

Solubility Equilibria

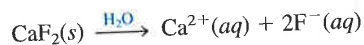
15.6 Solubility Equilibria and the Solubility Product

Purpose

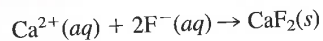
- To show how to calculate the solubility product of a salt given its solubility, and vice versa.
- To demonstrate the prediction of relative solubilities from K_{sp} values.
- To explain the effect of pH and a common ion on the solubility of a salt.

Solubility is a very important phenomenon. The fact that substances such as sugar and table salt dissolve in water allows us to flavor foods easily. The fact that calcium sulfate is less soluble in hot water than in cold water causes it to coat tubes in boilers, reducing thermal efficiency. Tooth decay involves solubility: when food lodges between the teeth, acids form that dissolve tooth enamel, which contains a mineral called hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Tooth decay can be reduced by treating teeth with fluoride (see Chemical Impact, p. 756). Fluoride replaces the hydroxide in hydroxyapatite to produce the corresponding fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, and calcium fluoride, CaF_2 , both of which are less soluble in acids than the original enamel. Another important consequence of solubility involves the use of a suspension of barium sulfate to improve the clarity of X rays of the gastrointestinal tract. The very low solubility of barium sulfate, which contains the toxic ion Ba^{2+} , makes ingestion of the compound safe.

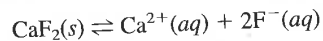
In this section we consider the equilibria associated with solids dissolving to form aqueous solutions. When a typical ionic solid dissolves in water, it dissociates completely into separate hydrated cations and anions. For example, calcium fluoride dissolves in water as follows:



When the solid salt is first added to the water, no Ca^{2+} and F^{-} ions are present. However, as the dissolution proceeds, the concentrations of Ca^{2+} and F^{-} increase, making it more and more likely that these ions will collide and re-form the solid phase. Thus two competing processes are occurring: the dissolution reaction and its reverse:



Ultimately, dynamic equilibrium is reached:



At this point no more solid dissolves (the solution is said to be **saturated**). We can write an equilibrium expression for this process according to the law of mass action:

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

where $[\text{Ca}^{2+}]$ and $[\text{F}^{-}]$ are expressed in mol/L. The constant K_{sp} is called the

Adding F^{-} to drinking water is controversial. See Bette Hileman, "Fluoridation of Water," *Chem. Eng. News*, Aug. 1, 1988, p. 26.



An X ray of the lower gastrointestinal tract using barium sulfate.

solubility product constant or simply the **solubility product** for the equilibrium expression.

Since CaF_2 is a pure solid, it is not included in the equilibrium expression. The fact that the amount of excess solid present does not affect the position of the solubility equilibrium might seem strange at first; more solid means more surface area exposed to the solvent, which would seem to result in greater solubility. This is not the case, however. When the ions in solution re-form the solid, they do so on the surface of the solid. Thus doubling the surface area of the solid not only doubles the rate of dissolving, it also doubles the rate of re-formation of the solid. The amount of excess solid present therefore has no effect on the equilibrium position. Similarly, although either increasing the surface area by grinding up the solid or stirring the solution speeds up the attainment of equilibrium, neither procedure changes the amount of solid dissolved at equilibrium. Neither the amount of excess solid nor the size of the particles present will shift the *position* of the solubility equilibrium.

It is very important to distinguish between the *solubility* of a given solid and its *solubility product*. The solubility product is an *equilibrium constant* and has only *one* value for a given solid at a given temperature. Solubility, on the other hand, is an *equilibrium position*. In pure water at a specific temperature a given salt has a particular solubility. On the other hand, if a common ion is present in the solution, the solubility varies according to the concentration of the common ion. However, in all cases the product of the ion concentrations must satisfy the K_{sp} expression. The K_{sp} values at 25°C for many common ionic solids are listed in Table 15.4. The units are customarily omitted.

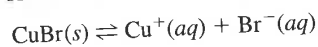
Solving solubility equilibria problems requires many of the same procedures we have used to deal with acid–base equilibria, as illustrated in Sample Exercises 15.12 and 15.13.

Sample Exercise 15.12

Copper(I) bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C . Calculate its K_{sp} value.

Solution

In this experiment the solid was placed in contact with water. Thus, before any reaction occurred, the system contained solid CuBr and H_2O . The process that occurs is the dissolving of CuBr to form the separated Cu^+ and Br^- ions:



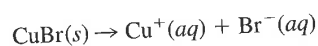
where

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

Initially, the solution contains no Cu^+ or Br^- , so the initial concentrations are

$$[\text{Cu}^+]_0 = [\text{Br}^-]_0 = 0$$

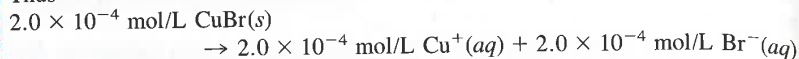
The equilibrium concentrations can be obtained from the measured solubility of CuBr , which is 2.0×10^{-4} mol/L. This means that 2.0×10^{-4} mol solid CuBr dissolves per 1.0 L of solution to come to equilibrium with the excess solid. The reaction is



Pure liquids and pure solids are never included in an equilibrium expression (Section 13.4).

