

product, K_{sp} is given by -

$$K_{sp} = a_{Ag^{\oplus}}^2 \cdot a_{CrO_4^{2\ominus}}$$
$$= (c_{Ag^{\oplus}}^2 \cdot c_{CrO_4^{2\ominus}}) \cdot \gamma_{\pm}^3$$

Suppose, The solubility of Ag_2CrO_4 in the solution is 's' gm. moles lit.⁻¹ then we have

$$c_{Ag^{\oplus}} = 2s \text{ (M)} \text{ and } c_{CrO_4^{2\ominus}} = s \text{ (M)}.$$

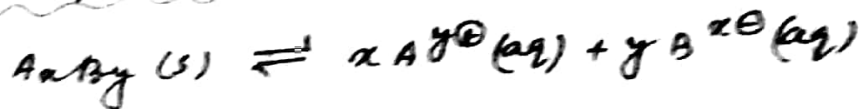
$$\therefore K_{sp} = (2s)^2 \cdot s \cdot \gamma_{\pm}^3$$
$$= 4s^3 \gamma_{\pm}^3$$

At very low ionic strength, $\gamma_{\pm} = 1$, we have

$$K_{sp} = 4s^3$$

This is the relation between solubility and solubility product of Ag_2CrO_4 .

Find out the general relation between solubility and solubility product of A_xB_y .



$$K_{sp} = a_{A^{y\oplus}}^x \cdot a_{B^{x\ominus}}^y$$
$$= (c_{A^{y\oplus}}^x \cdot c_{B^{x\ominus}}^y) (\gamma_{\pm})^{x+y}$$

In general, if 's' be the solubility of A_xB_y in water, which is sparingly soluble, we have

$$c_{A^{y\oplus}} = xs, \quad c_{B^{x\ominus}} = ys$$

assuming, $\gamma_{\pm} = 1$, we get

$$K_{sp} = (xs)^x \cdot (ys)^y$$
$$= (x^x \cdot y^y) s^{x+y}$$

$$\text{or, } s^{x+y} = \frac{K_{sp}}{x^x \cdot y^y}$$

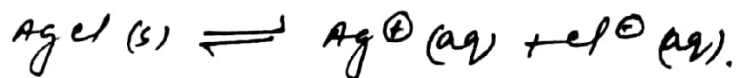
$$\text{or, } s = \left(\frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}}$$

This is the relation between solubility and solubility product of A_xB_y .

Q.46.

Why does precipitation take place?

⇒ Let us consider the saturated solution of $AgCl$. If excess solid is added then the following equilibrium exists:



The solubility product, K_{sp} is given by

$$K_{sp} = a_{Ag^+} \cdot a_{Cl^-}$$

When the product of ionic activities (or conc.) with appropriate power exceeds the solubility product of the salt, the excess ions are removed in the form of solid residue. Therefore precipitation occurs. Hence precipitation is nothing, but shifting the equilibrium from right to left. When ionic product $< K_{sp}$, there will be no precipitation. Again, when ionic product = K_{sp} , the solution will be saturated.

* Application of solubility product:-

Q.47. Why is the medium kept acidic in gr. II pptⁿ?

⇒ In qualitative analysis of both gr. II (Ca^{2+}, Pb^{2+} etc.) & gr. III B ($Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}$) metal ions are precipitated as their insoluble sulphides. To prevent the precipitation

of gr. III B metal sulphides in gr. II, the medium is kept acidic. This is because gr. II metal sulphides have extremely small solubility product and so negligible amount of S^{2-} ions can cause their precipitation. But gr. III B metal sulphides have relatively high solubility product and so comparatively large amount of sulphide ion is necessary for their precipitation. If H_2S is passed in acid medium, then due to common ion effect dissociation of H_2S is too small that amount of S^{2-} ions is just sufficient for gr. II metal precipitation, but is insufficient for gr. III B metal precipitation. That is why HCl is added.

48. Why is NH_4Cl added in gr. III A precipitation in presence of NH_4OH ?

\Rightarrow In qualitative analysis, gr. III A metal ions (Fe^{3+} , Al^{3+} , Cr^{3+}) are precipitated as their insoluble hydroxides. These hydroxides have very low solubility product. Now some metal hydroxides of gr. III B, gr. IV etc. have also comparatively high solubility product. Hence if the concentration of added OH^- ions become more, they may also be precipitated in gr. III A. In order to avoid this NH_4OH is added in presence of NH_4Cl . Since NH_4OH is a weak base, in presence of common ion NH_4^+ , its dissociation becomes very small. Thus OH^- ions produced is sufficient for gr. III A pptn, but not sufficient for other groups. That is why NH_4Cl is added.