

GENERAL CHEMISTRY.

UNI. CODE - USO1CCHE21.

CREDIT - 2. { 2 hr. Exam }

MARKS - 70 Marks External
30 Marks Internal.

UNIT - 3

IONIC EQUILIBRIUM.

In. Aqueous Solution

Ref. Book - Mahan B.H. Uni. Chem.

3rd Addition.

Mr. ATUL K KAPATEL

Chemistry Dept.

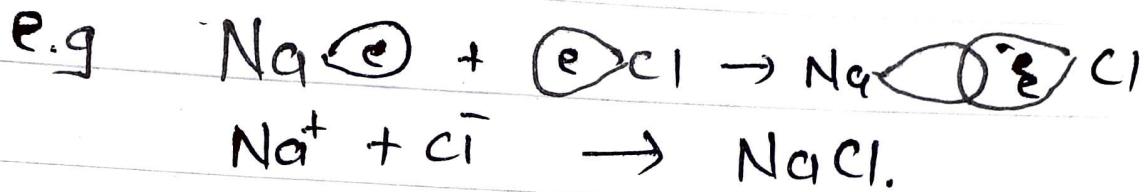
V. P & R.P.T.P. SCI COLLEGE

V. V. NAGAR

O1 Ionic Equilibrium.

Introduction.

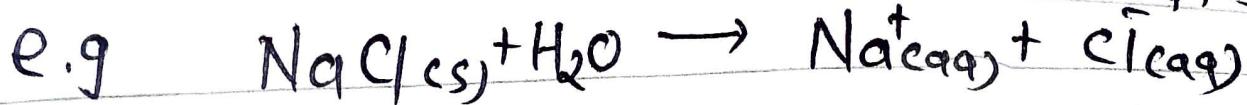
When one atom donate its outer electron to another atom via overlapping of their orbitals and form a bond is known as ionic bond.



* The substance made through ionic bond such type of substances are known as ionic sub. means inorganic substance.

* The detail study of ionic sub. is called Inorganic chemistry.

Generally ionic substance are soluble in aqueous, or ionic solvent via ionization of substance, and form a positive & negative ions. These are known as electrolytes.



Ionic substances are classified on base of their ionization factor.

* Strong electrolyte :- Such type of ionic substances are mostly ionized in aqueous solution e.g. strong Acid + strong base salt. NaCl , Na_2SO_4 , KBr , KCl ... etc.

* Weak electrolyte :- Such electrolyte substance has lower ionized in solvent approximately 1 to 20%. ionized.

* Sparingly soluble salt :- Such type of electrolyte are very low ionized & so very little amount are soluble in solvent. e.g. PbSO_4 , AgCl , CaF_2 , Ag_2CrO_4 ...

[Sparingly soluble salt are soluble in less than 1 gm soluble in 1 lit solvents]

Solubility :- Maximum soluble amount of electrolytic substance per liter solvent is called. Solubility.

Solubility is denoted by 'S'

Thus we can say that-

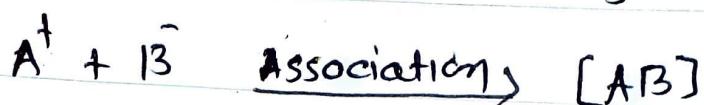
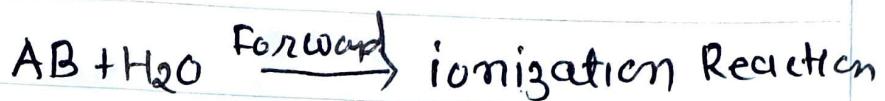
strong electrolyte has highest solubility while weak electrolytes has low solubility and sparingly soluble salt has lowest solubility

Ionic equilibrium and K_{sp} .

→ Consider AB is a sparingly soluble salt. Saturated solution of 'AB' in water, form an ionic equilibrium such as



where as



* thus forward Reaction is cleavage of ionic bond and backward Reaction is formation of ionic bond.

