

## 15.1: Precipitation and Dissolution

### Learning Objectives

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

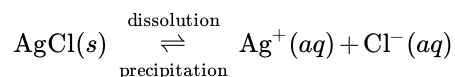
The preservation of medical laboratory blood samples, mining of sea water for magnesium, formulation of over-the-counter medicines such as Milk of Magnesia and antacids, and treating the presence of hard water in your home's water supply are just a few of the many tasks that involve controlling the equilibrium between a slightly soluble ionic solid and an aqueous solution of its ions.

In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the  $\text{CO}_3^{2-}$  ions produced in this process help soothe an upset stomach.

In this section, we will find out how we can control the dissolution of a slightly soluble ionic solid by the application of Le Chatelier's principle. We will also learn how to use the equilibrium constant of the reaction to determine the concentration of ions present in a solution.

### 15.1.1: The Solubility Product Constant

Silver chloride is what's known as a sparingly soluble ionic solid (Figure 15.1.1). Recall from the solubility rules in an earlier chapter that halides of  $\text{Ag}^+$  are not normally soluble. However, when we add an excess of solid  $\text{AgCl}$  to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions in equilibrium with undissolved silver chloride:



This equilibrium, like other equilibria, is dynamic; some of the solid  $\text{AgCl}$  continues to dissolve, but at the same time,  $\text{Ag}^+$  and  $\text{Cl}^-$  ions in the solution combine to produce an equal amount of the solid. At equilibrium, the opposing processes have equal rates.

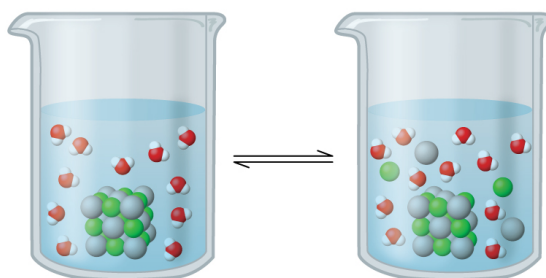
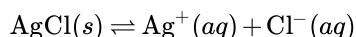


Figure 15.1.1: Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions in equilibrium with undissolved silver chloride.

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is called the solubility product ( $K_{\text{sp}}$ ) of the solid. Recall from the chapter on solutions and colloids that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:



with

$$K_{\text{sp}} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)]$$

When looking at dissolution reactions such as this, the solid is listed as a reactant, whereas the ions are listed as products. The solubility product constant, as with every equilibrium constant expression, is written as the product of the concentrations of each of

the ions, raised to the power of their stoichiometric coefficients. Here, the solubility product constant is equal to  $\text{Ag}^+$  and  $\text{Cl}^-$  when a solution of silver chloride is in equilibrium with undissolved  $\text{AgCl}$ . There is no denominator representing the reactants in this equilibrium expression since the reactant is a pure solid; therefore  $[\text{AgCl}]$  does not appear in the expression for  $K_{\text{sp}}$ .

Table 15.1.1: Common Solubility Products by Decreasing Equilibrium Constants

Substance	$K_{\text{sp}}$ at 25 °C
$\text{CuCl}$	$1.2 \times 10^{-6}$
$\text{CuBr}$	$6.27 \times 10^{-9}$
$\text{AgI}$	$1.5 \times 10^{-16}$
$\text{PbS}$	$7 \times 10^{-29}$
$\text{Al}(\text{OH})_3$	$2 \times 10^{-32}$
$\text{Fe}(\text{OH})_3$	$4 \times 10^{-38}$

Some common solubility products are listed in Table 15.1.1 according to their  $K_{\text{sp}}$  values, whereas a more extensive compilation of products appears in Table E3. Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small  $K_{\text{sp}}$  represents a system in which the equilibrium lies to the left, so that relatively few hydrated ions would be present in a saturated solution.

### ✓ Example 15.1.1: Writing Equations and Solubility Products

Write the ionic equation for the dissolution and the solubility product expression for each of the following slightly soluble ionic compounds:

- $\text{AgI}$ , silver iodide, a solid with antiseptic properties
- $\text{CaCO}_3$ , calcium carbonate, the active ingredient in many over-the-counter chewable antacids
- $\text{Mg}(\text{OH})_2$ , magnesium hydroxide, the active ingredient in Milk of Magnesia
- $\text{Mg}(\text{NH}_4)\text{PO}_4$ , magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium
- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , the mineral apatite, a source of phosphate for fertilizers

(Hint: When determining how to break (d) and (e) up into ions, refer to the list of polyatomic ions in the section on chemical nomenclature.)

