APPLICATIONS OF SOLUBILITY PRODUCT

(i) Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:

$$NaCl \leftrightarrow Na^+ + Cl^-$$

$$HCl \leftrightarrow H^+ + Cl^-$$

The concentration of Cl^- ions increases considerably in solution due to ionization HCl. Hence, the ionic product $[Na^+][Cl^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

Soap is a sodium salt of higher acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

$$C_nH_{2n+1}\,COONa \leftrightarrow C_nH_{2n+1}\,COO^- + Na^+$$

Soap

$$NaCl \leftrightarrow Na^+ + Cl^-$$

Thus, the concentration of Na+ ions increases considerably on addition of NaCl solution. Hence, the ionic product $[C_nH_{2n+1}COO^-]\,[Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda):

In Solvay's soda process. CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.

$$NH_4OH + CO_2 \rightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl, NH_3HCO_3 and NaCl.

Thus, baking soda ($NaHCO_3$) can be quantifiably estimated.

(iv) Application of solubility product in quantitative analysis

1. Estimation of barium as barium sulphate:

H_2SO_4 as precipitating agent is added to the aqueous solution of $BaCl_2$.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

Precipitation of $BaSO_4$ takes place when its ionic product exceeds solubility product. H_2SO_4 is added in slight excess to ensure complete precipitation. Large excess of H_2SO_4 is harmful for complex formation.

2. Estimation of silver as silver chloride:

NaCl solution is added to the silver nitrate solution, slight excess of NaCl is added to ensure complete precipitation.

$$AgNO_3 + NaCl \rightarrow AgCl + NaBO_3$$

Again, precipitation of AgCl takes place when ionic product of AgCl exceeds its solubility product.

3. In a similar manner. We estimate lead as lead chromate, calcium as calcium oxalate, etc.

(i) Precipitation of the sulphides of group II and IV

Hydrogen sulphide is a weak electrolyte and is used for the precipitation of various sulphides of group II and IV in quantitative analysis.

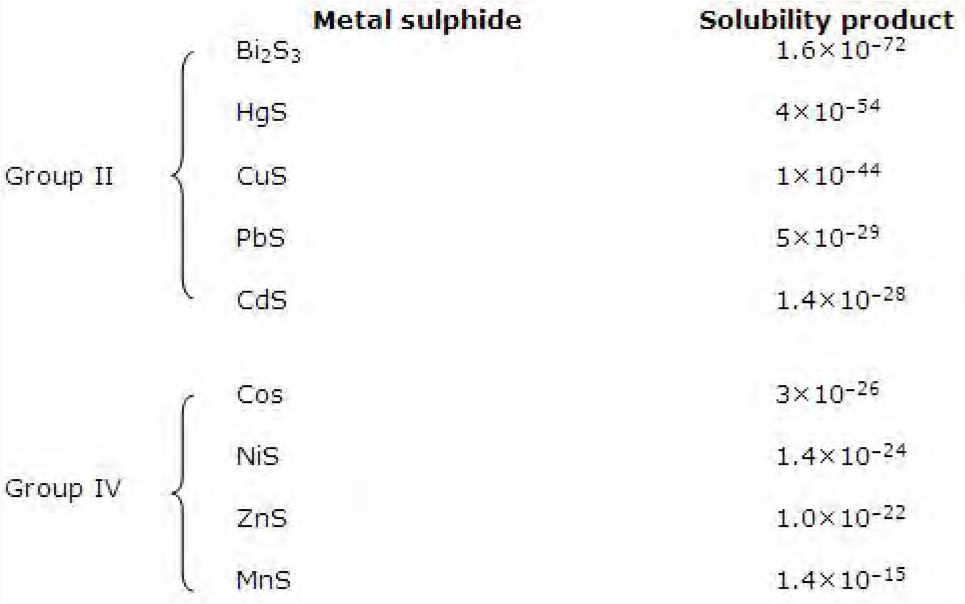
It ionizes to a small extent in water:

$$H_2S \leftrightarrow 2H^+ + S^{2-}$$

Applying law of mass action,

$K = ([H^+]^2 [S^{2-}])/[H_2 S]$

The concentrations of $S2^-$ ions can be decreased by increasing concentration of H^+ions and it can be increased by decreasing concentration of H^+ ions. In group II, lower concentration of sulphide ions is required as the solubility products of the sulphides of group II are low while higher concentration of sulphide ions is required in group IV as the solubility products of the suphides of group IV are high. The values of solubility products of various sulphides are given below.



	Metal sulphide	Solubility product
Group II	Bi_2S_3	1.6×10^{-72}
	HgS	4×10^{-54}
	CuS	1×10^{-44}
	PbS	5×10^{-29}
	CdS	1.4×10^{-28}
Group IV	Cos	3×10^{-26}
	NiS	1.4×10^{-24}
	ZnS	1.0×10^{-22}
	MnS	1.4×10^{-15}

The concentration of $S2^-$ ions in group II is lowered by maintaining acidic medium. In the presence of HCl, the ionization of H_2S is suppressed due to common ion effect. The concentration is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated. However, CdS has somewhat higher value. For its precipitation, dilution of the solution is done which increases ionization of H_2S and thereby increasing concentration of $S2^-$ ions.

