Solubility product:-

In a saturated situation of a salt, there exists a dynamic eqlbm b/w the excess of the solute and ions furnished by that part of the solute which has gone in solution.

Eg: When a sparingly soluble salt like AgCl is added to water, a very small amount dissolves and the rest of the salt remains in the solid state. ∴

$$AgCl\ (s,\ saturated\ soln) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

Acc. to law of chem eqlbm:

$$K = \frac{a_{Ag^+} \times a_{Cl^-}}{a_{AgCl}}$$

But activity of a solid is taken an unity by convention,

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

Where as K_{sp} is the solubility product

It is constant at a given temp. For convenience conc. terms can be used in place of activity (since ionic conc. are very low. activity of each ion is almost equal to its conc.

$\therefore K'sp = [Ag^+][Cl^-]$

$\Rightarrow K'sp = Ksp.$

$\therefore \boxed{Ksp = [Ag^+][Cl^-]}$

e.g

① $Ag_2SO_4\ (s, \text{Sald·sol}^n) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$

$\therefore Ksp = [Ag^+]^2[SO_4^{2-}].$

② $Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^-$

$Ksp = [Al^{+3}][OH^-]^3.$

③ $As_2S_3 \rightleftharpoons 2As^{+3} + 3S^{2-}$

$Ksp = [As^{+3}]^2[S^{2-}]^3.$

$\Rightarrow A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

$Ksp = [A^{y+}]^x[B^{x-}]^y$

∴ the solubility pdt of a sparingly soluble salt formuig a saturated sol^n in water is given by the product of the concentrations of the ions raised to a power equal to the number of times the ions occur in the eq^n representing dissociation of the electrolyte.

Molar solubility of sparingly soluble salt.

$$AB(s, \text{saturated sol}^n) \rightleftharpoons A^+(aq) + B^-(aq)$$

$[A^+] = S\ M$

$[B^-] = S\ M$

$\therefore K_{sp} = [A^+][B^-] = (S \text{ mol dm}^{-3})(S \text{ mol dm}^{-3})$

$= S^2 \text{ mol}^2 \text{ dm}^{-6}$

Q The solubility of AgCl in water at 25°C is 0.00179 g/L. Calculate its solubility product.

A: ~~Molar~~ Solubility $= 0.00179 \text{ g/dm}^{+3} = \frac{0.00179 \text{ g dm}^{-3}}{143.5 \text{ g mol}^{-1}}$

$= 1.25 \times 10^{-5} \text{ mol dm}^{-3}$

as $[Ag^+] = [Cl^-]$

$K_{sp} = [Ag^+][Cl^-] = (1.25 \times 10^{-5})(1.25 \times 10^{-5}) \text{ mol}^2 \text{ dm}^{-6}$

Q Calculate the solubility of $Al(OH)_3$ in g/L in water at 25°C.
Ksp of $Al(OH)_3 = 8.5 \times 10^{-32}$.

Ans $Al(OH)_3$ (S. sat. soln) $\rightleftharpoons Al^{+3}(aq) + 3OH^-(aq)$

If 's' is the molar solubility then:-

$1 dm^3 = 1L$

$Ksp = [Al^{+3}][OH^-]^3$
$= (S)(3S)^3$
$= 27 S^4$

8.5×10^{-8} mol $dm^{-3} = 27 \times S$

$\Rightarrow S = 0.749 \times 10^{-8}$ mol dm^{-3}.

or $S = 0.749 \times 10^{-8} \times 78$ g/mol
$= 5.842 \times 10^{-7}$ g/dm^3.

Applications of the solubility Product Principle:-

I) Determination of Solubilities of sparingly soluble Salts:

Let solubility of AgCl = S

Then $Ksp = [Ag^+][Cl^-] = S^2$.