#### Solution

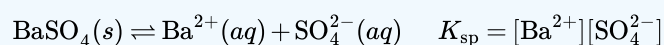
- $\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq) \quad K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$
- $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$
- $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \quad K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$
- $\text{Mg}(\text{NH}_4)\text{PO}_4(s) \rightleftharpoons \text{Mg}^{2+}(aq) + \text{NH}_4^+(aq) + \text{PO}_4^{3-}(aq) \quad K_{\text{sp}} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}]$
- $\text{Ca}_5(\text{PO}_4)_3\text{OH}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3\text{PO}_4^{3-}(aq) + \text{OH}^-(aq) \quad K_{\text{sp}} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-]$

### ? Exercise 15.1.1

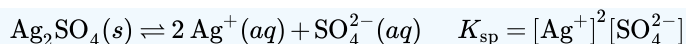
Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:

- $\text{BaSO}_4$
- $\text{Ag}_2\text{SO}_4$
- $\text{Al}(\text{OH})_3$
- $\text{Pb}(\text{OH})\text{Cl}$

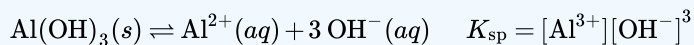
#### Answer a



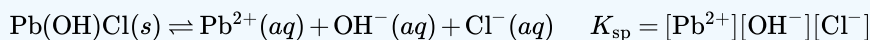
#### Answer b



**Answer c**



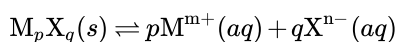
**Answer d**



Now we will extend the discussion of  $K_{\text{sp}}$  and show how the solubility product constant is determined from the solubility of its ions, as well as how  $K_{\text{sp}}$  can be used to determine the molar solubility of a substance.

### 15.1.2: $K_{\text{sp}}$ and Solubility

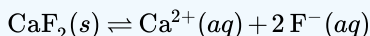
Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:



In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its molar solubility.

#### ✓ Example 15.1.2: Calculation of $K_{\text{sp}}$ from Equilibrium Concentrations

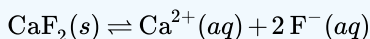
We began the chapter with an informal discussion of how the mineral fluorite is formed. Fluorite,  $\text{CaF}_2$ , is a slightly soluble solid that dissolves according to the equation:



The concentration of  $\text{Ca}^{2+}$  in a saturated solution of  $\text{CaF}_2$  is  $2.1 \times 10^{-4} \text{ M}$ ; therefore, that of  $\text{F}^-$  is  $4.2 \times 10^{-4} \text{ M}$ , that is, twice the concentration of  $\text{Ca}^{2+}$ . What is the solubility product of fluorite?

#### **Solution**

First, write out the  $K_{\text{sp}}$  expression, then substitute in concentrations and solve for  $K_{\text{sp}}$ :



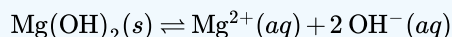
A saturated solution is a solution at equilibrium with the solid. Thus:

$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}][\text{F}^-]^2 \\ &= (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 \\ &= 3.7 \times 10^{-11} \end{aligned}$$

As with other equilibrium constants, we do not include units with  $K_{\text{sp}}$ .

#### ? Exercise 15.1.2

In a saturated solution that is in contact with solid  $\text{Mg}(\text{OH})_2$ , the concentration of  $\text{Mg}^{2+}$  is  $3.7 \times 10^{-5} \text{ M}$ . What is the solubility product for  $\text{Mg}(\text{OH})_2$ ?



#### **Answer**

$$2.0 \times 10^{-13}$$

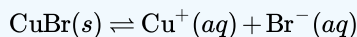
### ✓ Example 15.1.3: Determination of Molar Solubility from $K_{sp}$

The  $K_{sp}$  of copper(I) bromide, CuBr, is  $6.3 \times 10^{-9}$ . Calculate the molar solubility of copper bromide.

#### Solution

The solubility product constant of copper(I) bromide is  $6.3 \times 10^{-9}$ .

The reaction is:



First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [\text{Cu}^+][\text{Br}^-]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the CuBr column empty as it is a solid and does not contribute to the  $K_{sp}$ :

	CuBr	$\rightleftharpoons$	Cu <sup>+</sup>	+	Br <sup>-</sup>
Initial concentration (M)			0		0
Change (M)			x		x
Equilibrium concentration (M)			0 + x = x		0 + x = x

At equilibrium:

$$\begin{aligned}
 K_{sp} &= [\text{Cu}^+][\text{Br}^-] \\
 6.3 \times 10^{-9} &= (x)(x) = x^2 \\
 x &= \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5}
 \end{aligned}$$

Therefore, the molar solubility of CuBr is  $7.9 \times 10^{-5} M$ .

### ✓ Exercise 15.1.3

The  $K_{sp}$  of AgI is  $1.5 \times 10^{-16}$ . Calculate the molar solubility of silver iodide.

