medicine, and everyday life. For example, the preparation of many essential industrial chemicals such as sodium carbonate (Na_2CO_3) is based on precipitation reactions. The dissolving of tooth enamel, which is mainly made of hydroxyapatite [$Ca_5(PO_4)_3OH$], in an acidic medium leads to tooth decay. Barium sulfate ($BaSO_4$), an insoluble compound that is opaque to X rays, is used to diagnose ailments of the digestive tract. Stalactites and stalagmites, which consist of calcium carbonate ($CaCO_3$), are produced by a precipitation reaction, and so are many foods, such as fudge.

The general rules for predicting the solubility of ionic compounds in water were introduced in Section 4.2. Although useful, these solubility rules do not enable us to make quantitative predictions about how much of a given ionic compound will dissolve in water. To develop a quantitative approach, we start with what we already know about chemical equilibrium. Unless otherwise stated, in the following discussion the solvent is water and the temperature is 25°C.

$BaSO_4$ imaging of human large intestine.

Solubility Product

Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be represented as

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

Silver chloride is an insoluble salt (see Table 4.2). The small amount of solid AgCl that dissolves in water is assumed to dissociate completely into Ag^+ and Cl^- ions. We know from Chapter 14 that for heterogeneous reactions the concentration of the solid is a constant. Thus, we can write the equilibrium constant for the dissolution of AgCl (see Example 14.5) as

Recall that the activity of the solid is one (p. 624).

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

where K_{sp} is called the solubility product constant or simply *the solubility product*. In general, the ***solubility product*** of a compound is *the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.*

Because each AgCl unit contains only one Ag^+ ion and one Cl^- ion, its solubility product expression is particularly simple to write. The following cases are more complex:

- MgF_2

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Mg^{2+}][F^-]^2$$

- Ag_2CO_3

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[CO_3^{2-}]$$

- $Ca_3(PO_4)_2$

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \qquad K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

Table 16.2 lists the solubility products for a number of salts of low solubility. Soluble salts such as NaCl and KNO_3, which have very large K_{sp} values, are not listed in the table for essentially the same reason that we did not include K_a values for strong acids in Table 15.3. The value of K_{sp} indicates the solubility of an ionic compound—the smaller the value, the less soluble the compound in water. However, in using K_{sp} values to compare solubilities, you should choose compounds that have similar formulas, such as AgCl and ZnS, or CaF_2 and $Fe(OH)_2$.

A cautionary note: In Chapter 15 (p. 663) we assumed that dissolved substances exhibit ideal behavior for our calculations involving solution concentrations, but this assumption is not always valid. For example, a solution of barium fluoride (BaF_2) may contain both neutral and charged ion pairs, such as BaF_2 and BaF^+, in addition to free Ba^{2+} and F^- ions. Furthermore, many anions in the ionic compounds listed in Table 16.2 are conjugate bases of weak acids. Consider copper sulfide (CuS). The S^{2-} ion can hydrolyze as follows

$$S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$$
$$HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$$

TABLE 16.2 **Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C**

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [$Al(OH)_3$]	1.8×10^{-33}	Lead(II) chromate ($PbCrO_4$)	2.0×10^{-14}
Barium carbonate ($BaCO_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF_2)	4.1×10^{-8}
Barium fluoride (BaF_2)	1.7×10^{-6}	Lead(II) iodide (PbI_2)	1.4×10^{-8}
Barium sulfate ($BaSO_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi_2S_3)	1.6×10^{-72}	Magnesium carbonate ($MgCO_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$Mg(OH)_2$]	1.2×10^{-11}
Calcium carbonate ($CaCO_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF_2)	4.0×10^{-11}	Mercury(I) chloride (Hg_2Cl_2)	3.5×10^{-18}
Calcium hydroxide [$Ca(OH)_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$Ca_3(PO_4)_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$Cr(OH)_3$]	3.0×10^{-29}	Silver bromide (AgBr)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag_2CO_3)	8.1×10^{-12}
Copper(I) bromide (CuBr)	4.2×10^{-8}	Silver chloride (AgCl)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$Cu(OH)_2$]	2.2×10^{-20}	Silver sulfate (Ag_2SO_4)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag_2S)	6.0×10^{-51}
Iron(II) hydroxide [$Fe(OH)_2$]	1.6×10^{-14}	Strontium carbonate ($SrCO_3$)	1.6×10^{-9}
Iron(III) hydroxide [$Fe(OH)_3$]	1.1×10^{-36}	Strontium sulfate ($SrSO_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($PbCO_3$)	3.3×10^{-14}	Zinc hydroxide [$Zn(OH)_2$]	1.8×10^{-14}
Lead(II) chloride ($PbCl_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

