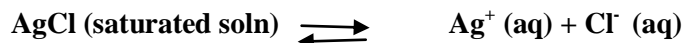## SOLUBILITY PRODUCT

In a saturated solution of a salt, there exists a dynamic equilibrium between the excess of the solute and the ions furnished by that part of the solute which has gone in solution. Consider, for example, the case when a sparingly soluble salt, like silver chloride, is added to water. A very small amount dissolves and the rest of it remains in the solid state. Here the solid silver chloride is in equilibrium with silver and chloride ions furnished by the dissolved silver chloride as shown below

AgCl (saturated soln) $\rightleftharpoons$ **Ag^+ (aq) + Cl^- (aq)**

Applying the law of chemical equilibrium, the equilibrium constant would be given by

$$K = a_{Ag+} \ X \ a_{Cl^-} / a_{AgCl} \qquad \ldots\ldots(1)$$

Since activity of a solid is taken as unity by convention, the above expression may be put as

$$Ksp = a_{Ag+} \ X \ a_{Cl-} \qquad \ldots\ldots(2)$$

is known as the solubility product of silver chloride. It is constant at a given temperature.

very often, in practice, it is more convenient to use concentration terms instead of activities. The constant is then known as concentration solubility product, denoted by K'_{sp}. Thus,

$$K'_{sp} = [Ag^+][Cl^-] \qquad \ldots\ldots(3)$$

where the square brackets, as usual, represent the concentrations of the entities enclosed within. In the case of sparingly soluble salts since the ionic concentration is very low, activity of each ion is almost equal to its concentration. Hence, $K_{sp} = K'_{sp}$ $\qquad \ldots\ldots(4)$

i.e., solubility product is almost equal to concentration solubility product. Therefore, without introducing any serious error, we may write: $K_{sp} = [Ag^+][Cl^-]$ $\qquad \ldots\ldots(5)$

Consider, in general, a salt of the type A_xB_y which dissociates as

$$A_xB_y \rightleftharpoons xA^{y+} + y\ B^{x-} \qquad \ldots\ldots(6)$$

The solubility product of the salt is now given by

$$Ksp = [A^{y+}]^x \ [B^{x-}]^y \qquad \ldots\ldots(7)$$

Thus, the solubility product of a sparingly soluble salt forming a saturated solution in water given by the product of the concentrations of the ions raised to a power equal to the number of the ions occur in the equation representing the dissociation of electrolyte.

Relation between Solubility Product and Molar Solubility of a Sparingly Soluble Salt.

For the saturated solution of a sparingly soluble salt AB, the following solubility equilibrium would exist :

$$AB(s, std.soln.) \rightleftharpoons A^+(aq) + B^-(aq) \qquad \qquad ……….(8)$$

If the molar solubility of the salt is s, then $[A^+]$ = s mol dm $^{-3}$, $[B^-]$ = s mol dm $^{-3}$ Hence

$Ksp = [A^+][B^-] = (s\ mol\ dm^{-3})(\ s\ mol\ dm^{-3}) = s^2\ mol^2\ dm^{-6}$ ……….(9)

Example. The solubility of silver chloride in water at 25°C is 0.00179 g per litre. Calculate its solubility product at 25°C.

Solution : Solubility of silver chloride = 0.00179 g dm = 0.00179 g dm^{-3} /143.5 g mol = - = 0.0000125 mol dm^{-3}

The dissolved salt would be present in the form of ions so that

$[Ag+] = [Cl-] = 0.0000125$ mol dm $^{-3}$

$Ksp= [Ag+][Cl-] = (0.0000125\ mol\ dm^{-3})^2 = 1.56x\ 10^{-10}\ mol^2\ dm^{-6}$

Application of Solubility product principle
1. Determination of solubilities of sparingly soluble salts
2. Predicting precipitation reactions
3. Fractional precipitation
4. Prefrential precipitation of an insoluble salt
5. Precipitation of soluble salts a) Purification of soluble salts b) salting out of soap
6. Inorganic Analysis a) Precipitation ofsulphides b) Precipitation of hydroxides
7. Other precipitation reactions
8. Dissolutions of precipitates of phosphates, carbonates sulphides etc.

