7.6 Solubility Equilibria and the Solubility Product Constant

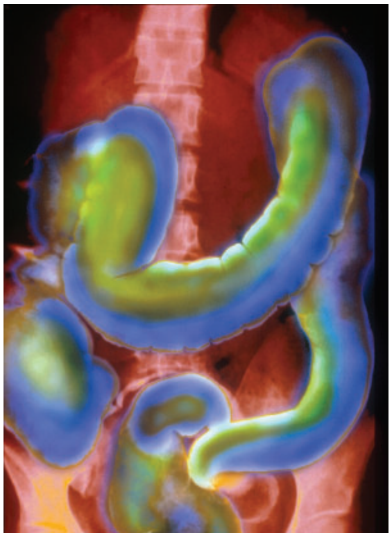


Figure 1 Barium sulfate makes the large intestine more visible in this X-ray image. Barium ions are toxic to humans, so the low solubility of barium sulfate also protects the patient from any toxic side effects.

solubility the quantity of solute that dissolves in a given quantity of solvent at a particular temperature; the concentration of a saturated solution at a particular temperature

Before undergoing an X-ray of the digestive tract, patients may be asked to consume a room-temperature (27 °C) barium "meal" composed of barium sulfate and water. At either 27 °C or body temperature (37 °C), the barium meal is mainly water and solid barium sulfate crystals, with a very small quantity of dissolved barium ions, $Ba^{2+}(aq)$, and sulfate ions, $SO_4^{2-}(aq)$. The undissolved crystals of barium sulfate block the transmission of X-rays through the digestive tract, creating a clear image of the structures of the digestive tract (**Figure 1**).

The low solubility of barium sulfate, $BaSO_4$, is one reason this compound is used in the diagnosis of gastrointestinal disorders. **Solubility** is the quantity of a solute that dissolves in a solvent under specific conditions, such as the amount of sugar that can dissolve in water at 100 °C. For example, calcium sulfate, $CaSO_4(s)$, is more soluble in cold water than in hot water. This can have significant effects on plumbing. In pipes carrying cold water, any calcium sulfate remains dissolved and is harmless. In hot water, such as in a water heater, the calcium sulfate is less soluble and so may precipitate out of solution along with other compounds, such as calcium carbonate. The resulting solid can harm parts of the plumbing system.

Solubility Equilibria of Ionic Compounds

Recall that ionic compounds are composed of ions joined by ionic bonds. In water, ionic compounds form a dynamic equilibrium. For example, silver iodide, AgI(s), is an ionic compound that is slightly soluble in water. Immediately after solid silver iodide is placed in water, all the silver ions, Ag^+, and iodide ions, I^-, are still tightly packed in a crystal lattice structure, as shown in **Figure 2**. The charged ends of polar water molecules, $H_2O(l)$, are attracted to the ions and pull some of them into solution. The oxygen atoms in the water molecules, which have a partial negative charge, orient to surround the positively charged silver ions. Similarly, the positively charged parts of the water molecules orient to surround the negatively charged iodide ions.

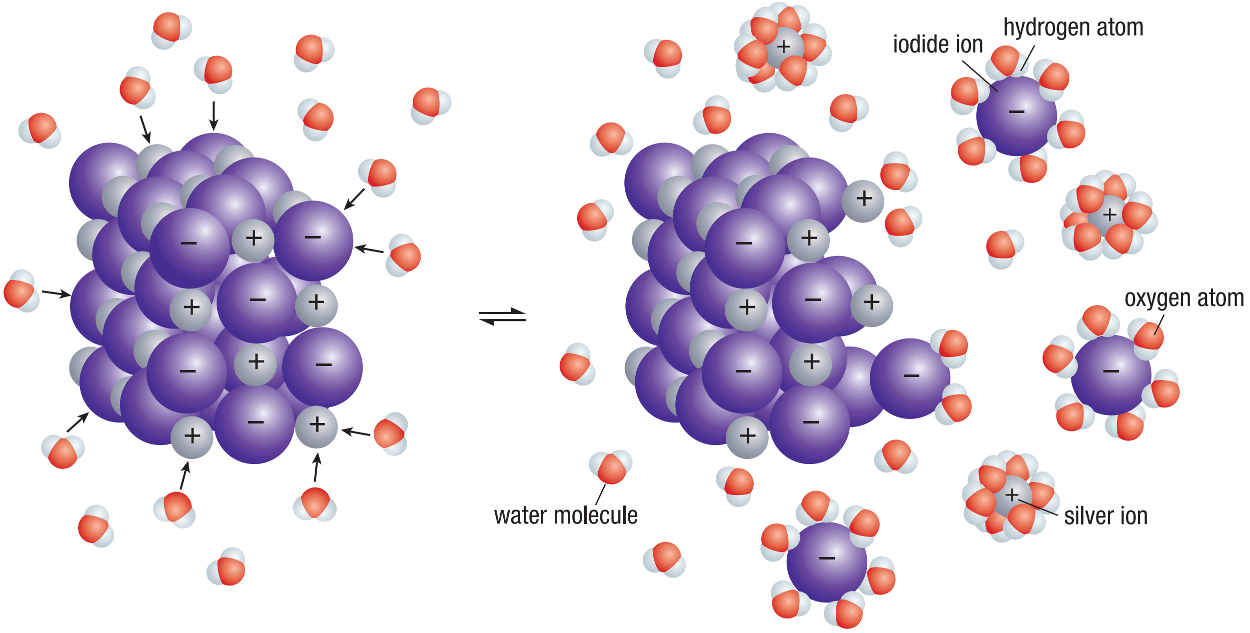


Figure 2 When a solid ionic compound, such as silver iodide, dissolves in water, ions are removed from the crystal lattice as they become surrounded by water molecules. The reverse reaction also takes place, eventually reaching equilibrium.