And highly charged small metal ions such as Al^{3+} and Bi^{3+} will undergo hydrolysis as discussed in Section 15.10. Both ion-pair formation and salt hydrolysis decrease the concentrations of the ions that appear in the K_{sp} expression, but we need not be concerned with the deviations from ideal behavior here.

For the dissolution of an ionic solid in aqueous solution, any one of the following conditions may exist: (1) the solution is unsaturated, (2) the solution is saturated, or (3) the solution is supersaturated. For concentrations of ions that do not correspond to equilibrium conditions we use the reaction quotient (see Section 14.4), which in this case is called the *ion product (Q),* to predict whether a precipitate will form. Note that Q has the same form as K_{sp} except that the concentrations of ions are *not* equilibrium concentrations. For example, if we mix a solution containing Ag^+ ions with one containing Cl^- ions, then the ion product is given by

$$Q = [Ag^+]_0[Cl^-]_0$$

The subscript 0 reminds us that these are initial concentrations and do not necessarily correspond to those at equilibrium. The possible relationships between Q and K_{sp} are

$Q < K_{sp}$ $[Ag^+]_0[Cl^-]_0 < 1.6 \times 10^{-10}$	Unsaturated solution (no precipitation)
$Q = K_{sp}$ $[Ag^+][Cl^-] = 1.6 \times 10^{-10}$	Saturated solution (no precipitation)
$Q > K_{sp}$ $[Ag^+]_0[Cl^-]_0 > 1.6 \times 10^{-10}$	Supersaturated solution; AgCl will precipitate out until the product of the ionic concentrations is equal to 1.6×10^{-10}

Depending on how a solution is made up, $[Ag^+]$ may or may not be equal to $[Cl^-]$.

Molar Solubility and Solubility

There are two other ways to express a substance's solubility: ***molar solubility,*** which is *the number of moles of solute in 1 L of a saturated solution (mol/L),* and ***solubility,*** which is *the number of grams of solute in 1 L of a saturated solution (g/L)*. Note that both these expressions refer to the concentration of saturated solutions at some given temperature (usually 25°C).

Both molar solubility and solubility are convenient to use in the laboratory. We can use them to determine K_{sp} by following the steps outlined in Figure 16.9(a). Example 16.8 illustrates this procedure.

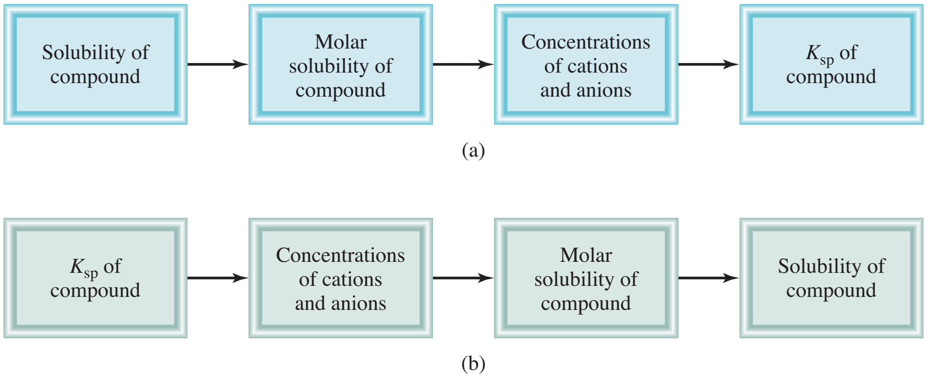


Figure 16.9 *Sequence of steps (a) for calculating K_{sp} from solubility data and (b) for calculating solubility from K_{sp} data.*

Calcium sulfate is used as a drying agent and in the manufacture of paints, ceramics, and paper. A hydrated form of calcium sulfate, called plaster of Paris, is used to make casts for broken bones.

