

Dr. L. K. Mishra
Deptt of Chemistry

Date:

Page No.

(1)

FOR. Deg II Chem Hons Paper - IV &
Deg II Sub Course

Solubility Product & Ostwald's dilution Law
For sparingly soluble salt the product of the total molecular concentration of the ions is constant, at constant temperature and that constant is known as the Solubility Product which is denoted by "S."

Let us suppose that AB is a given electrolyte for which we can write as



(solid) (dissolved) ions

Thus it can be expressed as

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

$$\text{or } [A^+][B^-] = K [AB] = S \text{ (Solubility Product)}$$

Where $[AB] = \text{Un-ionised}$ which is constant

For unsaturated solution $S > [A^+][B^-]$

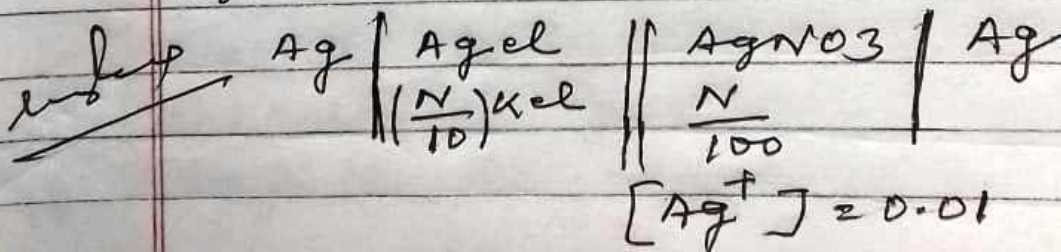
For saturated solution $S = [A^+][B^-]$

For the precipitation $S < [A^+][B^-]$
At a given temperature the value of S is constant.

For a given group the value of the solubility product is constant and thus for the precipitation it is necessary that $S < [A^+][B^-]$ and this is the reason that for the precipitation of the element of a given group, such type of reagent is required which can produce common ion effect in such a way that the above requirement i.e. $S < [A^+][B^-]$ must be fulfilled and this is the basic principle of the precipitation during qualitative analysis.

Determination of solubility product and solubility :-

Let us suppose that $AgCl$ is a given sparingly soluble salt by which a concentration cell is made by taking two metal electrodes



Since AgCl is a sparingly soluble salt thus it will not be ionised completely, therefore, KCl solution is utilised for the better flow of electricity, thus into the system $\frac{N}{10}$ KCl will also be decomposed along with the decomposition of AgCl but since KCl is a good electrolyte, therefore the Cl^- obtained by the decomposition of KCl will be greater than that of the decomposition of AgCl.

Thus we can neglect the concentration of Cl^- ion w.r. to the concentration of the Cl^- ions produced by the decomposition of KCl.

Let us suppose that KCl is completely decomposed then the concentration of Cl^- will be 0.1.

$$\text{i.e. } [\text{Cl}^-] = 0.1$$

~~and~~ Now the concentration of $[\text{Ag}^+]$ is calculated by measuring the emf of the above cell

$$E = 0.0591 \log \frac{0.1}{c}$$

By knowing the value of E in volts through potentiometer, c can be calculated.

$$\begin{aligned} \text{Solubility Product} &= [\text{Ag}^+][\text{Cl}^-] \\ &= c \times 0.1 \end{aligned}$$

$$\begin{aligned} \therefore \text{solubility} &= \sqrt{\text{Solubility Product}} \\ &= \sqrt{S} \\ &= \sqrt{c \times 0.1} \end{aligned}$$

Oswald's Dilution Law

This law is related with the equilibrium state between the ionised and un-ionised molecules in a given solution.

Let us suppose that

AB = An electrolyte

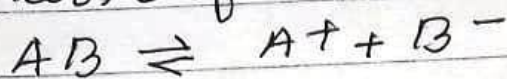
c = Dissolved moles

α = degree of dissociation

K = Equilibrium constant

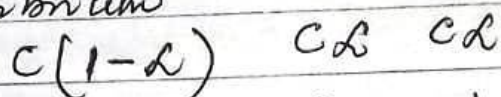
V = Volume of the aqueous solution in litre.

Now if the c moles of AB are dissolved in V litre of water then



Initially c 0 0

At equilibrium



Thus the concentration of AB , A^+ and B^- at the equilibrium will be

$$\frac{c(1-\alpha)}{V}, \quad \frac{c\alpha}{V}, \quad \frac{c\alpha}{V}, \text{ respectively}$$

$$\text{Equilibrium Constant } K = \frac{[A^+][B^-]}{[AB]}$$

$$= \frac{\frac{c\alpha}{V} \cdot \frac{c\alpha}{V}}{\frac{c(1-\alpha)}{V}} = \frac{c^2\alpha^2}{V^2} \cdot \frac{V}{c(1-\alpha)}$$

$$= \frac{c^2\alpha^2}{V^2} \times \frac{V}{c(1-\alpha)} = \frac{c\alpha^2}{V(1-\alpha)}$$

$$\therefore K = \frac{c\alpha^2}{V(1-\alpha)}$$

This expression is called Ostwald's dilution Law which is only applicable for the weak electrolyte such as CH_3COOH , NH_4OH etc and is not applicable for the case of strong electrolytes.