How does a dynamic equilibrium form? First, consider the chemical equation for the dissolving of silver iodide in water.

$$AgI(s) \rightarrow Ag^{+}(aq) + I^{-}(aq)$$

Once they have entered into solution, the aqueous silver and iodide ions can collide with each other, which can cause them to re-form solid silver iodide. When this happens, a precipitate will form or existing crystals might become larger. The chemical equation for the precipitation of silver iodide from an aqueous solution is

$$Ag^{+}(aq) + I^{-}(aq) \rightarrow AgI(s)$$

Notice how two opposing processes are occurring in the silver iodide solution: dissolution (dissolving) and precipitation. Eventually, these two opposing processes will reach a dynamic equilibrium. At this point the rate at which ions in the solid silver iodide dissolve is equal to the rate at which aqueous silver and iodide ions precipitate. At equilibrium, the solution is saturated: it contains the maximum quantity of solute at a given temperature and pressure. Therefore, the concentrations of aqueous silver ions and aqueous iodide ions remain constant in a saturated solution. This is an example of a **solubility equilibrium**, which is a dynamic equilibrium between a solute and a solvent that occurs in a saturated solution. It can be represented by this equation:

$$AgI(s) \rightleftharpoons Ag^{+}(aq) + I^{-}(aq)$$

solubility equilibrium a dynamic equilibrium between a solute and a solvent in a saturated solution in a closed system

The Solubility Product Constant (K_{sp})

A solubility equilibrium is a heterogeneous equilibrium system between a solid ionic compound and its ions dissolved in a saturated aqueous solution. The equilibrium law equation for the solubility equilibrium between solid silver iodide and its aqueous ions can be written as

$$K = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

$$K = \frac{[Ag^{+}(aq)][I^{-}(aq)]}{[AgI(s)]}$$

The concentration of silver and iodide ions may vary from one saturated solution to the next at the same temperature. However, the concentration of solid silver iodide remains constant. Therefore, we can ignore the concentration of the solid silver iodide in the equilibrium law equation for the solubility equilibrium. The equilibrium constant equation for silver iodide therefore becomes

$$K_{sp} = [Ag^{+}(aq)][I^{-}(aq)]$$

This equation gives us the **solubility product constant (K_{sp}),** which is the value of the equilibrium law equation for a solubility equilibrium. The subscript "sp" distinguishes this constant from the general equilibrium constant, K. As with K, K_{sp} is calculated using concentrations in mol/L, and K_{sp} values are not given units. A table of solubility product constants is provided in Appendix B4.

solubility product constant (K_{sp}) the value obtained from the equilibrium law applied to a saturated solution

The K_{sp} of AgI(s) at 25 °C is 8.5×10^{-17}. Temperature is always included when reporting values for the solubility product constant. K_{sp} values vary with temperature because the solubility of substances varies with temperature. We most commonly talk about the K_{sp} value for substances with low solubilities. However, even highly soluble substances, such as sodium chloride, have K_{sp} values. Therefore, any calculation you can perform for a low-solubility substance you can also perform for a highly soluble substance.

LEARNING **TIP**

Subscripts for *K*

The general equilibrium constant, K, is sometimes written as K_c or K_{eq} to distinguish it from other equilibrium constants, such as K_{sp}.

Tutorial 1 Writing Solubility Product Constant Equations and Calculating K_{sp} Values

When writing a solubility product constant equation or calculating the value of a solubility product constant, remember that the concentration of the solid can be ignored because it does not vary in a saturated solution.

Sample Problem 1: Writing a Solubility Product Constant Equation from a Balanced Equation

Write a solubility product constant equation for the solubility equilibrium at 25 °C given by the following balanced equation:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Solution: Since the concentration of $CaF_2(s)$ is constant, do not include it in the denominator of the equilibrium law equation.

Therefore,

$$K_{sp} = [Ca^{2+}(aq)][F^-(aq)]^2$$

Statement: The solubility product constant equation for the solubility equilibrium is

$$K_{sp} = [Ca^{2+}(aq)][F^-(aq)]^2$$

Sample Problem 2: Writing a Solubility Product Constant Equation from a Chemical Formula

Write the solubility product constant equation for a saturated solution of aluminum sulfate, $Al_2(SO_4)_3(aq)$, at 25 °C.

Solution:

Step 1. Write a balanced equation for the aluminum oxide solution equilibrium.

The saturated solution contains an equilibrium between $Al_2(SO_4)_3(s)$ and the dissolved ions, $Al^{3+}(aq)$ and $SO_4^{2-}(aq)$.

$$Al_2(SO_4)_3(s) \rightleftharpoons 2\,Al^{3+}(aq) + 3\,SO_4^{2-}(aq)$$

Step 2. Write the K_{sp} equation, omitting any solids.

$$K_{sp} = [Al^{3+}(aq)]^2[SO_4^{2-}(aq)]^3$$

Statement: The solubility product constant equation for a saturated solution of $Al_2(SO_4)_3(aq)$ is

$$K_{sp} = [Al^{3+}(aq)]^2[SO_4^{2-}(aq)]^3$$

Sample Problem 3: Calculating the K_{sp} Value from Ion Concentrations

A chemist has a closed vessel containing a chunk of solid zinc hydroxide, $Zn(OH)_2(s)$, surrounded by a saturated solution at 25 °C. He determines the concentrations of aqueous zinc ions, $Zn^{2+}(aq)$, and aqueous hydroxide ions, $OH^-(aq)$, to be 2.7×10^{-6} mol/L and 5.4×10^{-6} mol/L, respectively. Calculate the solubility product constant.

Given: $[Zn^{2+}(aq)] = 2.7 \times 10^{-6}$ mol/L;
$[OH^-(aq)] = 5.4 \times 10^{-6}$ mol/L

Required: K_{sp}

Solution:

Step 1. Write the balanced equation for the solution equilibrium.

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

Step 2. Write the K_{sp} equation for the equilibrium, omitting any solids.

$$K_{sp} = [Zn^{2+}(aq)][OH^-(aq)]^2$$

Step 3. Substitute the given ion concentrations into the K_{sp} equation and solve.

$$\begin{aligned} K_{sp} &= [Zn^{2+}(aq)][OH^-(aq)]^2 \\ &= (2.7 \times 10^{-6})(5.4 \times 10^{-6})^2 \\ K_{sp} &= 7.9 \times 10^{-17} \end{aligned}$$

Statement: The K_{sp} of zinc chloride in a saturated solution at 25 °C is 7.9×10^{-17}.