K_{sp} is an equilibrium constant; solubility is an equilibrium position.

• Thus



• We can now write the equilibrium concentrations:

$$\begin{aligned} [\text{Cu}^+] &= [\text{Cu}^+]_0 + \text{change to reach equilibrium} \\ &= 0 + 2.0 \times 10^{-4} \text{ mol/L} \end{aligned}$$

• and

$$\begin{aligned} [\text{Br}^-] &= [\text{Br}^-]_0 + \text{change to reach equilibrium} \\ &= 0 + 2.0 \times 10^{-4} \text{ mol/L} \end{aligned}$$

• These equilibrium concentrations allow us to calculate the value of K_{sp} for CuBr:

$$\begin{aligned} K_{sp} &= [\text{Cu}^+][\text{Br}^-] = (2.0 \times 10^{-4} \text{ mol/L})(2.0 \times 10^{-4} \text{ mol/L}) \\ &= 4.0 \times 10^{-8} \text{ mol}^2/\text{L}^2 = 4.0 \times 10^{-8} \end{aligned}$$

• The units for K_{sp} values are usually omitted.

Table 15.4

 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		Hg ₂ CrO ₄ *	2×10^{-9}	Co(OH) ₂	2.5×10^{-16}
BaF ₂	2.4×10^{-5}	BaCrO ₄	8.5×10^{-11}	Ni(OH) ₂	1.6×10^{-16}
MgF ₂	6.4×10^{-9}	Ag ₂ CrO ₄	9.0×10^{-12}	Zn(OH) ₂	4.5×10^{-17}
PbF ₂	4×10^{-8}	PbCrO ₄	2×10^{-16}	Cu(OH) ₂	1.6×10^{-19}
SrF ₂	7.9×10^{-10}	Carbonates		Hg(OH) ₂	3×10^{-26}
CaF ₂	4.0×10^{-11}	NiCO ₃	1.4×10^{-7}	Sn(OH) ₂	3×10^{-27}
Chlorides		CaCO ₃	8.7×10^{-9}	Cr(OH) ₃	6.7×10^{-31}
PbCl ₂	1.6×10^{-5}	BaCO ₃	1.6×10^{-9}	Al(OH) ₃	2×10^{-32}
AgCl	1.6×10^{-10}	SrCO ₃	7×10^{-10}	Fe(OH) ₃	4×10^{-38}
Hg ₂ Cl ₂ *	1.1×10^{-18}	CuCO ₃	2.5×10^{-10}	Co(OH) ₃	2.5×10^{-43}
Bromides		ZnCO ₃	2×10^{-10}	Sulfides	
PbBr ₂	4.6×10^{-6}	MnCO ₃	8.8×10^{-11}	MnS	2.3×10^{-13}
AgBr	5.0×10^{-13}	FeCO ₃	2.1×10^{-11}	FeS	3.7×10^{-19}
Hg ₂ Br ₂ *	1.3×10^{-22}	Ag ₂ CO ₃	8.1×10^{-12}	NiS	3×10^{-21}
Iodides		CdCO ₃	5.2×10^{-12}	CoS	5×10^{-22}
PbI ₂	1.4×10^{-8}	PbCO ₃	1.5×10^{-15}	ZnS	2.5×10^{-22}
AgI	1.5×10^{-16}	MgCO ₃	1×10^{-15}	SnS	1×10^{-26}
Hg ₂ I ₂ *	4.5×10^{-29}	Hg ₂ CO ₃ *	9.0×10^{-15}	CdS	1.0×10^{-28}
Sulfates		Hydroxides		PbS	7×10^{-29}
CaSO ₄	6.1×10^{-5}	Ba(OH) ₂	5.0×10^{-3}	CuS	8.5×10^{-45}
Ag ₂ SO ₄	1.2×10^{-5}	Sr(OH) ₂	3.2×10^{-4}	Ag ₂ S	1.6×10^{-49}
SrSO ₄	3.2×10^{-7}	Ca(OH) ₂	1.3×10^{-6}	HgS	1.6×10^{-54}
PbSO ₄	1.3×10^{-8}	AgOH	2.0×10^{-8}	Phosphates	
BaSO ₄	1.5×10^{-9}	Mg(OH) ₂	8.9×10^{-12}	Ag ₃ PO ₄	1.8×10^{-18}
Chromates		Mn(OH) ₂	2×10^{-13}	Sr ₃ (PO ₄) ₂	1×10^{-31}
SrCrO ₄	3.6×10^{-5}	Cd(OH) ₂	5.9×10^{-15}	Ca ₃ (PO ₄) ₂	1.3×10^{-32}
		Pb(OH) ₂	1.2×10^{-15}	Ba ₃ (PO ₄) ₂	6×10^{-39}
		Fe(OH) ₂	1.8×10^{-15}	Pb ₃ (PO ₄) ₂	1×10^{-54}

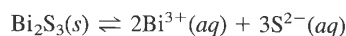
*Contains Hg₂²⁺ ions. $K_{sp} = [\text{Hg}_2^{2+}][\text{X}^-]^2$ for Hg₂X₂ salts, for example.

