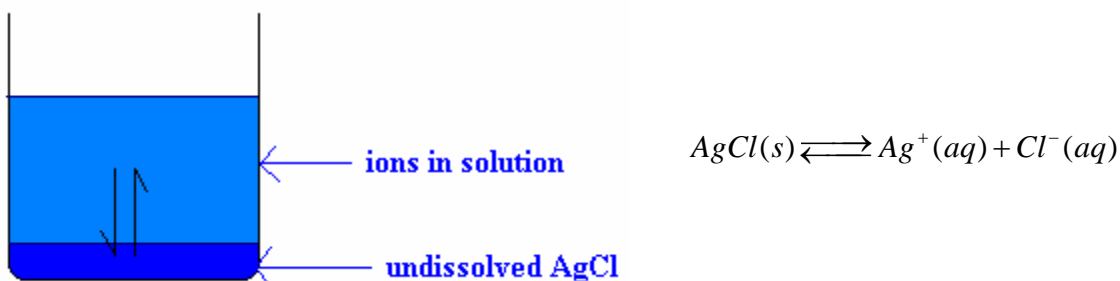


Solubility Equilibrium

Solubility is the ability of a substance to dissolve in water. The solubility is measured in terms of concentration of an ion that is present in a smaller ratio in solution. On the other hand, solubility equilibrium refers to the equilibrium between the dissolved salt (ions) and undissolved salt that usually exists in a saturated solution or a solution of a sparingly soluble salt. The word **sparingly soluble** salt refers to a salt that is partially (not completely) soluble in water, as results of which, the equilibrium between dissolved ions and undissolved salt is possible.

Solubility Product

To understand the concept of solubility product, consider the saturated solution of silver chloride (AgCl), where the equilibrium exists between dissolved ions and undissolved silver chloride according to the following equation.



Since this is an equilibrium reaction, we can write the equilibrium constant expression as

$$K = \frac{[Ag^+][Cl^-]}{[AgCl(s)]}$$

The concentrations of solids are either unknown or assumed to be constant. Hence we combine $[AgCl(s)]$ with K and label this constant as K_{sp} . Thus

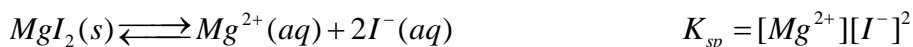
$$K[AgCl(s)] = K_{sp} = [Ag^+][Cl^-]$$

The K_{sp} is called the solubility product constant or simply solubility product.

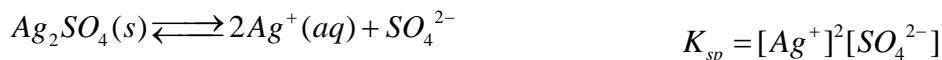
In general, *the solubility product of a compound is the product of molar concentrations of ions raised to the power of their respective stoichiometric coefficients in the equilibrium reaction.*

In the above example, writing the K_{sp} expression for AgCl is very simple because only one mole of Ag^+ ions and one mole of Cl^- ions are formed. If more than one mole of ions are formed, then the things get more complex. Consider the following examples:

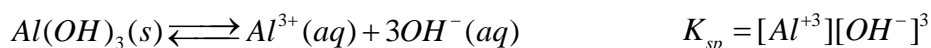
- MgI_2



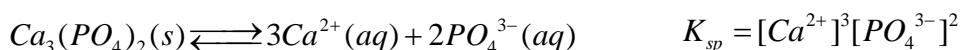
- Ag_2SO_4



- $Al(OH)_3$



- $Ca_3(PO_4)_2$



Important

Before you make an attempt to write K_{sp} for a given compound, few things you should know:

- How to break the compound into ions– identify the monatomic and polyatomic ions
- Number of moles of each ion formed
- Charge on each ion

Write the equilibrium reaction with double arrows going in opposite directions with proper phases first (s for solid, aq for solution) and then write K_{sp} .

The following table lists few K_{sp} values for low solubility hydroxides. You may refer to any general chemistry textbook for more salts.

