Pearson

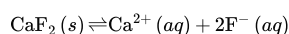# 17.5: Solubility Equilibria and the Solubility-Product Constant

Recall from Chapter 8 that a compound is considered *soluble* if it dissolves in water and *insoluble* if it does not. Recall also that the *solubility rules* in Table 8.1 allow us to classify ionic compounds simply as soluble or insoluble. Now we have the tools to examine *degrees* of solubility.

We can better understand the solubility of an ionic compound by applying the concept of equilibrium to the process of dissolution. For example, we can represent the dissolution of calcium fluoride in water as an equilibrium:

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

The equilibrium constant for a chemical equation representing the dissolution of an ionic compound is the **solubility-product constant** (K_{sp}). For CaF_2, the expression of the solubility-product constant is:

$$K_{sp} = \left[Ca^{2+}\right]\left[F^-\right]^2$$

Notice that, as we discussed in Section 15.5, solids are omitted from the equilibrium expression because the concentration of a solid is constant (it is determined by its density and does not change when more solid is added).

The value of K_{sp} is a measure of the solubility of a compound. Table 17.2 lists the values of K_{sp} for a number of ionic compounds. Appendix IIC includes a more complete list.

Table 17.2 **Selected Solubility-Product Constants (K_{sp}) at 25 °C**

Compound	Formula	K_{sp}	Compound	Fo
Barium fluoride	BaF_2	2.45×10^{-5}	Lead(II) chloride	Pb
Barium sulfate	$BaSO_4$	1.07×10^{-10}	Lead(II) bromide	Pb
Calcium carbonate	$CaCO_3$	4.96×10^{-9}	Lead(II) sulfate	Pb
Calcium fluoride	CaF_2	1.46×10^{-10}	Lead(II) sulfide*	Pb
Calcium hydroxide	$Ca(OH)_2$	4.68×10^{-6}	Magnesium carbonate	Mg
Calcium sulfate	$CaSO_4$	7.10×10^{-5}	Magnesium hydroxide	Mg
Copper(II) sulfide*	CuS	1.27×10^{-36}	Silver chloride	Ag
Iron(II) carbonate	$FeCO_3$	3.07×10^{-11}	Silver chromate	Ag
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}	Silver bromide	Ag
Iron(II) sulfide*	FeS	3.72×10^{-19}	Silver iodide	Ag

*Sulfide equilibrium is of the type: $MS(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-(aq)$.
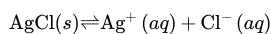
K_{sp} and Molar Solubility

Recall from Section 13.2 that the *solubility* of a compound is the quantity of the compound that dissolves in a certain amount of liquid. The **molar solubility** is the solubility in units of moles per liter (mol/L). We can calculate the molar solubility of a compound directly from K_{sp}.

Consider silver chloride:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq) \quad K_{sp} = 1.77 \times 10^{-10}$$
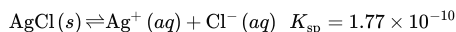
Notice that K_{sp} is *not* the molar solubility but the solubility-product constant. The solubility-product constant has only one value at a given temperature. The solubility, however, can have different values in different kinds of solutions. For example, due to the common ion effect, the solubility of AgCl in pure water is different from its solubility in an NaCl solution, even though the solubility-product constant is the same for both solutions. Notice also that the solubility of AgCl is directly related (by the reaction stoichiometry) to the amount of Ag^+ or Cl^- present in solution when equilibrium is reached. Consequently, determining molar solubility from K_{sp} involves solving an equilibrium problem.

For AgCl, we set up an ICE table for the dissolution of AgCl into its ions in pure water:

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

	$[Ag^+]$	$[Cl^-]$
Initial	0.00	0.00
Change	$+S$	$+S$
Equil	S	S

> Alternatively, we can use the variable *x* in place of *S*, as we have in other equilibrium calculations.