Practice

1. Write a solubility product constant equation for the following equilibrium: K/U

   $MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$

2. Write the solubility product constant equation for iron(III) hydroxide, $Fe(OH)_3(s)$. K/U
3. In a saturated solution of calcium phosphate, $Ca_3(PO_4)_2$, at 25 °C, the concentrations of the calcium ions and phosphate ions are 4.53×10^{-7} mol/L and 3.02×10^{-7} mol/L, respectively. Calculate the K_{sp} of calcium phosphate. T/I [ans: $K_{sp} = 8.48 \times 10^{-33}$]

Solubility and the Solubility Product Constant

The solubility of an ionic compound varies with the ions it contains. In general, the more highly charged the anions and cations are, the less soluble the ionic compound will be, because it takes more energy for a solvent to break the ionic bonds in the crystal lattice. Therefore, ionic compounds containing divalent ions, such as calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}), are generally less soluble than ionic compounds containing monovalent ions, such as sodium ions (Na^+) and nitrate ions (NO_3^-).

Keep in mind that the solubility of a given ionic compound is different from its solubility product constant. The solubility of an ionic compound tells us the maximum quantity that will dissolve in a given volume of solvent at a particular temperature to form a saturated solution. For example, the molar solubility of lithium carbonate, $Li_2CO_3(s)$, in water at 25 °C is 1.8×10^{-2} mol/L. Therefore, we could prepare a saturated solution of lithium carbonate by dissolving 1.3 g of solid lithium carbonate in 1000 mL of solution or 0.65 g in 500 mL of solution at 25 °C. Nevertheless, the solubility product constant of lithium carbonate at 25 °C is always 8.2×10^{-4}.

Investigation **7.6.1**

The K_{sp} of Calcium Hydroxide (page 476)

Calcium hydroxide, a compound used in the preparation of plaster and mortar, is only slightly soluble in water. In this investigation, you will prepare several solutions of calcium hydroxide, identify the one that is saturated, and use the concentrations of ions in this solution to determine the K_{sp} of calcium hydroxide.

Tutorial 2 Converting between K_{sp} and Solubility Values

Molar solubility and K_{sp} both describe the solubility of a substance, although in different ways. Therefore, it is possible to calculate the value of one if you know the value of the other.

Sample Problem 1: Calculating K_{sp} from Molar Solubility

A technician places a quantity of solid copper(I) bromide, CuBr(s), in a beaker of distilled water. The measured molar solubility of copper(I) bromide is 2.0×10^{-4} mol/L at 25 °C. Calculate the K_{sp} of copper(I) bromide at 25 °C.

Given: Molar solubility of copper(I) bromide: 2.0×10^{-4} mol/L

Required: K_{sp}

Solution:

Step 1. Write the balanced equation for the solubility equilibrium.

$$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$$

Step 2. Write the solubility product constant equation.

$$K_{sp} = [Cu^+(aq)][Br^-(aq)]$$

Step 3. Determine the equilibrium concentrations of the dissolved ions.

From the balanced equation, you know that the molar ratio is 1:1:1, so the concentrations of these ions are equal at any point in time. Since the solubility of solid copper(I) bromide is 2.0×10^{-4} mol/L, then a maximum of 2.0×10^{-4} mol of solid copper(I) bromide can dissolve in water to produce 1.0 L of solution at 25 °C. This will form 2.0×10^{-4} mol of copper(I) ions and 2.0×10^{-4} mol of bromide ions. Therefore, the equilibrium concentrations of these ions are also equal to 2.0×10^{-4} mol/L.

Step 4. Substitute the equilibrium concentrations into the K_{sp} equation and solve for K_{sp}.

$$\begin{aligned} K_{sp} &= [Cu^+(aq)][Br^-(aq)] \\ &= (2.0 \times 10^{-4})(2.0 \times 10^{-4}) \\ K_{sp} &= 4.0 \times 10^{-8} \end{aligned}$$

Statement: The solubility product constant of copper(I) bromide at 25 °C is 4.0×10^{-8}.

Sample Problem 2: Calculating K_{sp} from Solubility Expressed in Mass per Volume

Calculate the K_{sp} value for bismuth sulfide, $Bi_2S_3(s)$, which has a solubility of 4.68×10^{-14} g/100 mL at 25 °C.

Given: Solubility of Bi_2S_3: 4.68×10^{-14} g/100 mL

Required: K_{sp} of Bi_2S_3

Solution:

Step 1. Write the balanced equation.

$$Bi_2S_3(s) \rightleftharpoons 2\,Bi^{3+}(aq) + 3\,S^{2-}(aq)$$

Step 2. Write the solubility product constant equation.

$$K_{sp} = [Bi^{3+}(aq)]^2[S^{2-}(aq)]^3$$

Step 3. Determine the equilibrium concentrations in mol/L of the dissolved ions. Use an ICE table (**Table 1**). Since the concentration of solid Bi_2S_3 remains constant, it is not included.

Table 1 ICE Table for Calculating Equilibrium Concentrations

	$Bi_2S_3(s)$ $\rightleftharpoons$	$2\ Bi^{3+}(aq)$ +	$3\ S^{2-}(aq)$
I	—	0	0
C	—	$+2x$	$+3x$
E	—	$2x$	$3x$

Step 4. Calculate all concentrations in mol/L.

To convert given mass solubility of solid bismuth sulfide to molar solubility, first calculate the molar mass of bismuth sulfide. Then, use the molar mass to convert mass solubility to molar solubility.

$$\text{molar mass of } Bi_2S_3 = (2)\left(208.98\ \frac{\text{g}}{\text{mol}}\right) + (3)\left(32.07\ \frac{\text{g}}{\text{mol}}\right)$$

$$\text{molar mass of } Bi_2S_3 = 514.17\ \text{g/mol}$$

$$\text{molar solubility of } Bi_2S_3 = \frac{4.68 \times 10^{-14}\ \cancel{\text{g}}}{100\ \cancel{\text{mL}}} \times \frac{1\ \text{mol}}{514.17\ \cancel{\text{g}}} \times \frac{1000\ \cancel{\text{mL}}}{1\ \text{L}}$$

$$\text{molar solubility of } Bi_2S_3 = 9.10 \times 10^{-16}\ \text{mol/L}$$

Step 5. Write the K_{sp} equation using the expressions in the ICE table, and then substitute the molar solubility of solid bismuth sulfide for x.

$$\begin{aligned} K_{sp} &= [Bi^{3+}(aq)]^2[S^{2-}(aq)]^3 \\ &= (2x)^2(3x)^3 \\ &= 2^2 3^3 x^5 \\ &= 108(9.10 \times 10^{-16})^5 \\ K_{sp} &= 6.74 \times 10^{-74} \end{aligned}$$

Statement: The solubility product constant of solid bismuth sulfide is 6.74×10^{-74}.