Sample Exercise 15.13

Calculate the K_{sp} value for bismuth sulfide (Bi_2S_3), which has a solubility of 1.0×10^{-15} mol/L at 25°C .

Solution

The system initially contains H_2O and solid Bi_2S_3 , which dissolves as follows:



Therefore,

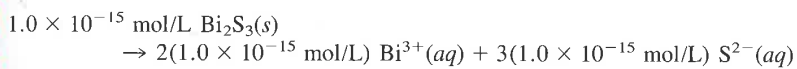
$$K_{sp} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3$$

Since no Bi^{3+} and S^{2-} ions were present in solution before the Bi_2S_3 dissolved,

$$[\text{Bi}^{3+}]_0 = [\text{S}^{2-}]_0 = 0$$

Thus the equilibrium concentrations of these ions will be determined by the amount of salt that dissolves to reach equilibrium, which in this case is 1.0×10^{-15} mol/L.

Since each Bi_2S_3 unit contains 2Bi^{3+} and 3S^{2-} ions:



The equilibrium concentrations are

$$[\text{Bi}^{3+}] = [\text{Bi}^{3+}]_0 + \text{change} = 0 + 2.0 \times 10^{-15} \text{ mol/L}$$

$$[\text{S}^{2-}] = [\text{S}^{2-}]_0 + \text{change} = 0 + 3.0 \times 10^{-15} \text{ mol/L}$$

Then

$$K_{sp} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3 = (2.0 \times 10^{-15})^2(3.0 \times 10^{-15})^3 = 1.1 \times 10^{-73}$$

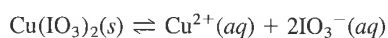
We have seen that the experimentally determined solubility of an ionic solid can be used to calculate its K_{sp} value.* The reverse is also possible: the solubility of an ionic solid can be calculated if its K_{sp} value is known.

Sample Exercise 15.14

The K_{sp} value for copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, is 1.4×10^{-7} at 25°C . Calculate its solubility at 25°C .

Solution

The system initially contains H_2O and solid $\text{Cu}(\text{IO}_3)_2$, which dissolves according to the following equilibrium:



Therefore,

$$K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$$

*This calculation assumes that all the dissolved solid is present as separated ions. In some cases, such as CaSO_4 , large numbers of ion pairs exist in solution, so this method yields an incorrect value for K_{sp} .



Precipitation of bismuth sulfide.

Sulfide is a very basic anion and really exists in water as HS^- . We will not consider this complication.

Solubilities must be expressed in mol/L in K_{sp} calculations.

To find the solubility of $\text{Cu}(\text{IO}_3)_2$, we must find the equilibrium concentrations of the Cu^{2+} and IO_3^- ions. We do this in the usual way by specifying the initial concentrations (before any solid has dissolved) and then defining the change required to reach equilibrium. Since in this case we do not know the solubility, we will assume that x mol/L of the solid dissolves to reach equilibrium. The 1:2 stoichiometry of the salt means that



The concentrations are as follows:

Initial Concentration (mol/L) [Before Any $\text{Cu}(\text{IO}_3)_2$ Dissolves]		Equilibrium Concentration (mol/L)
$[\text{Cu}^{2+}]_0 = 0$ $[\text{IO}_3^-]_0 = 0$	$\xrightarrow[\text{to reach equilibrium}]{x \text{ mol/L dissolves}}$	$[\text{Cu}^{2+}] = x$ $[\text{IO}_3^-] = 2x$

Substituting the equilibrium concentrations into the expression for K_{sp} gives

$$1.4 \times 10^{-7} = K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (x)(2x)^2 = 4x^3$$

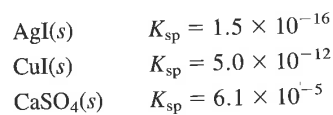
Then
$$x = \sqrt[3]{3.5 \times 10^{-8}} = 3.3 \times 10^{-3} \text{ mol/L}$$

Thus the solubility of solid $\text{Cu}(\text{IO}_3)_2$ is 3.3×10^{-3} mol/L.

Relative Solubilities

A salt's K_{sp} value gives us information about its solubility. However, we must be careful in using K_{sp} values to predict the *relative* solubilities of a group of salts. There are two possible cases:

1. The salts being compared produce the same number of ions. For example, consider



Each of these solids dissolves to produce two ions:



$$K_{sp} = [\text{cation}][\text{anion}]$$

If x is the solubility in mol/L, then at equilibrium

$$[\text{Cation}] = x$$

$$[\text{Anion}] = x$$

$$K_{sp} = [\text{cation}][\text{anion}] = x^2$$

$$x = \sqrt{K_{sp}} = \text{solubility}$$

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