$\therefore S = \sqrt{Ksp}$ mol dm^3

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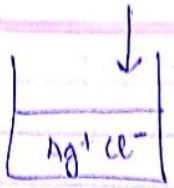

$KCl + Ag^+ + Cl^- \longrightarrow AgCl\downarrow$
(dissocⁿ due to sparingly soluble)

The conc. of Ag^+ determined by EMF method. Suppose this is 'a' M, then Cl^- will also be 'a' M (due to AgCl) ∴ total Cl^- will be (a+b) M (due to KCl + AgCl)

∴ $K_{sp} = a(a+b)$.

as both a & b are known, Ksp can be found.

II

Predicting Precipitation Reaction :-

With the knowledge of Ksp we can predict whether under given conditions that substance would be ppted or not.

If Ionic product > Solubility product — Insoluble / ppted
Ionic pdt < Solubility pdt — Soluble / not ppted

e.g. Ksp of $CaSO_4$ in water at 25°C is $2.4 \times 10^{-5}\ M^2$. A sample of hard water contains 0.01 M of $CaCl_2$. It is required

to precipitate $CaSO_4$ by add^n of dil. H_2SO_4. The conc of dil H_2SO_4 is 0.001M. Will Calcium sulphate be precipitated if equal volumes of both are mixed?

Ans The solubility eq^n

$$CaSO_4(s, \text{saturated sol}^n) \rightleftharpoons Ca^{+2}(aq) + SO_4^{2-}(aq).$$

$$K_{sp} = [Ca^{+2}][SO_4^{2-}] = 2.4 \times 10^{-5} M^2$$

Ca^{+2} in H_2O = 0.01M

Total volume is doubled $\therefore$ Ca^{+2} conc $= \frac{0.01}{2} = 0.005M$

conc. of H_2SO_4 = 0.001M

$\therefore [SO_4^{2-}] = 0.001M$.

In mixture effective $[SO_4^{2-}] = \frac{0.001M}{2} = 0.0005M$.

Ionic product $= [Ca^{+2}][SO_4^{2-}] = 0.005 \times 0.0005\ M.$

$= 2.5 \times 10^{-6} M^2$.

As I.P < S.P

$\therefore$ it will not be precipitated.

3. Precipitation of Soluble Salts:-

Purification of common salt in pure state from their saturated solutions. This phenomena is called "Salting out".

$$NaCl\ (s,\ Satd.\ Sol^n) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$
(Impure)

$$K'_{sp} = [Na^+][Cl^-]$$

Then HCl is passed through this solution as a result $[Cl^-]$ ↑es considerably. So the ionic product exceeds the solubility product of NaCl, ∴ it precipitates out & impurities remains in the solution.

Another example of is Salting out soap.

4. Inorganic Analysis

a) Precipitation of Sulphides

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

Hydrogen sulphide is a weak acid and its dissociation is further suppressed by the addition of dil HCl due to common ion effect ∴ the conc of S^{2-} which was already small

becomes smaller. But this is still enough that is required to exceed the solubility pdts of sulphides of Cu^{+2}, Cd^{+2}, Bi^{+3}, As^{+3}, Sb^{+3} & Sn^{+2}. ∴ these groups get precipitated as sulphides in acidic solution in second group of qualitative analysis

For ions like Zn^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2} a little more S^{2-} conc is reqd than grp II cations ∴ passing H_2S in the ammonical solution a larger amount of S^{2-} is available which exceeds the solubility pdts of ZnS, NiS etc.. ∴ Group IV gets ppted.

In case of Cd^{+2} (as CdS) the solubility pdt is higher than the other members of grp II ∴ the conc of S^{2-} should not be made very low So excess of HCl should be avoided or the solution should be diluted enough before passing H_2S for the detection of Cd^{+2}.

Similarly for Precipitation of hydroxides in grp III

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

Ammonium hydroxide a weak base & its dissociation is further supressed by addition of NH_4Cl, a strong electrolyte having an ion common to it. As a result a very small

(57).

amount of OH^- is available which can only exceed the solubility pdt of grp III cations not grp IV.