

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:



Solid unionized ions

(dissolved)

Applying the law of action to the **ionic equilibrium**,

$$\frac{[A^+][B^-]}{[AB]}$$

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, $[A^+][B^-] = K[AB] = KK = K_s$ (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:



Applying law of mass action,

$$\frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]} = K$$

When the solution is saturated,

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

or $[A^{y+}]^x[B^{x-}]^y = K [A_xB_y] = KK' = K_s$ (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.

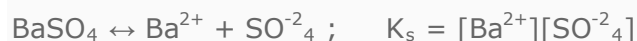
Different Expressions for Solubility Products

(i) Electrolyte of the type AB:

Its ionisation is represented as:



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

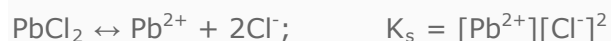


(ii) Electrolyte of the type AB₂:

Its ionisation is represented as:



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

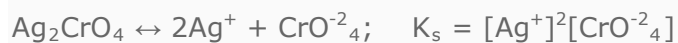


(iii) Electrolyte of the type A₂B:

Its ionisation is represented as:

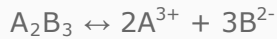


Thus, $K_s = [A^+]^2[B^{2-}]$



(iv) Electrolyte of the type A_2B_3 :

Its ionisation is represented as:



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

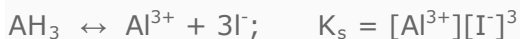


(v) Electrolyte of the type AB_3 :

Its ionisation is represented as:



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



Solubility product of a weak electrolyte:

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



$$t = 0 \quad \quad s \quad \quad 0 \quad \quad 0$$

$$t_{eq} \quad \quad s-sa \quad \quad msa \quad \quad nsa$$

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

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

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

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_2CrO_4 solution are mixed, the precipitation of Ag_2CrO_4 occurs as the **ionic product** exceeds the **solubility product** of Ag_2CrO_4 which is 2×10^{-12} .

In the resulting solution,

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

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

$$\begin{aligned} \text{Ionic product of } \text{Ag}_2\text{CrO}_4 &= [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ &= (1 \times 10^{-2})^2 (1 \times 10^{-2}) \\ &= 1 \times 10^{-6} \end{aligned}$$

1×10^{-6} is higher than 2×10^{-12} and thus precipitation of Ag_2CrO_4 occurs.

Source : <http://ciseche10.files.wordpress.com/2013/12/ionic-equilibrium.pdf>