We know that

Equilibrium constant K is define as

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

$$\therefore \boxed{K_a[AB] = K_{sp}} \quad \text{---(i)}$$

$$\therefore \boxed{K_{sp} = [A^+][B^-]} \quad \text{---(ii)}$$

Eq.(i) & Eq(ii) are mathematical statement of ' K_{sp} '.

Definition of K_{sp} :- it is mathematical statement It is define as

"Ionic equilibrium constant K_{sp} is multiplication of concentration of their ions."

$$K_{sp} = K_a \cdot [AB]$$

$$K_{sp} = [A^+] [B^-]$$

K_{sp} value of is an internal property of sparingly soluble salt. each sparingly soluble salt has particular value at $25^\circ C$ temp and 1 atm. pressure

K_{sp} value is very important. we can determine \rightarrow solubility of salt

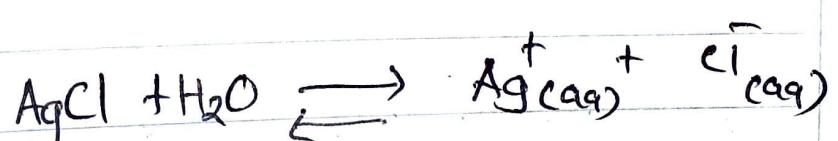
\rightarrow common ions effect

\rightarrow selective precipitation...etc.

Ex-1 Calculate solubility of AgCl in a water at $25^\circ C$ and 1 atm. pressure.

$$K_{sp}[\text{AgCl}] = 2.8 \times 10^{-10} \text{ mol/lit}$$

Ans-1 Consider, saturated solution of AgCl forming an ionic equilibrium such as



At initial stage 1 mol/lit

At Equi. stage $1 - s$ $-$ $s \text{ mol/lit}$ $s \text{ mol/lit}$

we know that

$$K_a = \frac{[\text{Ag}^+] [\text{Cl}^-]}{[\text{AgNO}_3]} = s$$

$$\therefore K_a[\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$$

we know that $K_a[\text{AgCl}] = K_{SP}$

$$\therefore K_{SP} = [\text{Ag}^+][\text{Cl}^-]$$

$$= [S][S].$$

where 'S' is solubility of AgCl

$$\therefore S^2 = K_{SP} = 2.8 \times 10^{-10} \text{ M.}$$

$$\therefore S = \sqrt{2.8 \times 10^{-10}}$$

$$S = 1.7 \times 10^{-5} \text{ mol/lit}$$

$$\therefore S = 1.7 \times 10^{-5} \times \text{Mol. Wt of AgCl (gm/lit)}$$

$$= 1.7 \times 10^{-5} \times 143 \text{ gm/lit}$$

$$= 243.1 \times 10^{-5}$$

$$S = 2.431 \times 10^{-3} \text{ gm/lit}$$

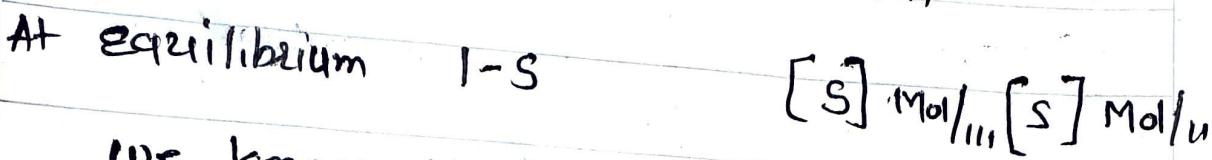
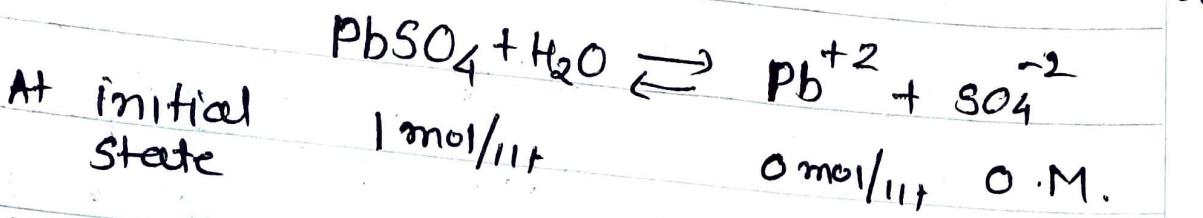
Thus, AgCl is only $2.431 \times 10^{-3} \text{ gm}$ soluble in one liter solution [less than 1.0 gm/lit]

