

What is Common-ion effect? Explain with example.

⇒ If there is no formation of complex ions to disturb the equilibrium, then solubility of any salt is less in a solution containing a common ion than in water alone. This effect is known as common-ion effect.

Let us consider a weak acid, HA. The equilibrium between undissociated molecules and the produced ions is



The dissociation constant, K_a of the weak acid in dilute solution is

$$K_a = \frac{C_{H^{\oplus}} \cdot C_{A^{\ominus}}}{C_{HA}}$$

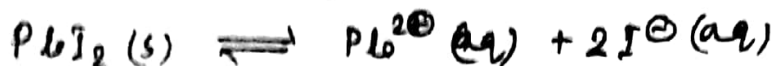
The addition of either H^{\oplus} ion or A^{\ominus} ion will affect the equilibrium. To keep K_a constant, some of the added ions will combine with opposite ions to produce undissociated HA molecule. The net result is a decrease in degree of dissociation. This is called common-ion effect.

Solubility of PbI_2 decreases in presence of $Pb(NO_3)_2$, ^{common ion} but increases in presence of KNO_3 . - Explain.

or,

Solubility of a sparingly soluble salt ^{uncommon ion} decreases in presence of common ion, but increases in presence of uncommon ion. - Explain.

⇒ we consider the saturated solution of the sparingly soluble salt, PbI_2 , if excess solid is added, then in aqueous medium the following equilibrium exists:



The solubility product is given by -

$$K_{sp} = a_{Pb^{2+}} \cdot a_{I^{-}}^2$$

$$= (c_{Pb^{2+}} \cdot \gamma_{\pm}^2) \cdot (c_{I^{-}}^2 \cdot \gamma_{\pm}^2) \quad \gamma_{\pm} \approx 1 \text{ so, neglected.}$$

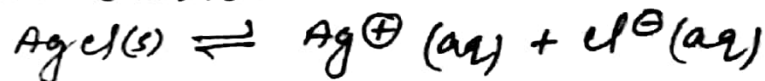
where 'c' is the concentration in moles per litre of the constituent ion and γ_{\pm} is the mean ionic activity co-efficient of the electrolyte. At a given temperature K_{sp} remains constant.

If we add $Pb(NO_3)_2$ in PbI_2 , then since there are already Pb^{2+} ion, so to keep K_{sp} constant concentration of I^{-} ion must decrease. But I^{-} ions are coming from PbI_2 alone, so solubility of PbI_2 will decrease.

But if we add KNO_3 in PbI_2 solution, then ionic strength of the solution will be increased. So from Debye-Hückel limiting law ($\log \gamma_{\pm} = -A z_+ z_- \sqrt{\mu}$) γ_{\pm} should decrease. To keep K_{sp} constant $c_{Pb^{2+}}$ and $c_{I^{-}}$ should increase. So solubility should increase. Thus, the solubility of a salt decreases in presence of common ion, but increases in presence of uncommon ion.

The solubility of $AgCl$ decreases in presence of KCl solution, but increases in presence of ammonia solution. — Explain.

\Rightarrow We consider the saturated solution of $AgCl$, if excess solid is added then following equilibrium exists:

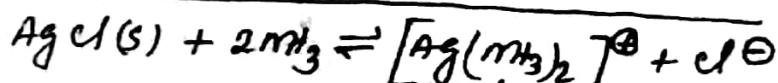
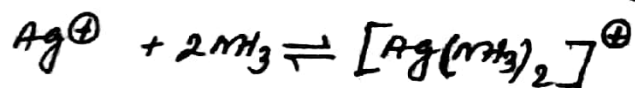
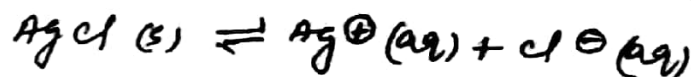


The thermodynamic solubility product is

$$K_{sp} = (c_{Ag^{+}} \cdot c_{Cl^{-}}) \cdot (\gamma_{\pm})^2$$

Since K_{sp} is constant at a given temperature. If we add KCl solution in $AgCl$, then due to common ion Cl^{-} , the solubility of $AgCl$ decreases.

But if we add ammonia solution to $AgCl$, then a soluble complex $Ag(NH_3)_2Cl$ is produced. The various equilibrium involved in the dissolution of $AgCl$ in aqueous ammonium solution are as follows:



The equilibrium is shifted towards right and so solubility of $AgCl$ increases in presence of ammonia solution.