#### Answer

$$1.2 \times 10^{-8} M$$

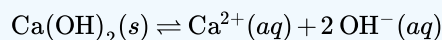
### ✓ Example 15.1.4: Determination of Molar Solubility from $K_{sp}$ , Part II

Determination of Molar Solubility from  $K_{sp}$ , Part II The  $K_{sp}$  of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , is  $8.0 \times 10^{-6}$ . Calculate the molar solubility of calcium hydroxide.

#### Solution

The solubility product constant of calcium hydroxide is  $1.3 \times 10^{-6}$ .

The reaction is:



First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

Create an ICE table, leaving the  $\text{Ca}(\text{OH})_2$  column empty as it is a solid and does not contribute to the  $K_{sp}$ :

	$\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$		
Initial concentration (M)		0	0
Change (M)		x	2x
Equilibrium concentration (M)		$0 + x = x$	$0 + 2x = 2x$

At equilibrium:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$

$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3}$$

Therefore, the molar solubility of  $\text{Ca(OH)}_2$  is  $6.9 \times 10^{-3} \text{ M}$ .

#### ✓ Exercise 15.1.4

The  $K_{\text{sp}}$  of  $\text{PbI}_2$  is  $1.4 \times 10^{-8}$ . Calculate the molar solubility of lead(II) iodide.

**Answer**

$$1.5 \times 10^{-3} \text{ M}$$

Note that solubility is not always given as a molar value. When the solubility of a compound is given in some unit other than moles per liter, we must convert the solubility into moles per liter (i.e., molarity) in order to use it in the solubility product constant expression. Example 15.1.5 shows how to perform those unit conversions before determining the solubility product equilibrium.

#### ✓ Example 15.1.5: Determination of $K_{\text{sp}}$ from Gram Solubility

Many of the pigments used by artists in oil-based paints (Figure 15.1.2) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow,  $\text{PbCrO}_4$ , is  $4.6 \times 10^{-6} \text{ g/L}$ . Determine the solubility product equilibrium constant for  $\text{PbCrO}_4$ .

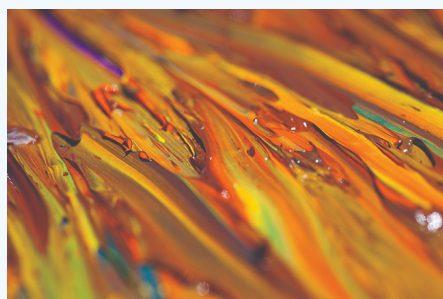
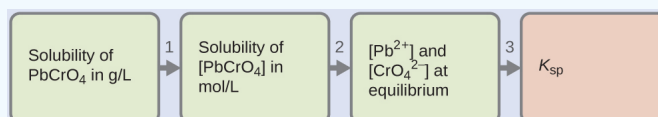


Figure 15.1.2: Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ( $\text{PbCrO}_4$ ), examples include Prussian blue ( $\text{Fe}_7(\text{CN})_{18}$ ), the reddish-orange color vermilion ( $\text{HgS}$ ), and green color veridian ( $\text{Cr}_2\text{O}_3$ ). (credit: Sonny Abesamis)

#### Solution

We are given the solubility of  $\text{PbCrO}_4$  in grams per liter. If we convert this solubility into moles per liter, we can find the equilibrium concentrations of  $\text{Pb}^{2+}$  and  $\text{CrO}_4^{2-}$ , then  $K_{\text{sp}}$ :



1. Use the molar mass of  $\text{PbCrO}_4$   $\left(\frac{323.2 \text{ g}}{1 \text{ mol}}\right)$  to convert the solubility of  $\text{PbCrO}_4$  in grams per liter into moles per liter:

$$[\text{PbCrO}_4] = \frac{4.6 \times 10^{-6} \text{ g PbCrO}_4}{1 \text{ L}} \times \frac{1 \text{ mol PbCrO}_4}{323.2 \text{ g PbCrO}_4}$$

$$= \frac{1.4 \times 10^{-8} \text{ mol PbCrO}_4}{1 \text{ L}}$$

$$= 1.4 \times 10^{-8} \text{ M}$$

- The chemical equation for the dissolution indicates that 1 mol of  $\text{PbCrO}_4$  gives 1 mol of  $\text{Pb}^{2+}(\text{aq})$  and 1 mol of  $\text{CrO}_4^{2-}(\text{aq})$ :  
 $\text{PbCrO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$

Thus, both  $[\text{Pb}^{2+}]$  and  $[\text{CrO}_4^{2-}]$  are equal to the molar solubility of  $\text{PbCrO}_4$ :

$$[\text{Pb}^{2+}] = [\text{CrO}_4^{2-}] = 1.4 \times 10^{-8} \text{ M}$$

- Solve.  $K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$

### ? Exercise 15.1.5

The solubility of  $\text{TlCl}$  [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.46 grams per liter at 20 °C. What is its solubility product?

