B.Sc. (Honours) Part-I
Paper-IA

Topic: Solubility Product

UG
Subject-Chemistry

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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:

$$AB \leftrightarrow AB \leftrightarrow \underbrace{A^+ + B^-}$$

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'= 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.

Or

The solubility product is a kind of equilibrium constant and its value depends on temperature. Ksp usually increases with an increase in temperature due to increased solubility.

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, $[A_xB_y] = K'$

(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.

Simpler way:

Suppose barium sulphate along with its saturated aqueous solution is taken. The following equation represents the equilibrium set up between the undissolved solids and ions:

$$BaSO_4 \rightleftharpoons_{\text{saturated solution in water}} Ba^{2+}(aq) + SO_4^{-}(aq)$$

The equilibrium constant in the above case is:

$$K = [Ba^{2+}][SO_4^{-}][BaSO_4]$$

In case of pure solid substances the concentration remains constant, and so we can say:

$$K_{sp} = K[BaSO_4] = [Ba^{2+}][SO_4^{-}]$$

Here Ksp is known as the solubility product constant. This further tells us that solid barium sulphate when in equilibrium with its saturated solution, the product of concentrations of ions of both barium and sulphate is equal to the solubility product constant.

Significance of Solubility Product

Solubility depends on a number of parameters amongst which lattice enthalpy of salt and solvation enthalpy of ions in the solution are of most importance.

- When a salt is dissolved in a solvent the strong forces of attraction of solute (lattice enthalpy of its ions) must be overcome by the interactions between ions and the solvent.
- The solvation enthalpy of ions is always negative which means that energy is released during this process.
- The nature of the solvent determines the amount of energy released during solvation that is solvation enthalpy.
- Non-polar solvents have a small value of solvation enthalpy, meaning that this energy is not sufficient to overcome the lattice enthalpy.

- So the salts are not dissolved in non-polar solvents. Hence, for salt to be dissolved in a solvent, its solvation enthalpy should be greater than its lattice enthalpy.
- Solubility depends on temperature and it is different for every salt.

Application of Solubility Product

(a) **In the purification of common salt:** A saturated solution of NaCl leads to precipitation of NaCl on passing HCl gas through it. An increase in $[Cl^-]$, shifts the equilibrium, $NaCl(s) \rightleftharpoons Na^+ + Cl^-$ to backward direction because of higher Ionic product concentration, i.e.,$[Na^+][Cl^-] > K_{sp}$.

(b) **In the preparation of $NaHCO_3$:** The precipitation of $NaHCO_3$ from its saturated solution in Solvay's ammonia soda process from its saturated solution is made by the addition of NH_4HCO_3.

(c) **Predicting precipitation in ionic reactions:** During an ionic reaction, the product's precipitation can be predicted when the product of ionic concentration of solute exceeds its K_{sp}.

(d) **Salting out action of soap:** A saturated solution of soap (RCOONa), the sodium salt of higher fatty acids show precipitation of soap on the addition of sodium chloride. This is because of the fact that an increase in Na^+ ion concentration helps in crossing over $[Na^+][RCOO^-]$ to their K_{sp} value.

(e) **In Qualitative Analysis:** The Qualitative analysis of a mixture is based on the principle of solubility product.