We let *S* represent the concentration of AgCl that dissolves (which is the molar solubility) and then represent the concentrations of the ions formed in terms of *S*. In this case, for every 1 mol of AgCl that dissolves, 1 mol of Ag^+ and 1 mol of Cl^- are produced. Therefore, the concentrations of Ag^+ and Cl^- present in solution are equal to *S*. Substituting the equilibrium concentrations of Ag^+ and Cl^- into the expression for the solubility-product constant, we get:

$$\begin{aligned} K_{sp} &= \left[Ag^+\right]\left[Cl^-\right] \\ &= S \times S \\ &= S^2 \end{aligned}$$

Therefore,

$$\begin{aligned} S &= \sqrt{K_{sp}} \\ &= \sqrt{1.77 \times 10^{-10}} \\ &= 1.33 \times 10^{-5}\,M \end{aligned}$$

The molar solubility of AgCl is 1.33×10^{-5} mol per liter.

Example 17.8 Calculating Molar Solubility from K_{sp}

Calculate the molar solubility of $PbCl_2$ in pure water.

SOLUTION   Begin by writing the reaction by which solid $PbCl_2$ dissolves into its constituent aqueous ions and write the corresponding expression for K_{sp}.

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-\,(aq)$$
$$K_{sp} = \left[Pb^{2+}\right]\left[Cl^-\right]^2$$
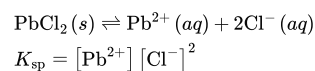
Refer to the stoichiometry of the reaction and prepare an ICE table, showing the equilibrium concentrations of Pb^{2+} and Cl^- relative to S, the amount of $PbCl_2$ that dissolves.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$
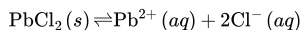
	$[Pb^{2+}]$	$[Cl^-]$
Initial	0.00	0.00
Change	$+S$	$+2S$
Equil	S	$2S$

Substitute the equilibrium expressions for $[Pb^{2+}]$ and $[Cl^-]$ from the previous step into the expression for K_{sp}.

Solve for S and substitute the numerical value of K_{sp} (from Table 17.2⬚) to calculate S.

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= S(2S)^2 = 4S^2 \end{aligned}$$

$$S = \sqrt[3]{\frac{K_{sp}}{4}}$$

$$S = \sqrt[3]{\frac{1.17 \times 10^{-5}}{4}} = 1.43 \times 10^{-2}\,M$$

FOR PRACTICE 17.8   Calculate the molar solubility of $Fe(OH)_2$ in pure water.

Interactive Worked Example 17.8   **Calculating Molar Solubility from K_{sp}**

Example 17.9 Calculating K_{sp} from Molar Solubility

The molar solubility of Ag_2SO_4 in pure water is $1.4 \times 10^{-2}\,M$. Calculate K_{sp}.

SOLUTION   Begin by writing the reaction by which solid Ag_2SO_4 dissolves into its constituent aqueous ions; then write the corresponding expression for K_{sp}.

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$
$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$
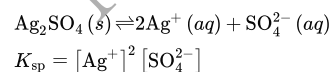
Use an ICE table to define $[Ag^+]$ and $[SO_4^{2-}]$ in terms of S, the amount of Ag_2SO_4 that dissolves.

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$
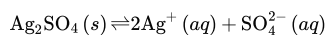
	$[Ag^+]$	$[SO_4^{2-}]$
Initial	0.00	0.00
Change	$+2S$	$+S$
Equil	$2S$	S

Substitute the expressions for $[Ag^+]$ and $[SO_4^{2-}]$ from the previous step into the expression for K_{sp}.

Substitute the given value *of the molar solubility for S and calculate* K_{sp}.

$$\begin{aligned} K_{sp} &= [Ag^+]^2 [SO_4^{2-}] \\ &= (2S)^2 S \\ &= 4S^3 \\ &= 4(1.4 \times 10^{-2})^3 \\ &= 1.1 \times 10^{-5} \end{aligned}$$

FOR PRACTICE 17.9   The molar solubility of AgBr in pure water is 7.3×10^{-7} M Calculate K_{sp}.

