Solubility and Complex-Ion Equilibria

References : 1.General Chemistry- principles and modern applications (Petrucci, Herring, Madura, Bissonnette).
2. Chemistry_10th_Edition_Raymond_Chang

Solubility Equilibria

Precipitation reactions are important in industry, medicine, and everyday life. For example, the preparation of many essential industrial chemicals such as sodium carbonate (Na_2CO_3) is based on precipitation reactions. The dissolving of tooth enamel, which is mainly made of hydroxyapatite [$Ca_5(PO_4)_3OH$], in an acidic medium leads to tooth decay. Barium sulfate (BaSO4), an insoluble compound that is opaque to X rays, is used to diagnose ailments of the digestive tract. Stalactites and stalagmites, which consist of calcium carbonate ($CaCO_3$), are produced by a precipitation reaction, and so are many foods, such as fudge.

Solubility Product

Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be represented as,

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

Silver chloride is an insoluble salt (see Table 4.2). The small amount of solid AgCl that dissolves in water is assumed to dissociate completely into Ag^+ and Cl^- ions. We know from Chapter 14 that for heterogeneous reactions the concentration of the solid is a constant. Thus, we can write the equilibrium constant for the dissolution of AgCl as,

$$K_{sp} = [Ag^+][Cl^-]$$

where K_{sp} is called the solubility product constant or simply the solubility product. In general, the solubility product of a compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coeffcient in the equilibrium equation.

Because each AgCl unit contains only one Ag^+ ion and one Cl^- ion, its solubility product expression is particularly simple to write. The following cases are more complex:

- MgF_2

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Mg^{2+}][F^-]^2$$

- Ag_2CO_3

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[CO_3^{2-}]$$

- $Ca_3(PO_4)_2$

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \qquad K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$
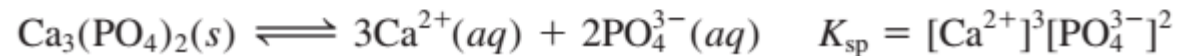
Table 16.2 lists the solubility products for a number of salts of low solubility. Soluble salts such as NaCl and KNO_3, which have very large K_{sp} values, are not listed in the table for essentially the same reason that we did not include K_a values for strong acids in Table 15.3. The value of K_{sp} indicates the solubility of an ionic compound— the smaller the value, the less soluble the compound in water. However, in using K_{sp} values to compare solubilities, you should choose compounds that have similar formulas, such as AgCl and ZnS, or CaF_2 and $Fe(OH)_2$.

TABLE 16.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [Al(OH)$_3$]	1.8×10^{-33}	Lead(II) chromate (PbCrO$_4$)	2.0×10^{-14}
Barium carbonate (BaCO$_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF$_2$)	4.1×10^{-8}
Barium fluoride (BaF$_2$)	1.7×10^{-6}	Lead(II) iodide (PbI$_2$)	1.4×10^{-8}
Barium sulfate (BaSO$_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi$_2$S$_3$)	1.6×10^{-72}	Magnesium carbonate (MgCO$_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [Mg(OH)$_2$]	1.2×10^{-11}
Calcium carbonate (CaCO$_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF$_2$)	4.0×10^{-11}	Mercury(I) chloride (Hg$_2$Cl$_2$)	3.5×10^{-18}
Calcium hydroxide [Ca(OH)$_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [Ca$_3$(PO$_4$)$_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [Cr(OH)$_3$]	3.0×10^{-29}	Silver bromide (AgBr)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag$_2$CO$_3$)	8.1×10^{-12}
Copper(I) bromide (CuBr)	4.2×10^{-8}	Silver chloride (AgCl)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [Cu(OH)$_2$]	2.2×10^{-20}	Silver sulfate (Ag$_2$SO$_4$)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag$_2$S)	6.0×10^{-51}
Iron(II) hydroxide [Fe(OH)$_2$]	1.6×10^{-14}	Strontium carbonate (SrCO$_3$)	1.6×10^{-9}
Iron(III) hydroxide [Fe(OH)$_3$]	1.1×10^{-36}	Strontium sulfate (SrSO$_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate (PbCO$_3$)	3.3×10^{-14}	Zinc hydroxide [Zn(OH)$_2$]	1.8×10^{-14}
Lead(II) chloride (PbCl$_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