**Answer**

$$2.08 \times 10^{-4}$$

### ✓ Example 15.1.6: Calculating the Solubility of $\text{Hg}_2\text{Cl}_2$

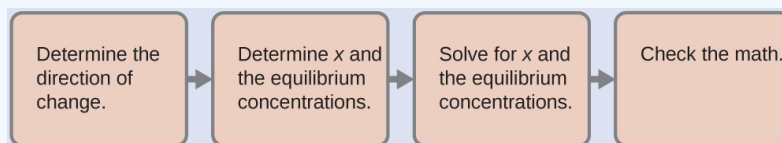
Calomel,  $\text{Hg}_2\text{Cl}_2$ , is a compound composed of the diatomic ion of mercury(I),  $\text{Hg}_2^{2+}$ , and chloride ions,  $\text{Cl}^-$ . Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel is quite insoluble:



Calculate the molar solubility of  $\text{Hg}_2\text{Cl}_2$ .

#### Solution

The molar solubility of  $\text{Hg}_2\text{Cl}_2$  is equal to the concentration of  $\text{Hg}_2^{2+}$  ions because for each 1 mol of  $\text{Hg}_2\text{Cl}_2$  that dissolves, 1 mol of  $\text{Hg}_2^{2+}$  forms:



- Determine the direction of change. Before any  $\text{Hg}_2\text{Cl}_2$  dissolves,  $Q$  is zero, and the reaction will shift to the right to reach equilibrium.
- Determine  $x$  and equilibrium concentrations. Concentrations and changes are given in the following ICE table:

	$\text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg}_2^{2+} + 2\text{Cl}^-$		
Initial concentration (M)		0	0
Change (M)		$x$	$2x$
Equilibrium concentration (M)		$0 + x = x$	$0 + 2x = 2x$

Note that the change in the concentration of  $\text{Cl}^-$  ( $2x$ ) is twice as large as the change in the concentration of  $\text{Hg}_2^{2+}$  ( $x$ ) because 2 mol of  $\text{Cl}^-$  forms for each 1 mol of  $\text{Hg}_2^{2+}$  that forms.  $\text{Hg}_2\text{Cl}_2$  is a pure solid, so it does not appear in the calculation.

3. *Solve for  $x$  and the equilibrium concentrations.* We substitute the equilibrium concentrations into the expression for  $K_{\text{sp}}$  and calculate the value of  $x$ :

$$\begin{aligned} K_{\text{sp}} &= [\text{Hg}_2^{2+}][\text{Cl}^-]^2 \\ 1.1 \times 10^{-18} &= (x)(2x)^2 \\ 4x^3 &= 1.1 \times 10^{-18} \\ x &= \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} = 6.5 \times 10^{-7} \text{ M} \end{aligned}$$

So the concentrations are

$$\begin{aligned} [\text{Hg}_2^{2+}] &= 6.5 \times 10^{-7} \text{ M} = 6.5 \times 10^{-7} \text{ M} \\ [\text{Cl}^-] &= 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6} \text{ M} \end{aligned}$$

The molar solubility of  $\text{Hg}_2\text{Cl}_2$  is equal to  $[\text{Hg}_2^{2+}]$ , or  $6.5 \times 10^{-7} \text{ M}$ .

#### Check the work.

At equilibrium,  $Q = K_{\text{sp}}$ :

$$Q = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (6.5 \times 10^{-7})(1.3 \times 10^{-6})^2 = 1.1 \times 10^{-18}$$

The calculations check.

#### ? Exercise 15.1.6

Determine the molar solubility of  $\text{MgF}_2$  from its solubility product:  $K_{\text{sp}} = 6.4 \times 10^{-9}$ .

#### Answer

$$1.2 \times 10^{-3} \text{ M}$$

Tabulated  $K_{\text{sp}}$  values can also be compared to reaction quotients calculated from experimental data to tell whether a solid will precipitate in a reaction under specific conditions:  $Q$  equals  $K_{\text{sp}}$  at equilibrium; if  $Q$  is less than  $K_{\text{sp}}$ , the solid will dissolve until  $Q$  equals  $K_{\text{sp}}$ ; if  $Q$  is greater than  $K_{\text{sp}}$ , precipitation will occur at a given temperature until  $Q$  equals  $K_{\text{sp}}$ .

#### 📌 Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the  $K_{\text{sp}}$  of barium sulfate is  $1.1 \times 10^{-10}$ , very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 15.1.3).

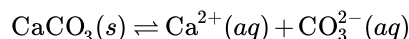


Figure 15.1.3: The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by “glitzy queen00”/Wikimedia Commons).