1. **Determination of solubilities of sparingly soluble salts**

  Suppose solubility of sparingly soluble salt silver chloride is given by s mole per litre, since conc. Is very small it is considered as compety dissociated so that conc. of silver and chloride ions will be s moles per litre each. Therefore, solubility product Ksp of silver chloride will be given by
$$\textbf{Ksp = [Ag}^+\textbf{] [Cl}^-\textbf{] = s}^2 \qquad ……….(10)$$
Or $\qquad\qquad\qquad$ **s = [Ksp]$^{1/2}$** ……….(11)

The solubility product of AgCl at a given temp is determined by adding AgCl in a solution of KCl of a known concentration say b moles per litre. The conc. of Ag+ ion in the solution produced by the dissociation of that part of AgCl which dissolves in water is determined by an EMF method. Suppose it is a mole per litre. The concentration of Cl$^-$ ion in solution will be (a+b) moles per litre due to AgCl and KCl both. Therefore, Ksp is given by
Ksp =a (a+b), since a and b are known,
hence **the solubility product of AgCl = [Ksp]$^{1/2}$ mole per litre** ……….(12)

2. Predicting precipitation reactions

With the knowledge of solubility product of a sparingly soluble substance, it can be predicted that under certain conditions that substance would be precipitated or not. **A substance is known to precipitate when the ionic product exceeds the solubility product of the substance.**

Example : 25 ml of 0-01 AgNO3 solution is mixed with 25 ml of 0.0005 M aqueous NaCl solution. Determine if the precipitate of AgCl will be formed. Given Ksp(AgCl) =1.7×10^{-10} M^2

Solution : Since the volume of the solution after mixing is doubled and $AgNO_3$ and $NaCl$ are strong electrolytes which are completely dissociated in solution, we have [Ag + = 1/2(0.01 M) = 5x 10-3 M

[Cl⁻] = 1/200 0005 M) = 2-25 x 10^{-4} M

ionic product [Ag+][Cl-] = (5x 10^{-3} M)(2 .25 x 10^{-4} M) = 1.125 x 10^{-6} M

Since ionic product > Ksp(AgCl), the precipitate of AgCl will be formed.

Question. 25 ml of 4×10^{-5} M solution of $Ba(NO_3)_2$, is mixed with 500 ml of 5x 10^{-5} M solution of Na₂SO4. Will a precipitate of $BaSO_4$, be formed ? Ksp(BaSO₄) = 1-08 x 10-10 M2.

3. **Fractional Precipitation**. Consider an aqueous solution of KCl and KI to which $AgNO_3$, solution is added. Since Ksp (Agl) is less than Ksp(AgCl), hence, Ksp(Agcl) will be exceeded and AgI will be precipitated first:

Ag+ (aq)   + I⁻(aq) ⟶ AgI (s)↓   Ksp = 0.94x10^{-16}

Ag+ (aq)   + Cl⁻(aq) ⟶ AgCl (s)↓   Ksp = 1.56x10^{-10}
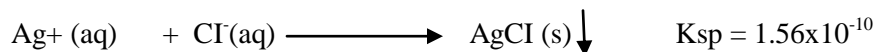
Thus, Agl will start precipitating out when [I⁻] is approximately one-millionth part of (Cl⁻).

AgCl will precipitate only when [Ag +) is greater than the value given below:

[Ag+] = ksp (AgCl)/ [Cl⁻] = 1.56x10^{-10}/ [Cl⁻]

At that point both Agl and AgCl will start precipitating simultaneously.

4. **Preferential Precipitation of an Insoluble Salt.** Silver chloride is 'insoluble" or sparingly soluble, to be more accurate. So is silver iodide. The question arises as to what would happen if potassium iodide solution is added to silver chloride. Would the ppt of AgCl change into ppt of AgI?