In group IV, higher concentration of $S2^-$ ions is needed. This is done by changing the medium for acidic to alkaline. Ammonium hydroxide is added, the OH^- ions furnished by NH_4OH remove H^+ ions from solution in the form of water molecules as,

$$H^+ + OH^- \leftrightarrow H_2O$$

More of the ionization of H_2S occurs and, thus, concentration of $S2^-$ ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products add they get precipitated.

(i) Precipitation of III group hydroxides

When NH_4OH is added in presence of NH_4Cl then precipitation of II group hydroxides takes place, i.e., $Al(OH)_3$, $Fe(OH)_3$ and $Cr(OH)_3$ are precipitated. Solubility product of III group hydroxides is less than those of higher group hydroxides.

$$NH_4Cl \rightarrow NH^+{}_4 + Cl^-$$

$$NH_4OH \leftrightarrow NH^+{}_4 + OH^-$$

NH^{+}_{4} ion furnished by NH_4Cl lowers the ionisatin of NH_4OH and hence the concentration of hydroxide ion OH^{-}. At low concentration of hydroxide ion only III group hydroxides precipitate.

Fractional Precipitation

It is a technique of separating two or more ions from a solution by adding a reagent that precipitates first one ion and then the second.

Let us suppose 0.1 M Ba^{2+} and 0.1 M Sr^{2+} in aqueous solution. K_2CrO_4 is added as precipitating agent. K_{sp} $BaCrO_4$ is 1.2×10^{-10} and K_{sp} $SrCrO_4$ is 3.5×10^{-5}.

$[CrO^{2-}_{4}]$concentration required to precipitate $BaCrO_4$

$$= K_{sp}/[Ba^{2+}] = 1.2 * 10^{-10}/0.1 = 1.2 * 10^{-9}$$

$BaCrO_4$ will precipitate first because it requires low concentration of CrO^{2-}_{4} ions. On addition of chromate ions, $BaCrO_4$ starts precipitating when chromate ion concentration reaches 1.2×10^{-9} M. When CrO^{2-}_{4} ion concentration reaches upto 3.5×10^{-4} M, then $SrCrO_4$ also starts precipitating.

Remaining concentration of Ba^{2+} when $SrCrO_4$ starts precipitation.

$$=(K_{sp}\ BaCrO_4)/[CrO_4^{2-}] = (1.2\times10^{-10})/(3.5\times10^{-4})= 3.4\times10^{-7}\ M$$

$$\%\ \text{remaining concentration} = (3.4 * 10^{-7})/0.1 * 100$$

$$= 0.00034\%$$

Stability Constant

Let us consider dissociation of the ion $FeBr^{+}$.

$$FeBr^{+} \leftrightarrow Fe^{2+} + Br^{-}$$

Dissociation constant for above equilibria may be given as

$$K_d = [Fe^{2+}][Br^{-}]/[FeBr^{+}]$$

Reciprocal of dissociation constant is called stability constant.

$$K_s = [FeBr^{+}]/([Fe^{2+}][Br^{-}])$$

Let us consider the formation of complex $K_2Cd(CN)_4$, Complex ion is $Cd(CN_4{}^{2-})$ where oxidation state of central metal Cd^{2+} is (2+). Complexing process proceeds in four steps as

$$Cd^{2+} + CN^- \rightleftharpoons CdCN^+ \qquad K_1 = \frac{[CdCN^+]}{[Cd^{2+}][CN^-]}$$

$$CdCN^+ + CN^- \rightleftharpoons Cd(CN)_2 \qquad K_2 = \frac{[Cd(CN)_2]}{[CdCN^+][CN^-]}$$

$$Cd(CN)_2 + CN^- \rightleftharpoons Cd(CN)_3^- \qquad K_3 = \frac{[Cd(CN)_3^-]}{[Cd(CN)_2][CN^-]}$$

$$Cd(CN)_3^- + CN^- \rightleftharpoons Cd(CN)_4^{2-} \qquad K_4 = \frac{[Cd(CN)_4^{2-}]}{[Cd(CN)_2^-][CN^-]}$$

Overall reaction may be given as

$$Cd2+ + 4CN- \rightleftharpoons [Cd(CN)_4^{2-}] \qquad K_s = \frac{[Cd(CN)_4^{2-}]}{[Cd^{2+}][CN^-]^4}$$

Here $Ks = K_1K_2K_3K_4$.

Significance of stability constant:

Greater will be the value of stability constant more stable will be the complex.

Note :

(a) If on addition of a common ion in a salt solution (sparingly soluble), formation of complex ion takes place, then ionization increases, i.e., equilibrium shifts towards right hand direction to maintain the value of K_{sp} constant. It means, addition of common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the concept of common ion effect.

(b) When we add an electrolyte to another electrolyte solution having no common ion, then ionization of the later increases.

(c) For a given electrolyte solubility product is always constant at a particular temperature.

Solubility of Metal Hydroxides in Acid Medium

H^+ ion furnished by the medium effects the solubility of metal hydroxide, say $M(OH)^2$, because of neutralization of OH^- ion by H^+ ion.

$$M(OH)^2 \leftrightarrow M^{2+} + 2OH^-$$

$$K_{sp} \text{ of } M(OH)^2 = [M2^+][OH^-]^2$$

$$[M^{2+}] = K_{sp}/[OH^-]^2$$

$[H^+]\ [OH^-] = K_w = 10^{-14}$

$[OH^-]^2 = 10^{-28}/[H^+]^2$

From Eqs. (i) and (ii), we have

$[M^{2+}] = K_{sp}[H^+]^2/10^{-28}$

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