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

### 15.1.3: Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

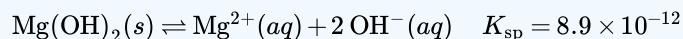


We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ( $Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$ ) is equal to the solubility product ( $K_{\text{sp}} = 4.8 \times 10^{-9}$ ). If we mix a solution of calcium nitrate, which contains  $\text{Ca}^{2+}$  ions, with a solution of sodium carbonate, which contains  $\text{CO}_3^{2-}$  ions, the slightly soluble ionic solid  $\text{CaCO}_3$  will precipitate, provided that the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions are such that  $Q$  is greater than  $K_{\text{sp}}$  for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of  $Q$  equals  $K_{\text{sp}}$ . A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that  $Q$  is less than  $K_{\text{sp}}$ , then the solution is not saturated and no precipitate will form.

We can compare numerical values of  $Q$  with  $K_{\text{sp}}$  to predict whether precipitation will occur, as Example 15.1.7 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

#### ✓ Example 15.1.7: Precipitation of $\text{Mg}(\text{OH})_2$

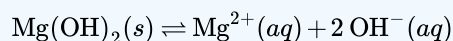
The first step in the preparation of magnesium metal is the precipitation of  $\text{Mg}(\text{OH})_2$  from sea water by the addition of lime,  $\text{Ca}(\text{OH})_2$ , a readily available inexpensive source of  $\text{OH}^-$  ion:



The concentration of  $\text{Mg}^{2+}(aq)$  in sea water is 0.0537 M. Will  $\text{Mg}(\text{OH})_2$  precipitate when enough  $\text{Ca}(\text{OH})_2$  is added to give a  $[\text{OH}^-]$  of 0.0010 M?

#### Solution

This problem asks whether the reaction:





shifts to the left and forms solid  $\text{Mg}(\text{OH})_2$  when  $[\text{Mg}^{2+}] = 0.0537 \text{ M}$  and  $[\text{OH}^-] = 0.0010 \text{ M}$ . The reaction shifts to the left if  $Q$  is greater than  $K_{\text{sp}}$ . Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because  $Q$  is greater than  $K_{\text{sp}}$  ( $Q = 5.4 \times 10^{-8}$  is larger than  $K_{\text{sp}} = 8.9 \times 10^{-12}$ ), we can expect the reaction to shift to the left and form solid magnesium hydroxide.  $\text{Mg}(\text{OH})_2(\text{s})$  forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of  $Q$  is equal to  $K_{\text{sp}}$ .

### ? Exercise 15.1.7

Use the solubility products in Table E3 to determine whether  $\text{CaHPO}_4$  will precipitate from a solution with  $[\text{Ca}^{2+}] = 0.0001 \text{ M}$  and  $[\text{HPO}_4^{2-}] = 0.001 \text{ M}$ .

#### Answer

No precipitation of  $\text{CaHPO}_4$ ;  $Q = 1 \times 10^{-7}$ , which is less than  $K_{\text{sp}}$

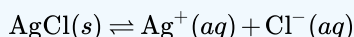
### ✓ Example 15.1.8: Precipitation of $\text{AgCl}$ upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a  $2.0 \times 10^{-4} \text{ M}$  solution of  $\text{AgNO}_3$  and a  $2.0 \times 10^{-4} \text{ M}$  solution of  $\text{NaCl}$  are mixed?

(Note: The solution also contains  $\text{Na}^+$  and  $\text{NO}_3^-$  ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

#### Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:



The solubility product is  $1.8 \times 10^{-10}$  (Table E3).

$\text{AgCl}$  will precipitate if the reaction quotient calculated from the concentrations in the mixture of  $\text{AgNO}_3$  and  $\text{NaCl}$  is greater than  $K_{\text{sp}}$ . The volume doubles when we mix equal volumes of  $\text{AgNO}_3$  and  $\text{NaCl}$  solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing,  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$  are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4}) \text{ M} = 1.0 \times 10^{-4} \text{ M}$$

The reaction quotient,  $Q$ , is *momentarily* greater than  $K_{\text{sp}}$  for  $\text{AgCl}$ , so a supersaturated solution is formed:

$$Q = [\text{Ag}^+][\text{Cl}^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{\text{sp}}$$

Since supersaturated solutions are unstable,  $\text{AgCl}$  will precipitate from the mixture until the solution returns to equilibrium, with  $Q$  equal to  $K_{\text{sp}}$ .