For the dissolution of an ionic solid in aqueous solution, any one of the following conditions may exist: (1) the solution is unsaturated, (2) the solution is saturated, or (3) the solution is supersaturated. For concentrations of ions that do not correspond to equilibrium conditions we use the reaction quotient (see Section 14.4), which in this case is called the *ion product (Q)*, to predict whether a precipitate will form. Note that Q has the same form as K_{sp} except that the concentrations of ions are *not* equilibrium concentrations. For example, if we mix a solution containing Ag^+ ions with one containing Cl^- ions, then the ion product is given by

$$Q = [Ag^+]_0[Cl^-]_0$$

The subscript 0 reminds us that these are initial concentrations and do not necessarily correspond to those at equilibrium. The possible relationships between Q and K_{sp} are

$Q < K_{sp}$ Unsaturated solution (no precipitation)
$[Ag^+]_0[Cl^-]_0 < 1.6 \times 10^{-10}$

$Q = K_{sp}$ Saturated solution (no precipitation)
$[Ag^+][Cl^-] = 1.6 \times 10^{-10}$

$Q > K_{sp}$ Supersaturated solution; AgCl will
$[Ag^+]_0[Cl^-]_0 > 1.6 \times 10^{-10}$ precipitate out until the product of the ionic concentrations is equal to 1.6×10^{-10}

- Precipitation *should occur* if $Q_{sp} > K_{sp}$.
- Precipitation *cannot occur* if $Q_{sp} < K_{sp}$.
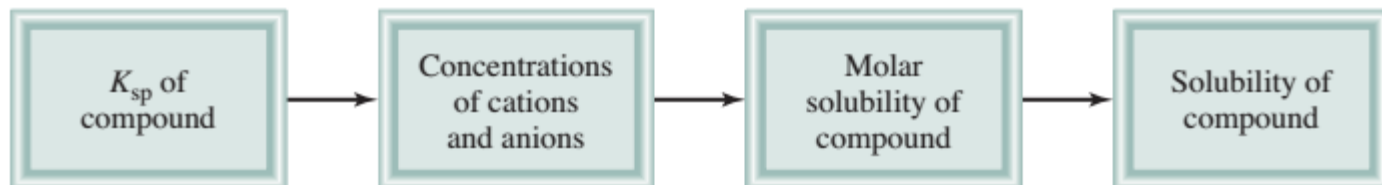- A solution is just saturated if $Q_{sp} = K_{sp}$.

Molar Solubility and Solubility

There are two other ways to express a substance's solubility: molar solubility, which is the number of moles of solute in 1 L of a saturated solution (mol/L), and solubility, which is the number of grams of solute in 1 L of a saturated solution (g/L). Note that both these expressions refer to the concentration of saturated solutions at some given temperature (usually 25oC).

Both molar solubility and solubility are convenient to use in the laboratory. We can use them to determine Ksp by following the steps outlined in Figure 16.9(a). Example 16.8 illustrates this procedure.

Solubility of compound	→	Molar solubility of compound	→	Concentrations of cations and anions	→	K_{sp} of compound

(a)

K_{sp} of compound	→	Concentrations of cations and anions	→	Molar solubility of compound	→	Solubility of compound
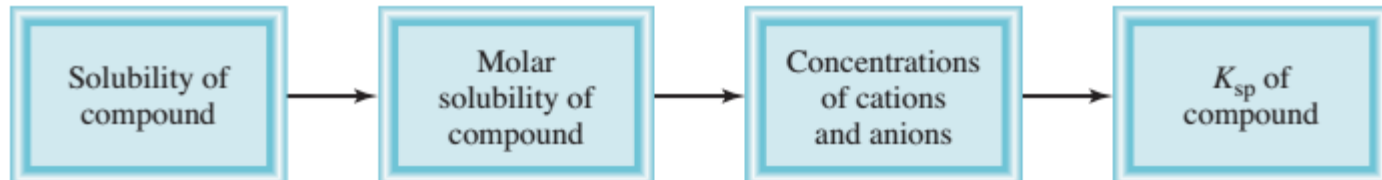
(b)

Figure 16.9 *Sequence of steps (a) for calculating K_{sp} from solubility data and (b) for calculating solubility from K_{sp} data.*