Sample Problem 3: Calculating Molar Solubility from K_{sp}

The solubility product constant of solid copper(II) iodate, $Cu(IO_3)_2(s)$, is 6.9×10^{-8} at 25 °C. Calculate the molar solubility of solid copper(II) iodate at 25 °C.

Given: K_{sp} of $Cu(IO_3)_2(s) = 6.9 \times 10^{-8}$

Required: molar solubility of $Cu(IO_3)_2(s)$ at 25 °C

Solution:

Step 1. Write the balanced chemical equation.

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ IO_3^-(aq)$$

Step 2. Write the solubility product constant equation.

$$K_{sp} = [Cu^{2+}(aq)][IO_3^-(aq)]^2$$

Step 3. Determine the equilibrium concentrations in mol/L of the dissolved ions.

Use an ICE table (**Table 2**).

Table 2 ICE Table for Calculating Equilibrium Concentrations

	$Cu(IO_3)_2(s)$ $\rightleftharpoons$	$Cu^{2+}(aq)$ +	$2\ IO_3^-(aq)$
I	—	0	0
C	—	$+x$	$+2x$
E	—	x	$2x$

Step 4. Substitute the equilibrium concentration expressions from the ICE table into the K_{sp} equation and solve for x.

$x = 2.5 \times 10^{-3}$

Statement: The molar solubility of copper(II) iodate at 25 °C is 2.5×10^{-3} mol/L.

Practice

1. The solubility of magnesium fluoride, $MgF_2(s)$, is 1.72×10^{-3} g/100 mL at 25 °C. What is the K_{sp} value for magnesium fluoride at 25 °C? T/I [ans: 8.41×10^{-11}]
2. Calculate the molar solubility of silver iodide, AgI(s), at 25 °C. Its K_{sp} value at this temperature is 8.5×10^{-17}. T/I [ans: 9.2×10^{-9} mol/L]
3. The K_{sp} of zinc hydroxide, $Zn(OH)_2(s)$, is 7.7×10^{-17} at 25 °C. What is its molar solubility at this temperature? T/I [ans: 2.7×10^{-6} mol/L]
4. Which has a greater solubility, mercury(I) chloride or copper(I) chloride? (Refer to Table 1 in Appendix B4.) Support your answer with calculations. T/I

Predicting Precipitation

What happens when two aqueous solutions containing dissolved ions are mixed? In some cases, ions will combine and form an ionic compound with low solubility, which then precipitates from the solution. For example, **Figure 3** shows what happens when a solution of potassium chromate, $K_2CrO_4(aq)$, is mixed with a solution of silver nitrate, $AgNO_3(aq)$. The reddish-brown precipitate is silver chromate, $Ag_2CrO_4(s)$. Could we have predicted if a precipitate of silver chromate would form before mixing these solutions? Solubility is a complex property and difficult to predict. The only reliable way to know if an ionic compound is soluble is to do the experiment. Solubility tables, such as **Table 3**, summarize the results of many such experiments.

Figure 3 A yellow solution of potassium chromate, $K_2CrO_4(aq)$, mixes with a colourless solution of silver nitrate, $AgNO_3(aq)$. A reddish-brown precipitate of silver chromate, $Ag_2CrO_4(s)$, forms as the solutions mix.

Table 3 Solubility of Some Ionic Compounds at SATP

	Cations	
Anions	**high solubility $\geq$ 0.1 mol/L at SATP**	**low solubility < 0.1 mol/L at SATP**
F^-	most	Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Fe^{2+}, $Hg_2^{\ 2+}$, Pb^{2+}
Cl^-, Br^-, I^-	most	Ag^+, Pb^{2+}, Tl^+, $Hg_2^{\ 2+}$, Hg^+, Cu^+
S^{2-}	Group 1, Group 2, $NH_4^{\ +}$	most
OH^-	Group 1, $NH_4^{\ +}$, Sr^{2+}, Ba^{2+}, Tl^+	most
$SO_4^{\ 2-}$	most	Ag^+, Pb^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Ra^{2+}
$CO_3^{\ 2-}$, $PO_4^{\ 3-}$, $SO_3^{\ 2-}$	Group 1, $NH_4^{\ +}$	most
$C_2H_3O_2^{\ -}$	most	Ag^+
$NO_3^{\ -}$	all	none
$IO_3^{\ -}$	$NH_4^{\ +}$, K^+, Na^+	most

It should also come as no surprise that a given cation may be quite soluble when paired with a particular anion, but be insoluble when paired with another. Even though Table 3 does not show all possible ion combinations, we can see important solubility trends and exceptions. For example, only the nitrate ion, $NO_3^{\ -}$, always forms a soluble compound. All other ions will form a highly soluble compound when combined with some ions but a compound of low solubility when paired with others.

To predict if a precipitate will form when two aqueous solutions are mixed, we can first use a solubility table to predict if any ionic compounds will form that will be of low solubility. For example, suppose you intend to mix an aqueous solution of sodium chloride, $NaCl(aq)$, with an aqueous solution of silver nitrate, $AgNO_3(aq)$. From Table 3, you see that these two ionic compounds are both highly soluble in water. They will dissolve in water according to the following net ionic equations:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$
$$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3^{\ -}(aq)$$

When you mix these two solutions, the combined solution therefore will contain aqueous sodium ions, chloride ions, silver ions, and nitrate ions. Table 3 shows that sodium chloride and all salts containing the nitrate ion are highly soluble in water. Therefore, dissolved sodium ions will not react with dissolved nitrate ions to produce a solid sodium nitrate precipitate. Silver chloride, however, has a low solubility in water. Therefore, when you mix sodium chloride solution and silver nitrate solution, a precipitate of silver chloride may form while the sodium and nitrate ions remain in solution (**Figure 4**). Whether a precipitate actually forms depends on the concentrations of the silver ions and the chloride ions in the solution.