### ? Exercise 15.1.8

Will  $\text{KClO}_4$  precipitate when 20 mL of a  $0.050 \text{ M}$  solution of  $\text{K}^+$  is added to 80 mL of a  $0.50 \text{ M}$  solution of  $\text{ClO}_4^-$ ? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

#### Answer

No,  $Q = 4.0 \times 10^{-3}$ , which is less than  $K_{\text{sp}} = 1.07 \times 10^{-2}$

In the previous two examples, we have seen that  $\text{Mg}(\text{OH})_2$  or  $\text{AgCl}$  precipitate when  $Q$  is greater than  $K_{\text{sp}}$ . In general, when a solution of a soluble salt of the  $\text{M}^{m+}$  ion is mixed with a solution of a soluble salt of the  $\text{X}^{n-}$  ion, the solid,  $\text{M}_p\text{X}_q$  precipitates if the value of  $Q$  for the mixture of  $\text{M}^{m+}$  and  $\text{X}^{n-}$  is greater than  $K_{\text{sp}}$  for  $\text{M}_p\text{X}_q$ . Thus, if we know the concentration of one of the ions of a

slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

### ✓ Example 15.1.9: Precipitation of Calcium Oxalate

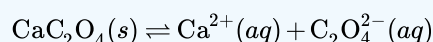
Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ , for this purpose (Figure 15.1.4). At sufficiently high concentrations, the calcium and oxalate ions form solid,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (which also contains water bound in the solid). The concentration of  $\text{Ca}^{2+}$  in a sample of blood serum is  $2.2 \times 10^{-3} \text{ M}$ . What concentration of  $\text{C}_2\text{O}_4^{2-}$  ion must be established before  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  begins to precipitate?



Figure 15.1.4: Anticoagulants can be added to blood that will combine with the  $\text{Ca}^{2+}$  ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

### Solution

The equilibrium expression is:



For this reaction (Table E3):

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 1.96 \times 10^{-8}$$

$\text{CaC}_2\text{O}_4$  does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid  $\text{CaC}_2\text{O}_4$  does not begin to form until  $Q$  equals  $K_{\text{sp}}$ . Because we know  $K_{\text{sp}}$  and  $[\text{Ca}^{2+}]$ , we can solve for the concentration of  $\text{C}_2\text{O}_4^{2-}$  that is necessary to produce the first trace of solid:

$$\begin{aligned} Q = K_{\text{sp}} &= [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 1.96 \times 10^{-8} \\ (2.2 \times 10^{-3})[\text{C}_2\text{O}_4^{2-}] &= 1.96 \times 10^{-8} \\ [\text{C}_2\text{O}_4^{2-}] &= \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6} \end{aligned}$$

A concentration of  $[\text{C}_2\text{O}_4^{2-}] = 8.9 \times 10^{-6} \text{ M}$  is necessary to initiate the precipitation of  $\text{CaC}_2\text{O}_4$  under these conditions.

### ? Exercise 15.1.9

If a solution contains 0.0020 mol of  $\text{CrO}_4^{2-}$  per liter, what concentration of  $\text{Ag}^+$  ion must be reached by adding solid  $\text{AgNO}_3$  before  $\text{Ag}_2\text{CrO}_4$  begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

### Answer

$$4.5 \times 10^{-9} \text{ M}$$

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of  $K_{\text{sp}}$  and the concentration of one ion in solution, we can calculate the

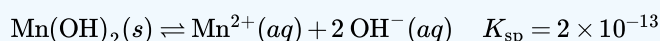
concentration of the second ion remaining in solution. The calculation is of the same type as that in Example 15.1.8—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

#### ✓ Example 15.1.10: Concentrations Following Precipitation

Clothing washed in water that has a manganese  $[\text{Mn}^{2+}(\text{aq})]$  concentration exceeding 0.1 mg/L ( $1.8 \times 10^{-6} \text{ M}$ ) may be stained by the manganese upon oxidation, but the amount of  $\text{Mn}^{2+}$  in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide,  $\text{Mn}(\text{OH})_2$ , what pH is required to keep  $[\text{Mn}^{2+}]$  equal to  $1.8 \times 10^{-6} \text{ M}$ ?

#### Solution

The dissolution of  $\text{Mn}(\text{OH})_2$  is described by the equation:



We need to calculate the concentration of  $\text{OH}^{-}$  when the concentration of  $\text{Mn}^{2+}$  is  $1.8 \times 10^{-6} \text{ M}$ . From that, we calculate the pH. At equilibrium:

$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^{-}]^2$$

or

$$(1.8 \times 10^{-6})[\text{OH}^{-}]^2 = 2 \times 10^{-13}$$

so

$$[\text{OH}^{-}] = 3.3 \times 10^{-4} \text{ M}$$

Now we calculate the pH from the pOH:

$$\text{pOH} = -\log[\text{OH}^{-}] = -\log(3.3 \times 10^{-4}) = 3.48$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.48 = 10.52$$

If the person doing laundry adds a base, such as the sodium silicate ( $\text{Na}_4\text{SiO}_4$ ) in some detergents, to the wash water until the pH is raised to 10.52, the manganese ion will be reduced to a concentration of  $1.8 \times 10^{-6} \text{ M}$ ; at that concentration or less, the ion will not stain clothing.

