

18.1: Solubility Product Constant, K_{sp}

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:



As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S²⁻, PO₄³⁻, and CO₃²⁻, react with water to produce OH⁻ and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as Ca₃(PO₄)₂ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2}{[\text{Ca}_3(\text{PO}_4)_2]} \quad (18.1.2)$$

$$[\text{Ca}_3(\text{PO}_4)_2]K = K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 \quad (18.1.3)$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07 × 10⁻³³, indicating that the concentrations of Ca²⁺ and PO₄³⁻ ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 18.1.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 18.1.2 and 18.1.3, changes in pH can affect the solubility of a compound as discussed later.

Note

As with K, the concentration of a pure solid does not appear explicitly in K_{sp}.

Table 18.1.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K _{sp}	Solid	Color	K _{sp}
Acetates			Iodides		
Ca(O ₂ CCH ₃) ₂ · 3H ₂ O	white	4 × 10 ⁻³	Hg ₂ I ₂ *	yellow	5.2 × 10 ⁻²⁹
Bromides			Oxalates		
AgBr	off-white	5.35 × 10 ⁻¹³	PbI ₂	yellow	9.8 × 10 ⁻⁹
Hg ₂ Br ₂ *	yellow	6.40 × 10 ⁻²³	Ag ₂ C ₂ O ₄	white	5.40 × 10 ⁻¹²
Carbonates			MgC ₂ O ₄ · 2H ₂ O	white	4.83 × 10 ⁻⁶
CaCO ₃	white	3.36 × 10 ⁻⁹	PbC ₂ O ₄	white	4.8 × 10 ⁻¹⁰
PbCO ₃	white	7.40 × 10 ⁻¹⁴	Phosphates		
Chlorides			Ag ₃ PO ₄	white	8.89 × 10 ⁻¹⁷
AgCl	white	1.77 × 10 ⁻¹⁰	Sr ₃ (PO ₄) ₂	white	4.0 × 10 ⁻²⁸
Hg ₂ Cl ₂ *	white	1.43 × 10 ⁻¹⁸	FePO ₄ · 2H ₂ O	pink	9.91 × 10 ⁻¹⁶
PbCl ₂	white	1.70 × 10 ⁻⁵	Sulfates		
Chromates			Ag ₂ SO ₄	white	1.20 × 10 ⁻⁵
CaCrO ₄	yellow	7.1 × 10 ⁻⁴	BaSO ₄	white	1.08 × 10 ⁻¹⁰
PbCrO ₄	yellow	2.8 × 10 ⁻¹³	PbSO ₄	white	2.53 × 10 ⁻⁸
Fluorides			Sulfides		
BaF ₂	white	1.84 × 10 ⁻⁷	Ag ₂ S	black	6.3 × 10 ⁻⁵⁰
PbF ₂	white	3.3 × 10 ⁻⁸	CdS	yellow	8.0 × 10 ⁻²⁷
Hydroxides			PbS	black	8.0 × 10 ⁻²⁸
Ca(OH) ₂	white	5.02 × 10 ⁻⁶	ZnS	white	1.6 × 10 ⁻²⁴
Cu(OH) ₂	pale blue	1 × 10 ⁻¹⁴			
Mn(OH) ₂	light pink	1.9 × 10 ⁻¹³			
Cr(OH) ₃	gray-green	6.3 × 10 ⁻³¹			
Fe(OH) ₃	rust red	2.79 × 10 ⁻³⁹			

*These contain the Hg₂²⁺ ion.

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} , like K , is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $\text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2$. Image used with permission from Wikipedia.

Example 18.1.1

Calcium oxalate monohydrate [$\text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$, also written as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$] is a sparingly soluble salt that is the other major component of kidney stones [along with $\text{Ca}_3(\text{PO}_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp} .

Given: solubility in g/100 mL

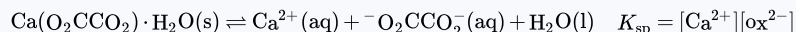
Asked for: K_{sp}

Strategy:

- A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.
 B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp} .

Solution:

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:



Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine $[\text{Ca}^{2+}]$ and $[\text{ox}^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4} \text{ g}}{146.1 \text{ g/mol}} = 5.04 \times 10^{-6} \text{ mol Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6} \text{ mol Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}}{100 \text{ mL}} \right) \left(\frac{1000 \text{ mL}}{1.00 \text{ L}} \right) = 5.04 \times 10^{-5} \text{ mol/L} = 5.04 \times 10^{-5} \text{ M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [\text{Ca}^{2+}][\text{ox}^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9} \quad (18.1.4)$$

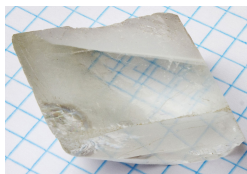
In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

Exercise 18.1.1

One crystalline form of calcium carbonate (CaCO_3) is the mineral sold as “calcite” in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp} .

Answer: 4.5×10^{-9}

The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.