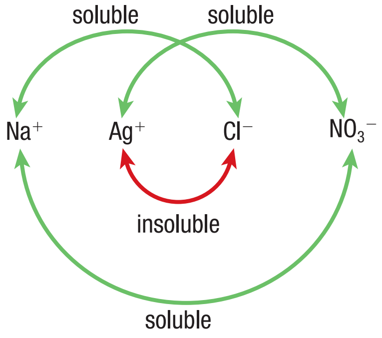


Figure 4 In a solution containing aqueous sodium, silver, chloride, and nitrate ions, only the combination of silver and chloride ions is likely to form a precipitate.

trial ion product (Q) the product of the concentrations of ions in a specific solution raised to powers equal to their coefficients in the balanced chemical equation; can be used to predict the formation of a precipitate

When we know the concentrations of ions in aqueous solution, we can use a quantitative method to predict whether a precipitate will form. The **trial ion product (Q)** is the reaction quotient applied to the initial ion concentrations of a slightly soluble ionic compound. We get a value for the trial ion product by multiplying the concentrations of ions in a specific solution raised to powers equal to their coefficients in a balanced chemical equation. For example, the dissolution equilibrium system of solid calcium fluoride, $CaF_2(s)$, is represented by the following balanced equation:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Note that we always write the equilibrium reaction equation so that the dissolution reaction occurs to the right. The trial ion product equation for the dissolution of solid calcium fluoride is

$$Q = [Ca^{2+}(aq)][F^-(aq)]^2$$

If we add a solution containing $Ca^{2+}(aq)$ ions to a solution containing $F^-(aq)$ ions, whether a precipitate will form depends on the concentrations of these ions in the combined solution. To calculate the trial ion product, we substitute the initial concentrations of $Ca^{2+}(aq)$ and $F^-(aq)$ ions into the trial ion product equation. Then, we compare the value of the trial ion product, Q, with the solubility product constant, K_{sp}. The following rules are used to predict whether precipitation will occur:

- If Q is greater than K_{sp}, the dissolution equilibrium system shifts to the left. Precipitation occurs and will continue until the solution reaches a new equilibrium.
- If Q is less than K_{sp}, the dissolution equilibrium system will shift to the right, and no precipitation occurs. The solution is unsaturated, so more solid can dissolve.
- If Q is equal to K_{sp}, the solution is at equilibrium. No precipitation or overall change in concentration will occur.

UNIT TASK **BOOKMARK**

How could you use information about predicting whether a precipitate will form as you work on the Unit Task on page 582?

Tutorial 3 Predicting whether a Precipitate Will Form

You can use a solubility table, such as Table 3, as a qualitative tool to predict if a precipitate is likely to form when aqueous solutions of ions are mixed. Comparing the trial ion product with the solubility product constant allows you to predict quantitatively if a precipitate will form when solutions of known concentrations of ions are mixed.

Sample Problem 1: Predicting Precipitation when Mixing Aqueous Solutions

A student is planning to combine a 1.0×10^{-3} mol/L aqueous solution of silver nitrate, $AgNO_3(aq)$, with a 5.0×10^{-3} mol/L aqueous solution of potassium bromide, KBr(aq) at 25 °C. Will a precipitate form when the solutions are mixed? If so, identify the precipitate.

Given: $[AgNO_3(aq)] = 1.0 \times 10^{-3}$ mol/L; $[KBr(aq)] = 5.0 \times 10^{-3}$ mol/L

Required: To predict if a precipitate will form and identify any predicted precipitate

Solution:

Step 1. Identify all of the ions that will be present in the mixture.

$AgNO_3(aq)$ will contribute aqueous ions of silver, $Ag^+(aq)$, and nitrate, $NO_3^-(aq)$.

KBr(aq) will contribute aqueous ions of potassium, $K^+(aq)$, and bromide, $Br^-(aq)$.

All four ions will be in the mixture: $Ag^+(aq)$, $NO_3^-(aq)$, $K^+(aq)$, and $Br^-(aq)$.

Step 2. Use the solubility rules in Table 3 to predict if a precipitate may form.

Table 3 indicates that $KNO_3(s)$ is highly soluble and that AgBr(s) has low solubility. Therefore, a precipitate of solid silver bromide, AgBr(s), may form.

Step 3. Determine the concentrations of the ions that may react to form a precipitate.

First, write the balanced dissolution equations for $AgNO_3(s)$ and KBr(s):

$$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3^-(aq)$$

$$KBr(s) \rightarrow K^+(aq) + Br^-(aq)$$

From these balanced equations, you can see that both dissolution reactions have a 1:1:1 molar ratio. Therefore, you know that the concentrations of both ions are equal to the given concentrations of the ionic compounds. Therefore,

$$[Ag^+(aq)] = [AgNO_3(aq)]$$

$$[Ag^+(aq)] = 1.0 \times 10^{-3}\text{ mol/L}$$

and

$$[Br^-(aq)] = [KBr(aq)]$$

$$[Br^-(aq)] = 5.0 \times 10^{-3}\text{ mol/L}$$

Step 4. Determine the trial ion product equation of the precipitate that may form.

You have determined that AgBr(s) may precipitate. First, write a balanced equation for the dissolution equilibrium system of AgBr(s).

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

Remember that you must write the balanced equation so that the dissolution reaction occurs to the right. From the balanced equation, the trial ion product equation is

$$Q = [Ag^+(aq)][Br^-(aq)]$$

Step 5. Calculate Q by substituting the concentrations of the dissolved ions in the mixture into the trial ion product equation.

$$Q = [Ag^+(aq)][Br^-(aq)]$$

$$= (1.0 \times 10^{-3}\text{ mol/L})(5.0 \times 10^{-3}\text{ mol/L})$$

$$Q = 5.0 \times 10^{-6}$$

Step 6. Compare the K_{sp} and Q values of the compound that may precipitate, and then predict if the position of this dissolution equilibrium system will shift and whether a precipitate will form.

From Table 1 in Appendix B4,

$$K_{sp}\text{ of }AgBr(s) = 5.4 \times 10^{-13}$$

$$Q = 5.0 \times 10^{-6}$$

Q is greater than K_{sp}, so the dissolution equilibrium system will shift to the left and a precipitate of AgBr(s) will form.

