SOLUBILITY PRODUCT:

If to a given amount of solvent at a particular temperature, a solute is added gradually in increasing amounts, a stage is reached when some of the solute remains undissolved, no matter how long we wait or how vigorously we stir. The solution is then said to be saturated. A solution which remains in contact with undissolved solute is said to be saturated. At saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

In case the solute is an electrolyte, its ionisation occurs in solution and degree of dissociation depends on the concentration of dissolved electrolyte at a particular temperature. Thus, in a saturated solution of an electrolyte two equilibria exist and can be represented as:

\[ AB \leftrightarrow AB \leftrightarrow A^+ + B^- \]

Solid unionized ions (dissolved)

Applying the law of action to the ionic equilibrium,

\[ [A^+][B^-]/[AB] \]

Since the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature, i.e., \([AB] = K' = \text{constant}\).

Hence, \([A^+] [B^-] = K[AB] = KK = K_s (\text{constant})\)

\(K_s\) is termed as the solubility product. It is defined as the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.

Consider, in general, the electrolyte of the type \(A_xB_y\) which is dissociated as:

\[ A_xB_y \leftrightarrow xA^{y+} + yB^{x-} \]

Applying law of mass action,

\[ [Ay+]x[Bx-]y/[A_xB_y] = K \]

When the solution is saturated,

\[ [A_xB_y] = K' (\text{constant}) \]

or \([A^{y+}]^x[B^{x-}]^y = K [A_xB_y] = KK' = K_s (\text{constant})\)
Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

Note: Solubility product is not the ionic product under all conditions but only when the solution is saturated.

**Different Expressions for Solubility Products**

(i) Electrolyte of the type AB:

Its ionisation is represented as:

\[
AB \leftrightarrow A^+ + B^-
\]

Thus, \( K_s = [A^+][B^-] \)

\( \text{AgCl} \leftrightarrow \text{Ag}^+ + \text{Cl}^-; \quad K_s = [\text{Ag}^+][\text{Cl}^-] \)

\( \text{BaSO}_4 \leftrightarrow \text{Ba}^{2+} + \text{SO}_{4}^-; \quad K_s = [\text{Ba}^{2+}][\text{SO}_{4}^-] \)

(ii) Electrolyte of the type AB\(_2\):

Its ionisation is represented as:

\[
AB_2 \leftrightarrow A^{2+} + 2B^-
\]

Thus, \( K_s = [A^{2+}][B^-]^2 \)

\( \text{PbCl}_2 \leftrightarrow \text{Pb}^{2+} + 2\text{Cl}^-; \quad K_s = [\text{Pb}^{2+}][\text{Cl}^-]^2 \)

\( \text{CaF}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{F}^-; \quad K_s = [\text{Ca}^{2+}][\text{F}^-]^2 \)

(iii) Electrolyte of the type A\(_2\)B:

Its ionisation is represented as:

\[
A_2B \leftrightarrow 2A^{2+} + B^{2-}
\]

Thus, \( K_s = [A^{+}]^2[B^{-}] \)

\( \text{Ag}_2\text{CrO}_4 \leftrightarrow 2\text{Ag}^+ + \text{CrO}_{4}^{2-}; \quad K_s = [\text{Ag}^+]^2[\text{CrO}_{4}^-] \)

\( \text{H}_2\text{S} \leftrightarrow 2\text{H}^+ + \text{S}^{2-}; \quad K_s = [\text{H}^+]^2[\text{S}^-] \)
(iv) Electrolyte of the type $A_2B_3$:

Its ionisation is represented as:

$$A_2B_3 \leftrightarrow 2A^{3+} + 3B^{-}$$

Thus, $K_s = [A^{3+}]^2[B^{-}]^3$

$As_2S_3 \leftrightarrow 2As^{3+} + 3S^{2-}$; $K_s = [As^{3+}]^2[S^{2-}]^3$

$Sb_2S_3 \leftrightarrow 2Sb^{3+} + 3S^{2-}$; $K_s = [Sb^{3+}]^2[S^{2-}]^3$

(v) Electrolyte of the type $AB_3$:

Its ionisation is represented as:

$$AB_3 \leftrightarrow A^{3+} + 3B^{-}$$

Thus, $K_s = [A^{3+}][B^{-}]^3$

$Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^{-}$; $K_s = [Fe^{3+}][OH^{-}]^3$

$AH_3 \leftrightarrow Al^{3+} + 3I^{-}$; $K_s = [Al^{3+}][I^{-}]^3$

**Solubility product of a weak electrolyte:**

Let degree of ionization of weak electrolyte $A_mB_n$ be 'a'.

$$A_mB_n \leftrightarrow mA^{n+} + nB^{m-}$$

$t = 0$

\[
\begin{array}{ccc}
  s & 0 & 0 \\
  t_{eq} & s-sa & msa & nsa \\
\end{array}
\]

$K_{sp} = [A^{n+}]^m[B^{m-}]^n$

$= [msa]^m[nsa]^n$

$K_{sp} = m^n n^m (sa)^{m+n}$

**Criteria of precipitation of an electrolyte:**

A very useful conclusion is derived from the **solubility product** concept. No precipitation of the electrolyte occurs if the **ionic product** is less than the **solubility product**, i.e., the solution has not reached the saturation stage.
Case I: When $K_{ip} < K_{sp}$, then solution is unsaturated in which more solute can be dissolved.

Case II: When $K_{ip} = K_{sp}$, then solution is saturated in which no more solute can be dissolved.

Case III: When $K_{ip} > K_{sp}$, then solution is supersaturated and precipitation takes place.

When the ionic product exceeds the solubility product, the equilibrium shifts towards left-hand side, i.e., increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solution as precipitate.

Thus, for the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product. For example, if equal volumes of 0.02 M AgNO$_3$ solution and 0.02 M K$_2$CrO$_4$ solution are mixed, the precipitation of Ag$_2$CrO$_4$ occurs as the ionic product exceeds the solubility product of Ag$_2$CrO$_4$ which is $2 \times 10^{-12}$.

In the resulting solution,

$[Ag^+] = 0.02/2 = 0.01 = 1 \times 10^{-2}$ M

and $[CrO^{2-}_4] = 0.02/2 = 0.01 = 1 \times 10^{-2}$ M

**Ionic product** of Ag$_2$CrO$_4 = [Ag^+]^2 [CrO^{2-}_4]$

\[
= (1 \times 10^{-2})^2 (1 \times 10^{-2})
\]

\[
= 1 \times 10^{-6}
\]

$1 \times 10^{-6}$ is higher than $2 \times 10^{-12}$ and thus precipitation of Ag$_2$CrO$_4$ occurs.