K_{sp} and Relative Solubility

As we have just seen, molar solubility and K_{sp} are related, and we can calculate each from the other; however, we cannot generally use the K_{sp} values of two different compounds to directly compare their relative solubilities.

For example, consider the following compounds, their K_{sp} values, and their molar solubilities:

Compound	K_{sp}	Solubility
$Mg(OH)_2$	2.06×10^{-13}	3.72×10^{-5} M
$FeCO_3$	3.07×10^{-11}	5.54×10^{-6} M

Magnesium hydroxide has a smaller K_{sp} than iron(II) carbonate but a higher molar solubility. Why? The relationship between K_{sp} and molar solubility depends on the stoichiometry of the dissociation reaction. Consequently, we can only make a direct comparison of K_{sp} values for different compounds if the compounds have the same dissociation stoichiometry.

Consider the following compounds with the same dissociation stoichiometry, their K_{sp} values, and their molar solubilities:

Compound	K_{sp}	Solubility
$Mg(OH)_2$	2.06×10^{-13}	3.72×10^{-5} M
CaF_2	1.46×10^{-10}	3.32×10^{-4} M

In this case, magnesium hydroxide and calcium fluoride have the same dissociation stoichiometry (1 mol of each compound produces 3 mol of dissolved ions); therefore, we can directly compare the K_{sp} values as a measure of relative solubility.

The Effect of a Common Ion on Solubility

How is the solubility of an ionic compound affected when the compound is dissolved in a solution that already contains one of its ions? For example, what is the solubility of CaF_2 in a solution that is 0.100 M in NaF? We can determine the change in solubility by considering the common ion effect, which we first encountered in Section 17.2. We represent the dissociation of CaF_2 in a 0.100 M NaF solution.

Common ion
0.100 M F$^-$(aq)

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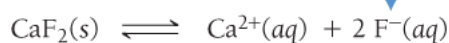
Equilibrium shifts left

In accordance with Le Châtelier's principle, the presence of the F^- ion in solution causes the equilibrium to shift to the left (compared to its position in pure water), which means that less CaF_2 dissolves—that is, its solubility is decreased:

> In general, the solubility of an ionic compound is lower in a solution containing a common ion than in pure water.

We can calculate the exact value of the solubility by working an equilibrium problem in which the concentration of the common ion is accounted for in the initial conditions, as shown in Example 17.10.

Example 17.10 Calculating Molar Solubility in the Presence of a Common Ion

What is the molar solubility of CaF_2 in a solution containing 0.100 M NaF?

SOLUTION   Begin by writing the reaction by which solid CaF_2 dissolves into its constituent aqueous ions. Write the corresponding expression for K_{sp}.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
$$K_{sp} = [Ca^{2+}][F^-]^2$$
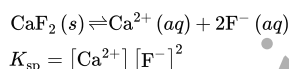
Use the stoichiometry of the reaction to prepare an ICE table showing the initial concentration of the common ion. Fill in the equilibrium concentrations of Ca^{2+} and F^- relative to S, the amount of CaF_2 that dissolves.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$
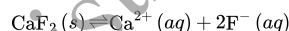
	$[Ca^{2+}]$	$[F^-]$
Initial	0.00	0.100
Change	$+S$	$+2S$
Equil	S	$0.100 + 2S$

Substitute the equilibrium expressions for $[Ca^{2+}]$ and $[F^-]$ from the previous step into the expression for K_{sp}. Since K_{sp} is small, you can make the approximation that $2S$ is much less than 0.100 and will therefore be insignificant when added to 0.100 (this is similar to the *x is small* approximation in equilibrium problems).

$$\begin{aligned} K_{sp} &= [Ca^{2+}][F^-]^2 \\ &= S(0.100 + 2S)^2 \ (S\ is\ small) \\ &= S(0.100)^2 \end{aligned}$$

Solve for S and substitute the numerical value of K_{sp} (from Table 17.2) to calculate S.