Statement: A precipitate of solid silver bromide, AgBr(s), will form when the two solutions are mixed.

Sample Problem 2: Predicting Precipitation when Mixing Aqueous Solutions

A student mixes 750.0 mL of an aqueous solution of magnesium nitrate, $Mg(NO_3)_2(aq)$, with 300.0 mL of ammonium hydroxide, $NH_4OH(aq)$. The concentration of the initial magnesium nitrate solution is 4.00×10^{-3} mol/L and of the initial ammonium hydroxide solution is 2.00×10^{-2} mol/L. Will a precipitate form? If so, identify the precipitate.

Given: $V_{Mg(NO_3)_2} = 750.0\text{ mL}$; $[Mg(NO_3)_2(aq)] = 4.00 \times 10^{-3}\text{ mol/L}$; $V_{NH_4OH} = 300.0\text{ mL}$; $[NH_4OH(aq)] = 2.00 \times 10^{-2}\text{ mol/L}$

Required: Predict if a precipitate will form and identify any predicted precipitate.

Solution:

Step 1. Identify all of the ions in the solution before any reaction occurs.

The initial $Mg(NO_3)_2(aq)$ solution and initial $NH_4OH(aq)$ solution will contribute these four ions to the mixture: $Mg^{2+}(aq)$, $NO_3^-(aq)$, $NH_4^+(aq)$, and $OH^-(aq)$.

Step 2. Use the solubility rules in Table 3 to predict if a precipitate may form.

Table 3 indicates that solid ammonium nitrate, $NH_4NO_3(s)$, is highly soluble and that solid magnesium hydroxide, $Mg(OH)_2(s)$, has low solubility. Therefore, a precipitate of $Mg(OH)_2(s)$ may form when the two initial solutions are mixed.

Step 3. Determine the concentrations of the ions that may react to form a precipitate.

$$Mg(NO_3)_2(s) \rightarrow Mg^{2+}(aq) + 2\,NO_3^-(aq)$$

$$NH_4OH(s) \rightarrow NH_4^+(aq) + OH^-(aq)$$

Since each dissolution reaction has a 1:1 mole ratio, the initial concentrations of both ions are the same as the given concentrations of the respective ionic compound. Therefore,

$$[Mg^{2+}(aq)]_{initial} = 4.00 \times 10^{-3}\text{ mol/L}$$

$$[OH^-(aq)]_{initial} = 2.00 \times 10^{-2}\text{ mol/L}$$

These concentrations are the concentration of $Mg^{2+}(aq)$ ions in the initial $Mg(NO_3)_2(aq)$ solution and the concentration of $OH^-(aq)$ in the initial $NH_4OH(aq)$ solution *before* these solutions are mixed. When the initial solutions are mixed, the volume of the final mixture, V_f, increases and is the sum of the volumes of the two initial solutions.

$$V_f = V_{Mg(NO_3)_2} + V_{NH_4OH}$$
$$= 750.0\text{ mL} + 300.0\text{ mL}$$
$$V_f = 1050.0\text{ mL}$$

The increase in volume reduces the concentration of the ions. Use the dilution formula to calculate the concentrations of Mg^{2+}(aq) and OH^-(aq) in the final mixture.

$$c_cV_c = c_dV_d$$
$$c_d = \frac{c_cV_c}{V_d}$$

where c_c is the initial, concentrated, ion concentration and c_d is the final, more dilute, ion concentration. V_c and V_d are the corresponding volumes.

Substitute the appropriate values for Mg^{2+}(aq) into the dilution equation.

$$[Mg^{2+}(aq)]_{final} = (4.00 \times 10^{-3}\text{ mol/L})\left(\frac{750.0\ \cancel{\text{mL}}}{1050\ \cancel{\text{mL}}}\right)$$
$$[Mg^{2+}(aq)]_{final} = 2.86 \times 10^{-3}\text{ mol/L}$$

Then, substitute the appropriate values for OH^-(aq) into the dilution equation.

$$[OH^-(aq)]_{final} = (2.00 \times 10^{-2}\text{ mol/L})\left(\frac{300.0\ \cancel{\text{mL}}}{1050\ \cancel{\text{mL}}}\right)$$
$$[OH^-(aq)]_{final} = 5.71 \times 10^{-3}\text{ mol/L}$$

Step 4. Determine the trial ion product equation of the precipitate that may form.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$$
$$Q = [Mg^{2+}(aq)][OH^-(aq)]^2$$

Step 5. Calculate Q.

$$Q = [Mg^{2+}(aq)_{final}][OH^-(aq)_{final}]^2$$
$$= (2.86 \times 10^{-3})(5.71 \times 10^{-3})^2$$
$$Q = 9.32 \times 10^{-8}$$

Step 6. Compare the K_{sp} and Q values of the compound that may precipitate, and then predict if the position of this dissolution equilibrium system will shift and whether a precipitate will form.

From the Table 1 in Appendix B4,

K_{sp} of $Mg(OH)_2 = 5.6 \times 10^{-12}$

$Q = 9.32 \times 10^{-8}$

Since Q is greater than K_{sp}, the dissolution equilibrium system shifts to the left and precipitation occurs.

Statement: A precipitate of $Mg(OH)_2$(s) will form when these solutions are mixed.