EXAMPLE 16.8

The solubility of calcium sulfate ($CaSO_4$) is found to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate.

Strategy We are given the solubility of $CaSO_4$ and asked to calculate its K_{sp}. The sequence of conversion steps, according to Figure 16.9(a), is

$$\begin{matrix}\text{solubility of}\\ CaSO_4\text{ in g/L}\end{matrix} \longrightarrow \begin{matrix}\text{molar solubility}\\ \text{of } CaSO_4\end{matrix} \longrightarrow \begin{matrix}[Ca^{2+}]\text{ and}\\ [SO_4^{2-}]\end{matrix} \longrightarrow \begin{matrix}K_{sp}\text{ of}\\ CaSO_4\end{matrix}$$

Solution Consider the dissociation of $CaSO_4$ in water. Let s be the molar solubility (in mol/L) of $CaSO_4$.

	$CaSO_4(s) \rightleftharpoons$	$Ca^{2+}(aq)$ +	$SO_4^{2-}(aq)$
Initial (M):		0	0
Change (M):	$-s$	$+s$	$+s$
Equilibrium (M):		s	s

The solubility product for $CaSO_4$ is

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = s^2$$

First, we calculate the number of moles of $CaSO_4$ dissolved in 1 L of solution:

$$\frac{0.67\ \cancel{\text{g } CaSO_4}}{1\text{ L soln}} \times \frac{1\text{ mol } CaSO_4}{136.2\ \cancel{\text{g } CaSO_4}} = 4.9 \times 10^{-3}\text{ mol/L} = s$$

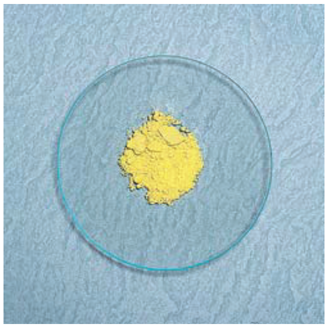
From the solubility equilibrium we see that for every mole of $CaSO_4$ that dissolves, 1 mole of Ca^{2+} and 1 mole of SO_4^{2-} are produced. Thus, at equilibrium,

$$[Ca^{2+}] = 4.9 \times 10^{-3}\ M \quad \text{and} \quad [SO_4^{2-}] = 4.9 \times 10^{-3}\ M$$

Now we can calculate K_{sp}:

$$\begin{aligned} K_{sp} &= [Ca^{2+}][SO_4^{2-}] \\ &= (4.9 \times 10^{-3})(4.9 \times 10^{-3}) \\ &= 2.4 \times 10^{-5} \end{aligned}$$

Sometimes we are given the value of K_{sp} for a compound and asked to calculate the compound's molar solubility. For example, the K_{sp} of silver bromide (AgBr) is 7.7×10^{-13}. We can calculate its molar solubility by the same procedure as that for acid ionization constants. First we identify the species present at equilibrium. Here we have Ag^+ and Br^- ions. Let s be the molar solubility (in mol/L) of AgBr. Because one unit of AgBr yields one Ag^+ and one Br^- ion, at equilibrium both $[Ag^+]$ and $[Br^-]$ are equal to s. We summarize the changes in concentrations as follows:



Silver bromide is used in photographic emulsions.

	$AgBr(s)$	$\rightleftharpoons$	$Ag^+(aq)$	$+$	$Br^-(aq)$
Initial (M):			0.00		0.00
Change (M):	$-s$		$+s$		$+s$
Equilibrium (M):			s		s

From Table 16.2 we write

$$\begin{aligned} K_{sp} &= [Ag^+][Br^-] \\ 7.7 \times 10^{-13} &= (s)(s) \\ s &= \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7}\,M \end{aligned}$$

Therefore, at equilibrium

$$\begin{aligned} [Ag^+] &= 8.8 \times 10^{-7}\,M \\ [Br^-] &= 8.8 \times 10^{-7}\,M \end{aligned}$$

Thus, the molar solubility of AgBr also is $8.8 \times 10^{-7}\,M$.

Example 16.9 makes use of this approach.

EXAMPLE 16.9

Using the data in Table 16.2, calculate the solubility of copper(II) hydroxide, $Cu(OH)_2$, in g/L.

Copper(II) hydroxide is used as a pesticide and to treat seeds.

Strategy We are given the K_{sp} of $Cu(OH)_2$ and asked to calculate its solubility in g/L. The sequence of conversion steps, according to Figure 16.9(b), is

$$\begin{matrix} K_{sp}\text{ of} \\ Cu(OH)_2 \end{matrix} \longrightarrow \begin{matrix} [Cu^{2+}]\text{ and} \\ [OH^-] \end{matrix} \longrightarrow \begin{matrix} \text{molar solubility} \\ \text{of } Cu(OH)_2 \end{matrix} \longrightarrow \begin{matrix} \text{solubility of} \\ Cu(OH)_2\text{ in g/L} \end{matrix}$$

Solution Consider the dissociation of $Cu(OH)_2$ in water:

	$Cu(OH)_2(s)$	$\rightleftharpoons$	$Cu^{2+}(aq)$	$+$	$2OH^-(aq)$
Initial (M):			0		0
Change (M):	$-s$		$+s$		$+2s$
Equilibrium (M):			s		$2s$

Note that the molar concentration of OH^- is twice that of Cu^{2+}. The solubility product of $Cu(OH)_2$ is

$$\begin{aligned} K_{sp} &= [Cu^{2+}][OH^-]^2 \\ &= (s)(2s)^2 = 4s^3 \end{aligned}$$

(Continued)

From the K_{sp} value in Table 16.2, we solve for the molar solubility of $Cu(OH)_2$ as follows:

$$2.2 \times 10^{-20} = 4s^3$$

$$s^3 = \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21}$$

Hence $$s = 1.8 \times 10^{-7}\, M$$

Finally, from the molar mass of $Cu(OH)_2$ and its molar solubility, we calculate the solubility in g/L:

$$\text{solubility of } Cu(OH)_2 = \frac{1.8 \times 10^{-7}\ \cancel{\text{mol Cu(OH)}_2}}{1\text{ L soln}} \times \frac{97.57\text{ g Cu(OH)}_2}{1\ \cancel{\text{mol Cu(OH)}_2}}$$

$$= 1.8 \times 10^{-5}\text{ g/L}$$

As Examples 16.8 and 16.9 show, solubility and solubility product are related. If we know one, we can calculate the other, but each quantity provides different information. Table 16.3 shows the relationship between molar solubility and solubility product for a number of ionic compounds.

When carrying out solubility and/or solubility product calculations, keep in mind the following important points:

1. Solubility is the quantity of a substance that dissolves in a certain quantity of water to produce a saturated solution. In solubility equilibria calculations, it is usually expressed as *grams* of solute per liter of solution. Molar solubility is the number of *moles* of solute per liter of solution.
2. Solubility product is an equilibrium constant.
3. Molar solubility, solubility, and solubility product all refer to a *saturated solution*.

TABLE 16.3 Relationship Between K_{sp} and Molar Solubility (s)

Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
$AgCl$	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	$2s$	s	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF_2	$[Pb^{2+}][F^-]^2$	s	$2s$	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$K_{sp} = 27s^4;\ s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$3s$	$2s$	$K_{sp} = 108s^5;\ s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

Predicting Precipitation Reactions

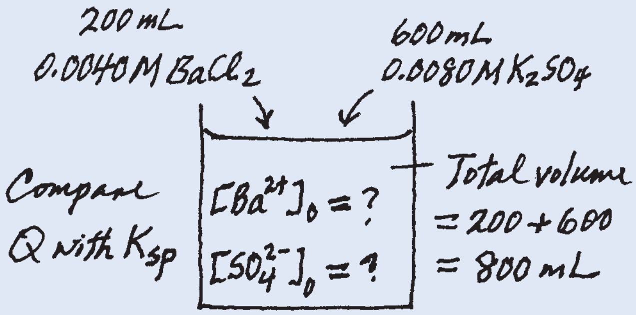
From a knowledge of the solubility rules (see Section 4.2) and the solubility products listed in Table 16.2, we can predict whether a precipitate will form when we mix two solutions or add a soluble compound to a solution. This ability often has practical value. In industrial and laboratory preparations, we can adjust the concentrations of ions until the ion product exceeds K_{sp} in order to obtain a given compound (in the form of a precipitate). The ability to predict precipitation reactions is also useful in medicine. For example, kidney stones, which can be extremely painful, consist largely of calcium oxalate, CaC_2O_4 ($K_{sp} = 2.3 \times 10^{-9}$). The normal physiological concentration of calcium ions in blood plasma is about 5 mM (1 mM = 1×10^{-3} M). Oxalate ions ($C_2O_4^{2-}$), derived from oxalic acid present in many vegetables such as rhubarb and spinach, react with the calcium ions to form insoluble calcium oxalate, which can gradually build up in the kidneys. Proper adjustment of a patient's diet can help to reduce precipitate formation. Example 16.10 illustrates the steps involved in predicting precipitation reactions.

A kidney stone.

EXAMPLE 16.10

Exactly 200 mL of 0.0040 M $BaCl_2$ are mixed with exactly 600 mL of 0.0080 M K_2SO_4. Will a precipitate form?

Strategy Under what condition will an ionic compound precipitate from solution? The ions in solution are Ba^{2+}, Cl^-, K^+, and SO_4^{2-}. According to the solubility rules listed in Table 4.2 (p. 125), the only precipitate that can form is $BaSO_4$. From the information given, we can calculate $[Ba^{2+}]$ and $[SO_4^{2-}]$ because we know the number of moles of the ions in the original solutions and the volume of the combined solution. Next, we calculate the reaction quotient Q ($Q = [Ba^{2+}]_0[SO_4^{2-}]_0$) and compare the value of Q with K_{sp} of $BaSO_4$ to see if a precipitate will form, that is, if the solution is supersaturated. It is helpful to make a sketch of the situation.



Solution The number of moles of Ba^{2+} present in the original 200 mL of solution is

$$200 \text{ mL} \times \frac{0.0040 \text{ mol } Ba^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 8.0 \times 10^{-4} \text{ mol } Ba^{2+}$$

The total volume after combining the two solutions is 800 mL. The concentration of Ba^{2+} in the 800 mL volume is

We assume that the volumes are additive.

$$\begin{aligned}[Ba^{2+}] &= \frac{8.0 \times 10^{-4} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \\ &= 1.0 \times 10^{-3}\ M\end{aligned}$$

(Continued)

The number of moles of SO_4^{2-} in the original 600 mL solution is

$$600\text{ mL} \times \frac{0.0080\text{ mol }SO_4^{2-}}{1\text{ L soln}} \times \frac{1\text{ L}}{1000\text{ mL}} = 4.8 \times 10^{-3}\text{ mol }SO_4^{2-}$$

The concentration of SO_4^{2-} in the 800 mL of the combined solution is

$$\begin{aligned}[SO_4^{2-}] &= \frac{4.8 \times 10^{-3}\text{ mol}}{800\text{ mL}} \times \frac{1000\text{ mL}}{1\text{ L soln}} \\ &= 6.0 \times 10^{-3}\,M\end{aligned}$$

Now we must compare Q and K_{sp}. From Table 16.2,

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = 1.1 \times 10^{-10}$$

As for Q,

$$\begin{aligned}Q &= [Ba^{2+}]_0[SO_4^{2-}]_0 = (1.0 \times 10^{-3})(6.0 \times 10^{-3}) \\ &= 6.0 \times 10^{-6}\end{aligned}$$

Therefore,

$$Q > K_{sp}$$

The solution is supersaturated because the value of Q indicates that the concentrations of the ions are too large. Thus, some of the $BaSO_4$ will precipitate out of solution until

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