AgCl   +   KI ⇌   KCl   + AgI
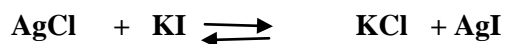
For answer, Ksp (AgCl) = [Ag+] [Cl-] = 1.56 x10^{-10}

And Ksp [AgI] = [Ag+] [I-] = 0.94 x 10^{-10}
So, [Cl⁻] /[I⁻]=   1.56 x10^{-10}/ 0.94 x 10^{-10} = 1.66 x 10^{6}

At equilibrium, the concentration of Cl⁻ ions in solution is more than a million times greater than that of I-ions,practically nothing of the l - ions can remain in solution at equilibrium. As the I⁻ ions can only be

removed as AgI, it means that the reaction proceeds virtually to completion towards the right. **As a rule, the compound with the lower solubility product gets precipitated in preference. Silver iodide has lower solubility product than silver chloride. Therefore, the former gets precipitated preference to the latter.**

5. Precipitation of Soluble Salts. (a) Purification of common salt. The principle of solubility product is also applicable in the precipitation of soluble salts in pure state from their saturated solution. This phenomenon, known as salting out, is used in the purification of sodium chloride. This is done by preparing a saturated solution of commercial NaCl in water when the following equilibrium exsist:

NaCl (s, satd soln) $\rightleftharpoons$ **Na$^+$ (aq) + Cl$^-$ (aq)**
  Ksp = [Na$^+$] [Cl$^-$]
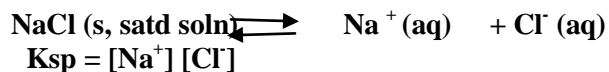
HCl gas is passed through this solution. The [Cl-], therefore increases considerably. Hence ionic product exceeds the concentration solubility product of Nacl and therefore, it precipitates out from the solution in pure state. The soluble impurities remain in solution.

(6) **Salting out of soap.** The same principle is made use of in the salting out of soap which may be considered as sodium salt of stearic acid for simplicity. The following equilibrium exists:

C17,H35COONa(s, std. soln.) $\rightleftharpoons$ C17H35Coo-(aq) + Na+ (aq)

$\qquad\qquad$ Ksp = [C17H35Coo-][Na+]
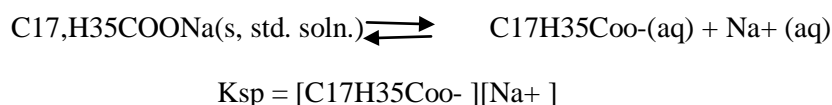
Some sodium chloride is now added. The [Na+], therefore, increases. Hence, the ionic product exceeds the concentration solubility product of sodium stearate. The soap, therefore, separates out from solution.

6. **Inorganic Analysis**. The application of solubility product principle to inorganic analysis is of great importance. A few illustrations are given below.

a. **Precipitation of sulphides.** Hydrogen sulphide is a weak acid. Its small dissociation is further suppressed by the addition of dilute hydrochloric acid (common ion effect).

  H_2S $\rightleftharpoons$ $2H^+$ + S^{2-}
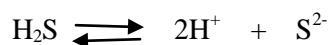
Therefore, the concentration of S^{2-} ions which was already small, becomes smaller still. But even then it is larger than that required for the solubility products of sulphides of copper, cadmium, bismuth, arsenic, antimony and tin, to be exceeded. Therefore, these cations get precipitated as sulphides in acidic solution in the Second Group of qualitative analysis. But, as the solubility products of sulphides of nickel, cobalt, manganese and zinc are comparatively higher, the sulphide ion concentration in the presence of hydrochloric acid is smaller than that required to cause their precipitation. These cations, therefore, do not get precipitated in Group II. Since they require a larger concentration of sulphide ions, a highly ionised sulphide, such as ammonium sulphide, is added (or which is the same thing as passing hydrogen sulphide through ammoniacal solution). By this means, the product [Zn2+[S2-], for example, in solution exceeds the solubility product of zinc sulphide. Therefore, zinc sulphide is precipitated. Similarly, the sulphides of nickel, cobalt and manganese, which all appear in Group IV of qualitative analysis, get precipitated. The solubility product of cadmium sulphide is greater than that of the other sulphides of the Second Group. Therefore, the sulphide ion concentration in this case should not be made very low. In other words, excess

of hydrochloric acid should be avoided or the solution should be diluted before passing hydrogen sulphide for the detection of Cd^{2+} in the second Group of qualitative analysis

Reference:
Principles of Physical Chemistry, Puri, Sharma and Pathania