#### ? Exercise 15.1.10

The first step in the preparation of magnesium metal is the precipitation of  $\text{Mg}(\text{OH})_2$  from sea water by the addition of  $\text{Ca}(\text{OH})_2$ . The concentration of  $\text{Mg}^{2+}(\text{aq})$  in sea water is  $5.37 \times 10^{-2} \text{ M}$ . Calculate the pH at which  $[\text{Mg}^{2+}]$  is diminished to  $1.0 \times 10^{-5} \text{ M}$  by the addition of  $\text{Ca}(\text{OH})_2$ .

#### Answer

10.97

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though  $\text{AgCl}$  ( $K_{\text{sp}} = 1.6 \times 10^{-10}$ ),  $\text{AgBr}$  ( $K_{\text{sp}} = 5.0 \times 10^{-13}$ ), and  $\text{AgI}$  ( $K_{\text{sp}} = 1.5 \times 10^{-16}$ ) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding  $\text{Ag}^{+}$  to a solution of  $\text{Cl}^{-}$ ,  $\text{Br}^{-}$ , and  $\text{I}^{-}$ ; essentially all of the  $\text{AgI}$  will precipitate before any of the other solid halides form because of its smaller value for  $K_{\text{sp}}$ . However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of  $\text{Cl}^{-}$ ,  $\text{Br}^{-}$ , and  $\text{I}^{-}$  to a solution of  $\text{Ag}^{+}$ .

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller  $K_{\text{sp}}$ ) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the  $K_{\text{sp}}$  values of the two compounds differ

by two orders of magnitude or more (e.g.,  $10^{-2}$  vs.  $10^{-4}$ ), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of selective precipitation, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

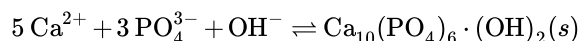
### 15.1.4: The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 15.1.5). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions ( $\text{PO}_4^{2-}$ ) are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.



Figure 15.1.5: Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, known as lime,  $\text{Ca}(\text{OH})_2$ . The lime is converted into calcium carbonate, a strong base, in the water. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , which then precipitates out of the solution:



The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of  $\text{CO}_2$  in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

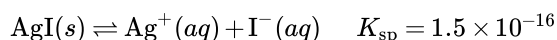
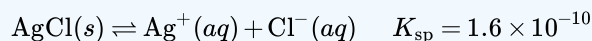
Selective precipitation can also be used in qualitative analysis. In this method, reagents are added to an unknown chemical mixture in order to induce precipitation. Certain reagents cause specific ions to precipitate out; therefore, the addition of the reagent can be used to determine whether the ion is present in the solution.

#### ✓ Example 15.1.11: Precipitation of Silver Halides

A solution contains 0.0010 mol of  $\text{KI}$  and 0.10 mol of  $\text{KCl}$  per liter.  $\text{AgNO}_3$  is gradually added to this solution. Which forms first, solid  $\text{AgI}$  or solid  $\text{AgCl}$ ?

#### Solution

The two equilibria involved are:



If the solution contained about *equal* concentrations of  $\text{Cl}^-$  and  $\text{I}^-$ , then the silver salt with the smallest  $K_{\text{sp}}$  ( $\text{AgI}$ ) would precipitate first. The concentrations are not equal, however, so we should find the  $[\text{Ag}^+]$  at which  $\text{AgCl}$  begins to precipitate and the  $[\text{Ag}^+]$  at which  $\text{AgI}$  begins to precipitate. The salt that forms at the lower  $[\text{Ag}^+]$  precipitates first.

For  $\text{AgI}$ :  $\text{AgI}$  precipitates when  $Q$  equals  $K_{\text{sp}}$  for  $\text{AgI}$  ( $1.5 \times 10^{-16}$ ). When  $[\text{I}^-] = 0.0010 \text{ M}$ :

$$Q = [\text{Ag}^+][\text{I}^-] = [\text{Ag}^+](0.0010) = 1.5 \times 10^{-16}$$

$$[\text{Ag}^+] = \frac{1.5 \times 10^{-16}}{0.0010} = 1.5 \times 10^{-13}$$

AgI begins to precipitate when  $[Ag^+]$  is  $1.5 \times 10^{-13} M$ .

For AgCl: AgCl precipitates when  $Q$  equals  $K_{sp}$  for AgCl ( $1.6 \times 10^{-10}$ ). When  $[Cl^-] = 0.10 M$ :

$$Q_{sp} = [Ag^+][Cl^-] = [Ag^+](0.10) = 1.6 \times 10^{-10}$$

$$[Ag^+] = \frac{1.6 \times 10^{-10}}{0.10} = 1.6 \times 10^{-9} M$$

AgCl begins to precipitate when  $[Ag^+]$  is  $1.6 \times 10^{-9} M$ .

AgI begins to precipitate at a lower  $[Ag^+]$  than AgCl, so AgI begins to precipitate first.