Note that the calculated value of S is indeed small compared to 0.100; your approximation is valid.

$$K_{sp} = S(0.100)^2$$
$$S = \frac{K_{sp}}{} = \frac{1.46 \times 10^{-10}}{} = 1.46 \times 10^{-8}\,M$$

$$\approx \quad 0.0100 \quad \overline{\quad} \quad 0.0100$$

For comparison, the molar solubility of CaF_2 in pure water is $3.32 \times 10^4 M$ which means CaF_2 is over 20,000 times more soluble in water than in the NaF solution. (Confirm this for yourself by calculating its solubility in pure water from the value of K_{sp}).
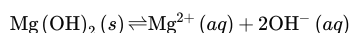
FOR PRACTICE 17.10

Calculate the molar solubility of CaF_2 in a solution containing 0.250 M $Ca(NO_3)_2$


Conceptual Connection 17.10   **Common Ion Effect**

The Effect of pH on Solubility

The pH of a solution can affect the solubility of a compound in that solution. For example, consider the dissociation of $Mg(OH)_2$ the active ingredient in Milk of Magnesia:

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

The solubility of this compound is highly dependent on the pH of the solution into which it dissolves. If the pH is high, then the concentration of OH^- in the solution is high. In accordance with the common ion effect, this shifts the equilibrium to the left, lowering the solubility:

High $[OH^-]$

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

Equilibrium shifts left
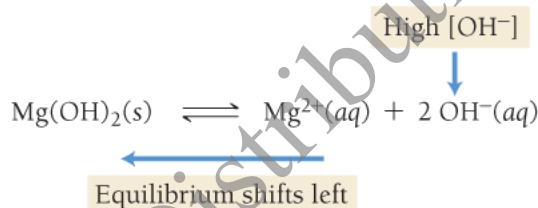
If the pH is low, then the concentration of $H_3O^+ (aq)$ in the solution is high. As the $Mg(OH)_2$ dissolves, these H_3O^+ ions neutralize the newly dissolved OH^- ions, driving the reaction to the right:

H_3O^+ reacts with OH^-

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

Equilibrium shifts right
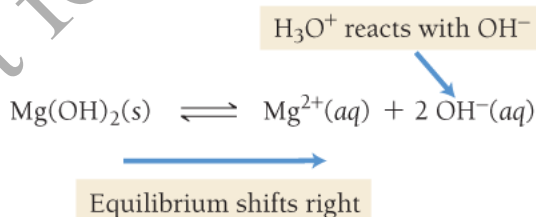
Consequently, the solubility of $Mg(OH)_2$ in an acidic solution is higher than that in a pH-neutral or basic solution.

> In general, the solubility of an ionic compound with a strongly basic or weakly basic anion increases with increasing acidity (decreasing pH).

Common basic anions include OH^-, S^2, and CO_3^{2-}. Therefore, hydroxides, sulfides, and carbonates are more soluble in acidic water than in pure water. Rainwater is naturally acidic due to dissolved carbon dioxide, so it can dissolve rocks high in limestone ($CaCO_3$) as it flows through the ground, sometimes resulting in huge underground caverns such as those at Carlsbad Caverns National Park in New Mexico. Dripping water saturated in $CaCO_3$ within the cave creates the dramatic mineral formations known as stalagmites and stalactites.

Stalactites (which hang from the ceiling) and stalagmites (which grow up from the ground) form as calcium carbonate precipitates out of the water evaporating in underground caves.

Example 17.11 **The Effect of pH on Solubility**

Determine whether each compound is more soluble in an acidic solution than in a neutral solution.

a. BaF_2
b. AgI
c. $Ca(OH)_2$

SOLUTION

a. BaF_2 is more soluble in acidic solution because the F^- ion is a weak base. F^- is the conjugate base of the weak acid HF and is therefore a weak base.)

b. The solubility of AgI is not greater in acidic solution because the I^- is *not* a base. (I^- is the conjugate base of the *strong* acid HI and is therefore pH-neutral.)

c. $Ca(OH)_2$ is more soluble in acidic solution because the OH^- ion is a strong base.

FOR PRACTICE 17.11   Which compound, $FeCO_3$ or $PbBr_2$, is more soluble in acid than in base? Why?