Ex 2

Calculate solubility of P sparingly soluble salt PbSO_4 in water at 25°C Temp and 1.0 atm pressure [$K_{SP}(\text{PbSO}_4) = 1.8 \times 10^{-8} \text{ M}^2$]

Consider saturated aqueous soln of PbSO_4 form a following ionic equilibrium

such as.



We know that-

$$K_a = \frac{[\text{Pb}^{+2}][\text{SO}_4^{-2}]}{[\text{PbSO}_4]}$$

$$\therefore K_a[\text{PbSO}_4] = K_{sp} = [\text{Pb}^{+2}][\text{SO}_4^{-2}]$$

$$1.8 \times 10^{-8} \text{ M} = [\text{S}][\text{S}]$$

$$\therefore [\text{S}]^2 = 1.8 \times 10^{-8}$$

$$\therefore S = \sqrt{1.8 \times 10^{-8} \text{ mol/lit}}$$

$$= 1.34 \times 10^{-4} \text{ mol/lit}$$

Thus, the only 1.34×10^{-4} mol PbSO_4 soluble in a one lit. solution it is confirm that PbSO_4 is sparingly soluble salt

EXA = 03

calculate solubility of sparingly soluble salt - Ag_2CrO_4 in aqueous solution at 25°C .

Temp and 1. atm. Pressure.

$$K_{sp}[\text{Ag}_2\text{CrO}_4] = 1.9 \times 10^{-12} \text{ M}.$$

Ans-3. → Consider saturated aqueous solution of Ag_2CrO_4 forming a ionic equilibrium such as.



At initial stage

$$1 \text{ mol/litr}$$

$$0 \text{ mol/litr} \quad 0 \text{ mol/litr}$$

At equilibrium

$$1 - S$$

$$2S + S$$

$$\therefore K_a = \frac{[2\text{Ag}^+]^2 [2\text{CrO}_4^{2-}]}{[\text{Ag}_2\text{CrO}_4]}$$

$$\therefore K_a [\text{Ag}_2\text{CrO}_4] = K_{SP} = [2\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$= [2S]^2 [S]$$

$$= 4S^3$$

$$\therefore 4S^3 = 1.9 \times 10^{-12}$$

$$S^3 = \frac{1.9 \times 10^{-12}}{4} = 0.475 \times 10^{-12}$$

$$\therefore S = (0.475 \times 10^{-12})^{1/3}$$

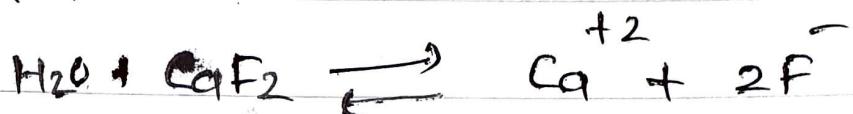
$$= 7.8 \times 10^{-5} \text{ mol/litr}$$

Thus only 7.8×10^{-5} mol Ag_2CrO_4 is dissolve in one lit soln.

ExA = 04

Calculate solubility of sparingly soluble salt CaF_2 in aqueous soln. at 25°C temp and 1 atm pressure $[K_{\text{sp}}[\text{CaF}_2]] = 1.7 \times 10^{-10} \text{ M}$

Ans. 4 → Consider saturated aqueous solution of CaF_2 forming a following ionic equilibrium.