A crystal of calcite (CaCO_3), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. Image used with permission from Wikipedia

Calcite, a structural material for many organisms, is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 18.1.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (**ICE Tables**), remembering that the concentration of the pure solid is essentially constant.

Example 18.1.2

We saw that the K_{sp} for $\text{Ca}_3(\text{PO}_4)_2$ is 2.07×10^{-33} at 25°C . Calculate the aqueous solubility of $\text{Ca}_3(\text{PO}_4)_2$ in terms of the following:

- the molarity of ions produced in solution
- the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

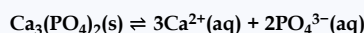
Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

- Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C .
- Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

- The dissolution equilibrium for $\text{Ca}_3(\text{PO}_4)_2$ (Equation 18.1.2) is shown in the following **ICE table**. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $\text{Ca}_3(\text{PO}_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in moles per liter, then the change in $[\text{Ca}^{2+}]$ will be $+3x$, and the change in $[\text{PO}_4^{3-}]$ will be $+2x$. We can insert these values into the table.



	$\text{Ca}_3(\text{PO}_4)_2$	$[\text{Ca}^{2+}]$	$[\text{PO}_4^{3-}]$
initial	pure solid	0	0
change	–	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $\text{Ca}_3(\text{PO}_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3x)^3(2x)^2 \quad (18.1.5)$$

$$2.07 \times 10^{-33} = 108x^5 \quad (18.1.6)$$

$$1.92 \times 10^{-35} = x^5 \quad (18.1.7)$$

$$1.14 \times 10^{-7} \text{ M} = x \quad (18.1.8)$$

This is the molar solubility of calcium phosphate at 25°C . However, the molarity of the ions is $2x$ and $3x$, which means that $[\text{PO}_4^{3-}] = 2.28 \times 10^{-7}$ and $[\text{Ca}^{2+}] = 3.42 \times 10^{-7}$.

- To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7} \text{ mol}}{1 \text{ L}}\right) 100 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) \left(\frac{310.18 \text{ g Ca}_3(\text{PO}_4)_2}{1 \text{ mol}}\right) = 3.54 \times 10^{-6} \text{ g Ca}_3(\text{PO}_4)_2$$

Exercise 18.1.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C . Calculate the following:

- the molarity of a saturated solution
- the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer:

- $1.28 \times 10^{-4} \text{ M}$
- 3.54 mg

The Ion Product

The **ion product (Q)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (Q) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

▮ *The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.*

As summarized in Figure 18.1.1 "The Relationship between ", there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

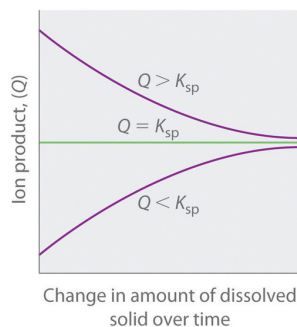


Figure 18.1.1: The Relationship between Q and K_{sp} . If Q is less than K_{sp} , the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp} , the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 18.1.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C , so it is ideally suited for this purpose because of its low solubility when a “barium milkshake” is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M BaCl_2 ? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

- Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp} .
- Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).
- Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution:

A The only slightly soluble salt that can be formed when these two solutions are mixed is BaSO_4 because NaCl is highly soluble. The equation for the precipitation of BaSO_4 is as follows:



The solubility product expression is as follows:

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product— $Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ —using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of BaCl_2 solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\begin{aligned} \text{moles Ba}^{2+} &= 100 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}} \right) = 3.2 \times 10^{-5} \text{ mol Ba}^{2+} \\ [\text{Ba}^{2+}] &= \left(\frac{3.2 \times 10^{-5} \text{ mol Ba}^{2+}}{110 \text{ mL}} \right) \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) = 2.9 \times 10^{-4} \text{ M Ba}^{2+} \end{aligned}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\begin{aligned} \text{moles SO}_4^{2-} &= 10.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.0020 \text{ mol}}{1 \text{ L}} \right) = 2.0 \times 10^{-5} \text{ mol SO}_4^{2-} \\ [\text{SO}_4^{2-}] &= \left(\frac{2.0 \times 10^{-5} \text{ mol SO}_4^{2-}}{110 \text{ mL}} \right) \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) = 1.8 \times 10^{-4} \text{ M SO}_4^{2-} \end{aligned}$$

We can now calculate Q :

$$Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (2.9 \times 10^{-4})(1.8 \times 10^{-4}) = 5.2 \times 10^{-8}$$

C We now compare Q with the K_{sp} . If $Q > K_{sp}$, then BaSO_4 will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that BaSO_4 will precipitate when the two solutions are mixed. In fact, BaSO_4 will continue to precipitate until the system reaches equilibrium, which occurs when $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

Exercise 18.1.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11} . If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5} M solution of $\text{Ca}(\text{NO}_3)_2$, will CaF_2 precipitate?

Answer: yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed.