

16.2: Ionic Equilibria between Solids and Solutions

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 more advanced chemistry courses, basic anions, such as S^{2-} , PO_4^{3-} , and CO_3^{2-} , 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 $\text{Ca}_3(\text{PO}_4)_2$ 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

$$K = \frac{[\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2}{[\text{Ca}_3(\text{PO}_4)_2]} \quad (16.2.2)$$

$$[\text{Ca}_3(\text{PO}_4)_2]K = K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 \quad (16.2.3)$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33} , indicating that the concentrations of Ca^{2+} and PO_4^{3-} 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 16.2.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 16.2.2 and 16.2.3, changes in pH can affect the solubility of a compound as discussed later.

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

Table 16.2.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	Ksp	Solid	Color	Ksp
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			PbI ₂	yellow	9.8 × 10 ⁻⁹
AgBr	off-white	5.35 × 10 ⁻¹³	Oxalates		
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		
*These contain the Hg ₂ ²⁺ ion.					

Solid	Color	K _{sp}	Solid	Color	K _{sp}
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 $\text{Ca}_3(\text{PO}_4)_2$. from Wikipedia.

✓ Example 16.2.1: Kidney Stones

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

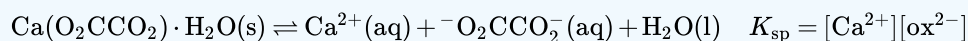
Asked for: K_{sp}

Strategy:

- Write the balanced dissolution equilibrium and the corresponding solubility product expression.
- 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 $5.04 \times 10^{-5} \text{ M}$. Inserting these values into the solubility product expression,

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

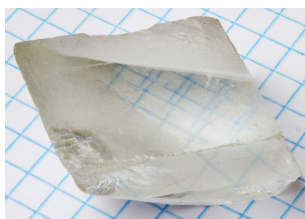
In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 16.2.1

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 16.2.1. 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 16.2.2

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}

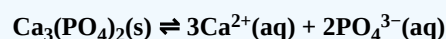
Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

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:

- A.** The dissolution equilibrium for $\text{Ca}_3(\text{PO}_4)_2$ (Equation 16.2.2) 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):

$$\begin{aligned}
 K_{sp} &= [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3x)^3 (2x)^2 \\
 2.07 \times 10^{-33} &= 108x^5 \\
 1.92 \times 10^{-35} &= x^5 \\
 1.14 \times 10^{-7} \text{ M} &= x
 \end{aligned}$$

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 $[\text{Ca}^{2+}] = 3.42 \times 10^{-7}$.

b. **B** 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 16.2.2

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 a

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

Answer a

$$3.54 \text{ mg}$$

Relating Solubilities to Solubility Constants

The *solubility* (by which we usually mean the *molar solubility*) of a solid is expressed as the concentration of the "dissolved solid" in a *saturated solution*. In the case of a simple 1:1 solid such as AgCl , this would just be the concentration of Ag^+ or Cl^- in the saturated solution. But for a more complicated stoichiometry such as silver chromate, the solubility would be only one-half of the Ag^+ concentration.

For example, let us denote the solubility of Ag_2CrO_4 as $S \text{ mol L}^{-1}$. Then for a saturated solution, we have

- $[\text{Ag}^+] = 2S$
- $[\text{CrO}_4^{2-}] = S$

Substituting this into Eq 5b above,

$$(2S)^2(S) = 4S^3 = 2.76 \times 10^{-12} \quad (16.2.4)$$

$$S = (\text{frac}K_{sp}4)^{1/3} = (6.9 \times 10^{-13})^{1/3} = 0.88 \times 10^{-4} \quad (16.2.5)$$

thus the solubility is $8.8 \times 10^{-5} \text{ M}$.

Note that the relation between the solubility and the solubility product constant depends on the stoichiometry of the dissolution reaction. For this reason it is meaningless to compare the solubilities of two salts having the formulas A_2B and AB_2 , say, on the basis of their K_s values.

It is *meaningless* to compare the solubilities of two salts having different formulas on the basis of their K_s values.

✓ Example 16.2.2

The solubility of CaF_2 (molar mass 78.1) at 18°C is reported to be 1.6 mg per 100 mL of water. Calculate the value of K_s under these conditions.

Solution

moles of solute in 100 mL; $S = 0.0016 \text{ g} / 78.1 \text{ g/mol} = 2.05 \times 10^{-5} \text{ mol}$

$$\begin{aligned} S &= \frac{2.05 \times 10^{-5} \text{ mol}}{0.100 \text{ L}} \\ &= 2.05 \times 10^{-4} \text{ M} \end{aligned}$$

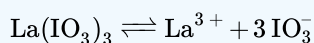
$$\begin{aligned}
 K_{sp} &= [Ca^{2+}][F^{-}]^2 \\
 &= (S)(2S)^2 \\
 &= 4 \times (2.05 \times 10^{-4})^3 \\
 &= 3.44 \times 10^{-11}
 \end{aligned}$$

✓ Example 16.2.3

Estimate the solubility of $La(IO_3)_3$ and calculate the concentration of iodate in equilibrium with solid lanthanum iodate, for which $K_s = 6.2 \times 10^{-12}$.

Solution

The equation for the dissolution is



If the solubility is S , then the equilibrium concentrations of the ions will be

$$\begin{aligned}
 [La^{3+}] &= S \text{ and } [IO_3^{-}] = 3S. \text{ Then } K_s = [La^{3+}][IO_3^{-}]^3 = S(3S)^3 = 27S^4 \\
 27S^4 &= 6.2 \times 10^{-12}, S = ((6.2 \div 27) \times 10^{-12})^{1/4} = 6.92 \times 10^{-4} \text{ M} \\
 [IO_3^{-}] &= 3S = 2.08 \times 10^{-3} \text{ (M)}
 \end{aligned}$$

✓ Example 16.2.4: Cadmium

Cadmium is a highly toxic environmental pollutant that enters wastewaters associated with zinc smelting (Cd and Zn commonly occur together in ZnS ores) and in some electroplating processes. One way of controlling cadmium in effluent streams is to add sodium hydroxide, which precipitates insoluble $Cd(OH)_2$ ($K_s = 2.5E-14$). If 1000 L of a certain wastewater contains Cd^{2+} at a concentration of $1.6E-5$ M, what concentration of Cd^{2+} would remain after addition of 10 L of 4 M NaOH solution?

Solution

As with most real-world problems, this is best approached as a series of smaller problems, making simplifying approximations as appropriate.

Volume of treated water: $1000 \text{ L} + 10 \text{ L} = 1010 \text{ L}$

Concentration of OH^{-} on addition to 1000 L of pure water:

$$(4 \text{ M}) \times (10 \text{ L}) / (1010 \text{ L}) = 0.040 \text{ M}$$

Initial concentration of Cd^{2+} in 1010 L of water:

$$(1.6 \times 10^{-5} \text{ M}) \left(\frac{100}{101} \right) \approx 1.6 \times 10^{-5} \text{ M} \quad (16.2.6)$$

The easiest way to tackle this is to start by assuming that a stoichiometric quantity of $Cd(OH)_2$ is formed — that is, *all* of the Cd^{2+} gets precipitated.

Concentrations	$[Cd^{2+}], \text{ M}$	$[OH^{-}], \text{ M}$
initial	$1.6E-5$	0.04
change	$-1.6E-5$	$-3.2E-5$
final:	0	$0.04 - 3.2E-5 \approx .04$

Now "turn on the equilibrium" — find the concentration of Cd^{2+} that can exist in a $0.04 \text{ M } OH^{-}$ solution:

Concentrations	$[Cd^{2+}], \text{ M}$	$[OH^{-}], \text{ M}$
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Concentrations	$[\text{Cd}^{2+}], \text{ M}$	$[\text{OH}^{-}], \text{ M}$
initial	0	0.04
change	+x	+2x
at equilibrium	x	.04 + 2x \approx .04

Substitute these values into the solubility product expression:

$$\text{Cd}(\text{OH})_2(s) = [\text{Cd}^{2+}] [\text{OH}^{-}]^2 = 2.5\text{E-}14$$

$$[\text{Cd}^{2+}] = (2.5\text{E-}14) / (16\text{E-}4) = 1.6\text{E-}13 \text{ M}$$

Note that the effluent will now be very alkaline:

$$pH = 14 + \log 0.04 = 12.6 \quad (16.2.7)$$

so in order to meet environmental standards an equivalent quantity of strong acid must be added to neutralize the water before it is released.

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.

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