Practice

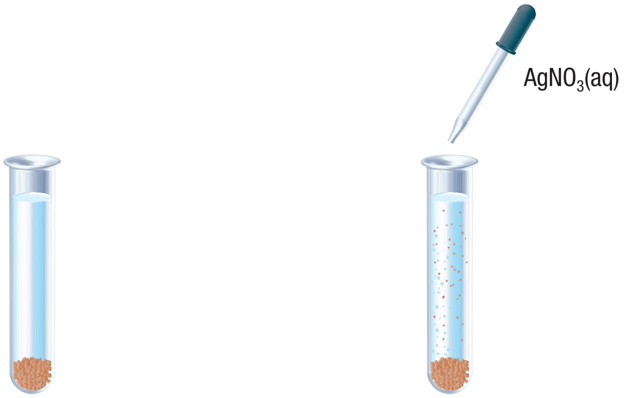
1. Will a precipitate form in an aqueous solution in which the concentration of copper(I) nitrate, $CuNO_3$(aq), is 0.015 mol/L and the concentration of potassium iodide, KI(aq), is 0.075 mol/L? Explain. T/I
2. A scientist mixes 100.0 mL of a 0.0500 mol/L aqueous solution of lead(II) nitrate, $Pb(NO_3)_2$(aq), with 200.0 mL of a 0.100 mol/L aqueous solution of sodium iodide, NaI(aq). Will solid lead(II) iodide, PbI_2(s), precipitate? Explain your answer. T/I
3. Predict whether a calcium hydroxide precipitate, $Ca(OH)_2$(s), will form when 250.0 mL of a 0.0025 mol/L aqueous solution of calcium chloride, $CaCl_2$, is mixed with 300.0 mL of a 0.0015 mol/L aqueous potassium hydroxide solution. Explain your reasoning. T/I
4. Will a precipitate form if a student mixes 100.0 mL of an aqueous solution of 0.100 mol/L calcium chloride, $CaCl_2$(aq), with 100.0 mL of an aqueous solution of 0.0400 mol/L sodium sulfate, Na_2SO_4(aq)? If so, identify the precipitate. T/I

The Common Ion Effect

The position of a solubility equilibrium system can be shifted by changing the temperature, the concentration of the dissolved ions, or both. Now that we can predict if a given set of ion concentrations will produce a precipitate or stay dissolved in solution, we are ready to investigate how we can influence a dissolution equilibrium system. How can a chemist shift a dissolution equilibrium system to favour more precipitate (reactants) or more dissolved ions (products)? A dissolution equilibrium system is just a specific type of a chemical equilibrium, so all the techniques that shift general reaction equilibrium systems can be applied to dissolution equilibrium systems. Consider a saturated solution of silver chromate, Ag_2CrO_4(aq), in equilibrium with a small quantity of undissolved silver chromate, Ag_2CrO_4(s).

$$Ag_2CrO_4(s) \rightleftharpoons 2\ Ag^+(aq) + CrO_4^{2-}(aq)$$

We may use Le Châtelier's principle to predict what will happen if we add a few drops of silver nitrate solution, $AgNO_3(aq)$, to the equilibrium mixture. Silver nitrate solution contains silver ions, $Ag^+(aq)$, and nitrate ions, $NO_3^-(aq)$. Since they are not part of the equilibrium system, the nitrate ions will not affect the equilibrium position. However, the additional silver ions will increase the concentration of silver ions in solution (a product) and shift the equilibrium to the left, toward the reactant. This leftward equilibrium shift may cause solid silver chromate, $Ag_2CrO_4(s)$, to precipitate (**Figure 5**). A precipitate will form only if the new concentrations of aqueous silver ions and chromate ions push the equilibrium system past the solubility limit represented by the solubility product constant, K_{sp}. We can determine if this will happen by comparing the trial ion product, Q, with the solubility product constant. WEB LINK



(a) $Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4^{2-}(aq)$ **(b)** $Ag_2CrO_4(s) \xleftarrow{\text{shift}} 2\,Ag^+(aq) + CrO_4^{2-}(aq)$

Figure 5 The common ion effect. (a) A solution of silver chromate is in equilibrium with solid silver chromate. (b) When silver nitrate is added to the solution, the extra silver ion shifts the equilibrium to the left, causing more silver chromate to precipitate.

In this example, the equilibrium shifted to the left because the saturated silver chromate solution and the silver nitrate solution both contained aqueous silver ions. We could expect a similar result if we added a solution that contained chromate ions, $CrO_4^{2-}(aq)$. In general, we can predict that adding a solution that contains a common ion will shift a dissolution equilibrium system toward the solid and may cause some of the ions to precipitate from solution. Lowering the solubility of an ionic compound by the addition of a common ion is called the **common ion effect**.

The common ion effect does not occur only in solutions of substances with low solubility. Highly soluble substances also demonstrate the common ion effect. For example, if you added hydrochloric acid to a saturated solution of sodium chloride, a sodium chloride precipitate might form.

common ion effect a reduction in the solubility of an ionic compound due to the presence of a common ion in solution

Tutorial 4 Calculating the Effect of Common Ions

The amount of an ionic compound that can dissolve in a solution decreases if mixed with a second solution that contains a common ion. You can calculate this effect quantitatively by using the molar solubility values and the solubility product constant, K_{sp}.

Sample Problem 1: Calculating the Molar Solubility of Solid Calcium Fluoride

Calculate the molar solubility of solid calcium fluoride, $CaF_2(s)$, in a 0.025 mol/L solution of sodium fluoride, $NaF(aq)$, at 25 °C. That is, determine the maximum amount of solid calcium fluoride that will dissolve into the aqueous sodium fluoride solution, noting that the two solutions have a common ion.

Solution:

Step 1. Identify the common ion.

The ion present in both $CaF_2(s)$ and NaF(s) is the fluoride ion, $F^-(aq)$.

Step 2. Determine the concentration in mol/L of the common ion in solution before any solid is dissolved.

You need to find the concentration of $F^-(aq)$ in the NaF(aq) solution before $CaF_2(s)$ was added. Table 3 indicates that NaF(s) has high solubility and dissolves completely in water to form $Na^+(aq)$ and $F^-(aq)$ ions.

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

Since the ions dissolve in a 1:1 molar ratio, the concentrations of sodium and fluoride ions are equal to the concentration of the NaF(aq) solution.

$[Na^+(aq)] = 0.025$ mol/L

$[F^-(aq)] = 0.025$ mol/L

Step 3. Determine the concentration in mol/L of the common ion once the solid has dissolved.

Table 3 indicates that $CaF_2(s)$ has a low solubility in water at 25 °C. Therefore, it will establish a dynamic equilibrium in solution.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

If the $CaF_2(s)$ were dissolving in pure water, you could calculate molar solubility the same way you did in Tutorial 2. However, the $CaF_2(s)$ is being dissolved in solution that already contains some $F^-(aq)$ ions. Therefore, the $CaF_2(s)$ equilibrium will shift to the left relative to its position in pure water and so you should expect less $CaF_2(s)$ to dissolve in the NaF(aq) solution than in pure water. The final concentration of $F^-(aq)$ ions will be equal to the initial concentration (0.025 mol/L) plus the change in concentration caused by adding $CaF_2(s)$ to the solution. **Table 4** is an ICE table summarizing these changes.