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [Al(OH) ₃]	1.8×10^{-33}	Iron(II) hydroxide [Fe(II)(OH) ₂]	1.6×10^{-14}
Calcium hydroxide [Ca(OH) ₂]	8.0×10^{-6}	Iron (III) hydroxide [Fe(OH) ₃]	1.1×10^{-36}
Chromium(III) hydroxide [Cr(OH) ₃]	3.0×10^{-29}	Magnesium hydroxide [Mg(OH) ₂]	1.2×10^{-11}
Copper(II) hydroxide [Cu(OH) ₂]	2.2×10^{-20}	Zinc hydroxide [Zn(OH) ₂]	1.8×10^{-14}

What do the K_{sp} values tell us?

K_{sp} values are derived from the concentrations of ions in equilibrium reactions; higher the concentrations of ions, greater the K_{sp} . Higher the concentrations of ions means greater

the solubility of the salt. Therefore, the magnitude of K_{sp} directly indicates the solubility of the salt in water. For example, comparing the K_{sp} of aluminum hydroxide and calcium hydroxide, it is evident that calcium hydroxide is more soluble in water than aluminum hydroxide.

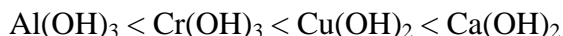
Example

Arrange the following salts in order of increasing solubility.

- (a) Aluminum hydroxide $[Al(OH)_3]$ ($K_{sp}=1.8 \times 10^{-33}$)
- (b) Calcium hydroxide $[Ca(OH)_2]$ ($K_{sp}=8.0 \times 10^{-6}$)
- (c) Chromium (III) hydroxide $[Cr(OH)_3]$ ($K_{sp} = 3.0 \times 10^{-29}$)
- (d) Copper (II) hydroxide $[Cu(OH)_2]$ ($K_{sp}=2.2 \times 10^{-20}$)

Answer

Higher the K_{sp} means greater the solubility. Arranging the above salts from low K_{sp} to high K_{sp} , we have



Solubility

In a simple term, solubility is the dissolving ability of a salt in a fixed amount of water. It is measured by the concentration of an ion that is present in a smaller proportion (smaller number of moles). The above discussed K_{sp} values are useful in comparing the solubilities of group of salts, but not in assessing their actual solubilities. When we need to calculate the actual solubility of the salt, we use either the **molar solubility**, which is defined as the number moles of solute in 1 L of saturated solution (moles per liter), or **solubility** that is defined as the number of grams of solute in 1 L saturated solution (grams per liter). Thus you can see there are two ways to define solubility. However, both are related through the molar mass.

Suppose, you want to convert solubility (g/L) to molar solubility (mol/L), you divide solubility by molar mass (g/mol):

$$\frac{mol}{L} = \frac{g}{L} \times \frac{1}{molar\ mass(g/mol)} = \frac{g}{L} \times \frac{mol}{g} = \frac{mol}{L}$$

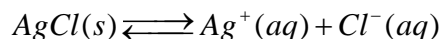
Suppose, you want to convert molar solubility (mol/L) to solubility(g/L), you multiply molar solubility by molar mass (g/mol):

$$\frac{g}{L} = \frac{mol}{L} \times \frac{molar\ mass(g/mol)}{1} = \frac{mol}{L} \times \frac{g}{mol} = \frac{g}{L}$$

Relationship between K_{sp} and solubility

Solubility is the molar concentration and K_{sp} is the product of molar concentrations, and hence both are related to one another. In the following, we develop relationships between these two for various salts.

Let us illustrate the concept using a simple example of AgCl that dissociates into one cation (Ag^+) and one anion (Cl^-) at equilibrium:



The K_{sp} expression for this is

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

Let s be the molar solubility (mol/L) of Ag^+ ion. This will also be the molar solubility of Cl^- ion because number of Ag^+ ions is equal to number of Cl^- ions that can be seen by the above equilibrium reaction. That is,

$$s = [Ag^+] \text{ and } s = [Cl^-]$$

Substituting these into K_{sp} equation, we get

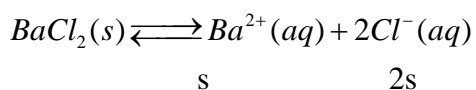
$$K_{sp} = [Ag^+][Cl^-] = (s)(s) = s^2$$

or
$$s = \sqrt{K_{sp}}$$

Thus, the molar solubility is just square root of the K_{sp} .