Sometimes we are given the value of K_{sp} for a compound and asked to calculate the compound's molar solubility. For example, the K_{sp} of silver bromide (AgBr) is 7.7×10^{-13}. We can calculate its molar solubility by the same procedure as that for acid ionization constants. First we identify the species present at equilibrium. Here we have Ag^+ and Br^- ions. Let s be the molar solubility (in mol/L) of AgBr. Because one unit of AgBr yields one Ag^+ and one Br^- ion, at equilibrium both $[Ag^+]$ and $[Br^-]$ are equal to s. We summarize the changes in concentrations as follows:

	AgBr(s) $\rightleftharpoons$ Ag$^+$(aq)	+ Br$^-$(aq)
Initial (M):	0.00	0.00
Change (M):	$-s$	$+s$	$+s$
Equilibrium (M):	s	s

From Table 16.2 we write

$$K_{sp} = [Ag^+][Br^-]$$
$$7.7 \times 10^{-13} = (s)(s)$$
$$s = \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7}\,M$$

Therefore, at equilibrium

$$[Ag^+] = 8.8 \times 10^{-7}\,M$$
$$[Br^-] = 8.8 \times 10^{-7}\,M$$

Thus, the molar solubility of AgBr also is $8.8 \times 10^{-7}\,M$.
Example 16.9 makes use of this approach.

When carrying out solubility and/or solubility product calculations, keep in mind the following important points:

1. Solubility is the quantity of a substance that dissolves in a certain quantity of water to produce a saturated solution. In solubility equilibria calculations, it is usually expressed as *grams* of solute per liter of solution. Molar solubility is the number of *moles* of solute per liter of solution.

2. Solubility product is an equilibrium constant.

3. Molar solubility, solubility, and solubility product all refer to a *saturated solution*.

TABLE 16.3 Relationship Between K_{sp} and Molar Solubility (s)

| Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
AgCl	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2; s = (K_{sp})^{\frac{1}{2}}$
BaSO$_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2; s = (K_{sp})^{\frac{1}{2}}$
Ag$_2$CO$_3$	$[Ag^+]^2[CO_3^{2-}]$	$2s$	s	$K_{sp} = 4s^3; s = \left(\dfrac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF$_2$	$[Pb^{2+}][F^-]^2$	s	$2s$	$K_{sp} = 4s^3; s = \left(\dfrac{K_{sp}}{4}\right)^{\frac{1}{3}}$
Al(OH)$_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$K_{sp} = 27s^4; s = \left(\dfrac{K_{sp}}{27}\right)^{\frac{1}{4}}$
Ca$_3$(PO$_4$)$_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$3s$	$2s$	$K_{sp} = 108s^5; s = \left(\dfrac{K_{sp}}{108}\right)^{\frac{1}{5}}$

Common-Ion Effect in Solubility Equilibria

As we have noted, the solubility product is an equilibrium constant; precipitation of an ionic compound from solution occurs whenever the ion product exceeds K_{sp} for that substance. In a saturated solution of AgCl, for example, the ion product $[Ag^+][Cl^-]$ is, of course, equal to K_{sp}. Furthermore, simple stoichiometry tells us that $[Ag^+] = [Cl^-]$. But this equality does not hold in all situations.

Suppose we study a solution containing two dissolved substances that share a common ion, say, AgCl and $AgNO_3$. In addition to the dissociation of AgCl, the following process also contributes to the total concentration of the common silver ions in solution:

$$AgNO_3(s) \xrightarrow{\text{H}_2\text{O}} Ag^+(aq) + NO_3^-(aq)$$
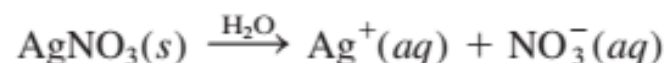
The solubility equilibrium of AgCl is

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
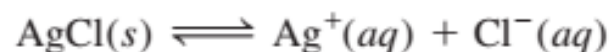
If $AgNO_3$ is added to a saturated AgCl solution, the increase in $[Ag^+]$ will make the ion product greater than the solubility product:

$$Q = [Ag^+]_0[Cl^-]_0 > K_{sp}$$

To reestablish equilibrium, some AgCl will precipitate out of the solution, as Le Châtelier's principle would predict, until the ion product is once again equal to K_{sp}. The effect of adding a common ion, then, is a *decrease* in the solubility of the salt (AgCl) in solution. Note that in this case $[Ag^+]$ is no longer equal to $[Cl^-]$ at equilibrium; rather, $[Ag^+] > [Cl^-]$.