Table 4 ICE Table for Calculating Equilibrium Concentrations

	$CaF_2(s)$	$\rightleftharpoons$	**$Ca^{2+}(aq)$**	+	**$2\,F^-(aq)$**
I	—		0		0.025
C	—		$+x$		$+2x$
E	—		x		$0.025 + 2x$

Step 4. Write the equation for the solubility product, K_{sp}, and substitute in the value of K_{sp} for $CaF_2(s)$ from Table 1 in Appendix B4, and the equilibrium concentration expressions from the ICE table. Solve for x.

$$\begin{aligned} K_{sp} &= [Ca^{2+}(aq)][F^-(aq)]^2 \\ 4.0 \times 10^{-11} &= (x)(0.025 + 2x)^2 \\ x &= \frac{4.0 \times 10^{-11}}{(0.025 + 2x)^2} \end{aligned}$$

Since $CaF_2(s)$ has a very low solubility, the amount of $F^-(aq)$ ions that the $CaF_2(s)$ will add to the solution will be very small compared to the 0.025 mol/L provided by the NaF(aq) solution. You can therefore make the simplifying assumption that $0.025 + 2x \approx 0.025$.

$$\begin{aligned} x &\approx \frac{4.0 \times 10^{-11}}{(0.025)^2} \\ &\approx \frac{4.0 \times 10^{-11}}{6.25 \times 10^{-4}} \\ x &\approx 6.4 \times 10^{-8} \text{ mol/L} \end{aligned}$$

Since x represents the amount of calcium ions that can dissolve in this equilibrium system and there is a 1:1 ratio of calcium ions to solid calcium fluoride, then x is also the solubility of $CaF_2(s)$. Since this value is nearly 5 orders of magnitude smaller than the initial concentration of $F^-(aq)$, you know the simplifying assumption was warranted.

Statement: The molar solubility of calcium fluoride in this solution is 6.4×10^{-8} mol/L.

Practice

1. Make a prediction about the solubility of silver acetate in each of the following: pure water, 0.001 mol/L of silver nitrate, 0.01 mol/L of silver nitrate, 0.001 mol/L of sodium acetate, and 0.01 mol/L of sodium nitrate. Explain your reasoning. T/I
2. The K_{sp} of solid silver chloride, AgCl(s), is 1.8×10^{-10} at 25 °C. T/I A
   (a) What is the molar solubility of solid silver chloride in pure water? [ans: 1.3×10^{-5} mol/L]
   (b) What is the molar solubility of solid silver chloride in a 0.10 mol/L aqueous solution of sodium chloride? [ans: 1.8×10^{-9} mol/L]
   (c) Compare your answers to (a) and (b) and determine if they make sense. Explain.
3. What amount of solid lead (II) chloride, $PbCl_2(s)$, can dissolve in 1.00 L of a 0.200 mol/L aqueous solution of lithium chloride, LiCl(aq)? T/I [ans: 3.0×10^{-4} mol]

7.6 Review

Summary

- A solubility equilibrium is a heterogeneous equilibrium system between a solid ionic compound and its ions dissolved in a saturated aqueous solution.
- The solubility product constant, K_{sp}, is the value of the equilibrium law equation for a solubility equilibrium and does not include the concentration of the solid. K_{sp} varies with temperature and the nature of the ionic solid.
- The trial ion product, Q, is the reaction quotient applied to the ion concentrations of a slightly soluble ionic compound.
- The common ion effect explains why the solubility of an ionic compound may decrease when a common ion is added to the equilibrium system.

Questions

1. What is the difference between molar solubility and the product solubility constant, K_{sp}? K/U
2. What is a common ion? How does its presence affect solubility? Why? K/U
3. (a) Show the balanced equation for the solubility equilibrium that would occur when a solution of barium nitrate, $Ba(NO_3)_2(aq)$, is mixed with a solution of sodium sulfate, $Na_2SO_4(aq)$.
   (b) Write the solubility product constant equation for this equilibrium system. K/U
4. Which is less soluble in water, solid silver chloride, AgCl(s), with a solubility product constant, K_{sp}, of 1.8×10^{-10}, or solid silver bromide, AgBr(s), with a K_{sp} of 5.0×10^{-13}? Explain. K/U
5. Calculate the solubility product constant at 25 °C for silver iodide, AgI(s), given that its solubility at this temperature is 2.14×10^{-7} g/100 mL. T/I
6. Calculate the molar solubility of solid zinc hydroxide, $Zn(OH)_2(s)$, at 25 °C, using the K_{sp} value given in Appendix B4. T/I
7. A student prepares a solution containing 0.01 mol/L calcium nitrate, $Ca(NO_3)_2(aq)$, and 0.025 mol/L sodium phosphate, $Na_3PO_4(aq)$. Will a precipitate form when the student makes this solution? If so, identify the precipitate. T/I
8. A chemist adds 100.0 mL of 4.0×10^{-4} mol/L magnesium nitrate, $Mg(NO_3)_2(aq)$, solution to 100.0 mL of 2.0×10^{-3} mol/L sodium hydroxide, NaOH(aq), solution. Will a precipitate form? Justify your answer. T/I
9. Calculate the molar solubility of solid silver chromate, $Ag_2CrO_4(s)$, in 0.10 mol/L sodium chromate, Na_2CrO_4 (aq). T/I
10. Describe the relationship between the solubility product constant, K_{sp}, and the trial ion product, Q. T/I
11. A water treatment plant tests the water and determines that there are high levels of phosphate in the water.
    (a) What are two solutions that could be used to precipitate out the phosphate from the water? A
    (b) Use Le Châtelier's principle to explain how adding these solutions causes a decrease in the phosphate ion concentration. K/U T/I
12. The formation of stalactites and stalagmites in limestone caves (**Figure 6**) is an example of solubility equilibrium in the natural environment. Investigate the formation of stalactites and stalagmites in terms of solubility equilibrium and K_{sp}. Write a short essay to summarize your findings. C A

WEB LINK

Figure 6 Cueva del Vienta in the Guajataca Forest Reserve, Puerto Rico