### ? Exercise 15.1.11

If silver nitrate solution is added to a solution which is  $0.050 M$  in both  $Cl^-$  and  $Br^-$  ions, at what  $[Ag^+]$  would precipitation begin, and what would be the formula of the precipitate?

#### Answer

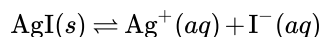
$[Ag^+] = 1.0 \times 10^{-11} M$ ; AgBr precipitates first

### 15.1.5: Common Ion Effect

As we saw when we discussed buffer solutions, the hydronium ion concentration of an aqueous solution of acetic acid decreases when the strong electrolyte sodium acetate,  $NaCH_3CO_2$ , is added. We can explain this effect using Le Chatelier's principle. The addition of acetate ions causes the equilibrium to shift to the left, decreasing the concentration of  $H_3O^+$  to compensate for the increased acetate ion concentration. This increases the concentration of  $CH_3CO_2H$ :



Because sodium acetate and acetic acid have the acetate ion in common, the influence on the equilibrium is called **the common ion effect**. The common ion effect can also have a direct effect on solubility equilibria. Suppose we are looking at the reaction where silver iodide is dissolved:



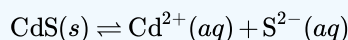
If we were to add potassium iodide (KI) to this solution, we would be adding a substance that shares a common ion with silver iodide. Le Chatelier's principle tells us that when a change is made to a system at equilibrium, the reaction will shift to counteract that change. In this example, there would be an excess of iodide ions, so the reaction would shift toward the left, causing more silver iodide to precipitate out of solution.

### ✓ Example 15.1.12: Common Ion Effect

Calculate the molar solubility of cadmium sulfide ( $CdS$ ) in a  $0.010-M$  solution of cadmium bromide ( $CdBr_2$ ). The  $K_{sp}$  of  $CdS$  is  $1.0 \times 10^{-28}$ .

#### Solution

The first thing you should notice is that the cadmium sulfide is dissolved in a solution that contains cadmium ions. We need to use an ICE table to set up this problem and include the  $CdBr_2$  concentration as a contributor of cadmium ions:



	CdS	$\rightleftharpoons$	Cd <sup>2+</sup>	+	S <sup>2-</sup>
Initial concentration (M)			0.010		0
Change (M)			x		x
Equilibrium concentration (M)			0.010 + x		0 + x = x

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration ( M ), Change ( M ), and Equilibrium concentration ( M ). The second column has the header, “C d S equilibrium arrow C d to the second power plus S to the second power superscript negative sign.” Under the second column is a subgroup of three rows and three columns. The first column is blank. The second column has the following: 0.010, x, 0.010 plus x. The third column has the following: 0, x, 0 plus x equals x.

$$K_{sp} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$

$$(0.010 + x)(x) = 1.0 \times 10^{-28} \quad x^2 + 0.010x - 1.0 \times 10^{-28} = 0$$

We can solve this equation using the quadratic formula, but we can also make an assumption to make this calculation much simpler. Since the  $K_{sp}$  value is so small compared with the cadmium concentration, we can assume that the change between the initial concentration and the equilibrium concentration is negligible, so that  $0.010 + x \sim 0.010$ . Going back to our  $K_{sp}$  expression, we would now get:

$$\begin{aligned} K_{sp} &= [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28} \\ (0.010)(x) &= 1.0 \times 10^{-28} \\ x &= 1.0 \times 10^{-26} \end{aligned}$$

Therefore, the molar solubility of CdS in this solution is  $1.0 \times 10^{-26} \text{ M}$ .

### ? Exercise 15.1.12

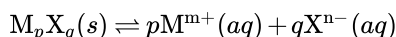
Calculate the molar solubility of aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , in a 0.015-M solution of aluminum nitrate,  $\text{Al}(\text{NO}_3)_3$ . The  $K_{sp}$  of  $\text{Al}(\text{OH})_3$  is  $2 \times 10^{-32}$ .

**Answer**

$$4 \times 10^{-11}$$

## Summary

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product,  $K_{sp}$ , of the solid. When we have a heterogeneous equilibrium involving the slightly soluble solid  $\text{M}_p\text{X}_q$  and its ions  $\text{M}^{m+}$  and  $\text{X}^{n-}$ :



We write the solubility product expression as:

$$K_{sp} = [\text{M}^{m+}]^p [\text{X}^{n-}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its  $K_{sp}$ , provided the only significant reaction that occurs when the solid dissolves is the formation of its ions. A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product. A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Chatelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

## Glossary

### common ion effect

effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

**molar solubility**

solubility of a compound expressed in units of moles per liter (mol/L)

**selective precipitation**

process in which ions are separated using differences in their solubility with a given precipitating reagent

**solubility product ( $K_{sp}$ )**

equilibrium constant for the dissolution of a slightly soluble electrolyte

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