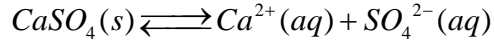
We can extend similar procedure to develop the relationship between K_{sp} and s for more complicated compounds:

Barium chloride ($BaCl_2$)



$$K_{sp} = [Ba^{2+}][Cl^-]^2 = (s)(2s)^2 = 4s^3$$

or
$$s = (K_{sp}/4)^{1/3}$$



The K_{sp} is written as

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

In order to evaluate K_{sp} , we need the molar concentrations (mol/L), but the solubility is given g/L. First, we need to convert g/L to mol/L:

$$\frac{0.56 \text{ g } CaSO_4}{1 \text{ L soln}} \times \frac{1 \text{ mol } CaSO_4}{136.2 \text{ g } CaSO_4} = 4.1 \times 10^{-3}$$

Thus we have

$$[Ca^{2+}] = [SO_4^{2-}] = 4.1 \times 10^{-3}$$

Now we can determine K_{sp} :

$$\begin{aligned} K_{sp} &= [Ca^{2+}][SO_4^{2-}] = (4.1 \times 10^{-3})(4.1 \times 10^{-3}) \\ &= 1.7 \times 10^{-5} \end{aligned}$$

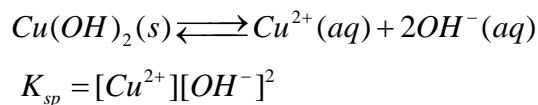
Calculating solubility from K_{sp}

Example

Calculate the molar solubility of $Cu(OH)_2$ if $K_{sp} = 2.2 \times 10^{-20}$.

Answer

First we write the K_{sp} expression for $Cu(OH)_2$ as



Let s be the molar solubility of Cu^{2+} , i.e., $[Cu^{2+}] = s$. Then $2s$ will be the concentration of OH^{-} , i.e., $[OH^{-}] = 2s$. Then K_{sp} becomes

$$\begin{aligned} K_{sp} &= 2.2 \times 10^{-20} = (s)(2s)^2 = 4s^3 \\ s^3 &= 2.2 \times 10^{-20} / 4 \end{aligned}$$

Hence $s = (2.2 \times 10^{-20} / 4)^{1/3} = 1.8 \times 10^{-7} \text{ mol/L} = 1.8 \times 10^{-7} \text{ M}$

Predicting the Formation of Precipitate

Precipitate is the solid formed as a result of chemical reaction between two or more solutions. Let say that you mix two solutions, how do you know whether the precipitate forms or not? Before you can answer this question, you got to know what kind of precipitate is going to form using the solubility rules. From the information given in the problem, first calculate the molar concentrations of the ions responsible for the precipitate. Next calculate the reaction quotient Q (this is exactly the same as K_{sp} except it is based on the initial (given) concentrations) and compare it with K_{sp} .

If $Q > K_{sp}$ precipitate will form otherwise no.

Example

Exactly 100 ml of 0.05 M AgNO_3 are added to exactly 500 ml of 0.05 M HCl . Will a precipitate form?

Answer

The ions present in solution are Ag^+ , NO_3^- , H^+ and Cl^- . According to the solubility rules, only AgCl precipitate is possible. From the given information, first we calculate the molar concentrations of Ag^+ and Cl^- ions:

$$[\text{Ag}^+] = \frac{100\text{ml}}{600\text{ml}} \times 0.05\text{M} = 8.3 \times 10^{-3}\text{M}$$

$$[\text{Cl}^-] = \frac{500\text{ml}}{600\text{ml}} \times 0.05\text{M} = 4.2 \times 10^{-2}\text{M}$$

Note the 600ml is the total volume of the solution. Then we calculate Q

$$Q = [\text{Ag}^+][\text{Cl}^-] = (8.3 \times 10^{-3})(4.2 \times 10^{-2}) \\ = 3.5 \times 10^{-4}$$

Therefore

$$Q (= 3.5 \times 10^{-4}) > K_{sp} (= 1.6 \times 10^{-10})$$

The precipitate of AgCl will form.