At initial	1 mol/lit	0.0 M	0.0 M
Step			

At equilibrium	1 - s	s	+ 2s
Step			

$$\therefore K_a = \frac{[\text{Ca}^{+2}][2\text{F}^-]^2}{[\text{CaF}_2]}$$

$$\therefore K_a[\text{CaF}_2] = K_{\text{sp}} = [\text{Ca}^{+2}][2\text{F}^-]^2 \\ = [s][2s]^2$$

$$\therefore 4s^3 = K_{\text{sp}} = 1.7 \times 10^{-10} \text{ M}$$

$$s^3 = \frac{1.7 \times 10^{-10}}{4}$$

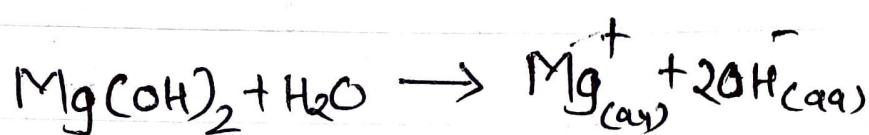
$$\therefore s = [0.425 \times 10^{-10}]^{1/3}$$

$$= 3.4 \times 10^{-4} \text{ mol/lit (M)}$$

ExA-05 → Calculate solubility of sparingly soluble salt $Mg(OH)_2$ in aqueous solution at $25^\circ C$ Temp and 1 atm pressure

$$K_{sp}(Mg(OH)_2) = 1.4 \times 10^{-12} M.$$

Ans-05 :- Consider, Saturated aqueous solution of $Mg(OH)_2$ is forming a following ionic equilibrium such as



At initial stage 1 M 0 M + 0.0 M

At equilibrium 1 - s s + 2s

$$\therefore K_a = \frac{[Mg]^{+2}[2OH]}{[Mg(OH)_2]}$$

$$\therefore K_a [Mg(OH)_2] = K_{sp} = [Mg]^{+2}[2OH]$$

$$= [s][2s]^2 \\ = 4s^3$$

$$\therefore s^3 = \frac{K_{sp}}{4} = 1.4 \times 10^{-12} M$$

$$s = [0.35 \times 10^{-12}]^{1/3}$$

$$s = 1.4 \times 10^{-4} \text{ mol/lit (M)}$$

Thus solubility of $Mg(OH)_2$ is $1.4 \times 10^{-4} \text{ mol/lit}$

COMMON IONS EFFECT

In 1884, French chemist Henry Le Chatelier introduce principle for all system in equilibrium. He stated as "When a stress is applied on a system in equilibrium. The system tends to adjust itself so as to reduce the stress".

In case of ionic equilibrium, suppression of the dissociation of weak electrolyte [backward reaction] done by addition of own ions. - is called common ions effects.

Mean Presence of common ions is increase rate of reaction of back ward reaction. is called common ion effect.

* Solubility of sparingly soluble salt is always decreases by effect of common ions present in ionic equilibrium system. Thus According to Le Chatelier principle. the reverse process is favored to reach the new state of equl. by common ions effect.

We can experimentally derive common ion effect by following illustration

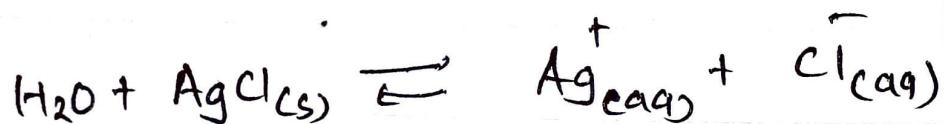
Exa. 06

* Calculate solubility of AgCl in pure water and 0.01 M NaCl solution and justify le Chatelier principle.

$$[K_{sp} \text{ [AgCl]}] = 2.8 \times 10^{-10} \text{ M}$$

Ans. 06

Consider, saturated aqueous solution of AgCl form a following equil. eqn.



At initial	1 M	0	0
Step 1			

At Equi.	1 - s	s	s
Step 2			

$$\therefore \text{Ionic equi } K_a = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

$$\therefore K_a [\text{AgCl}] = K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$\therefore 2.8 \times 10^{-10} \text{ M} = [s][s]$$

$$\therefore s^2 = 2.8 \times 10^{-10}$$

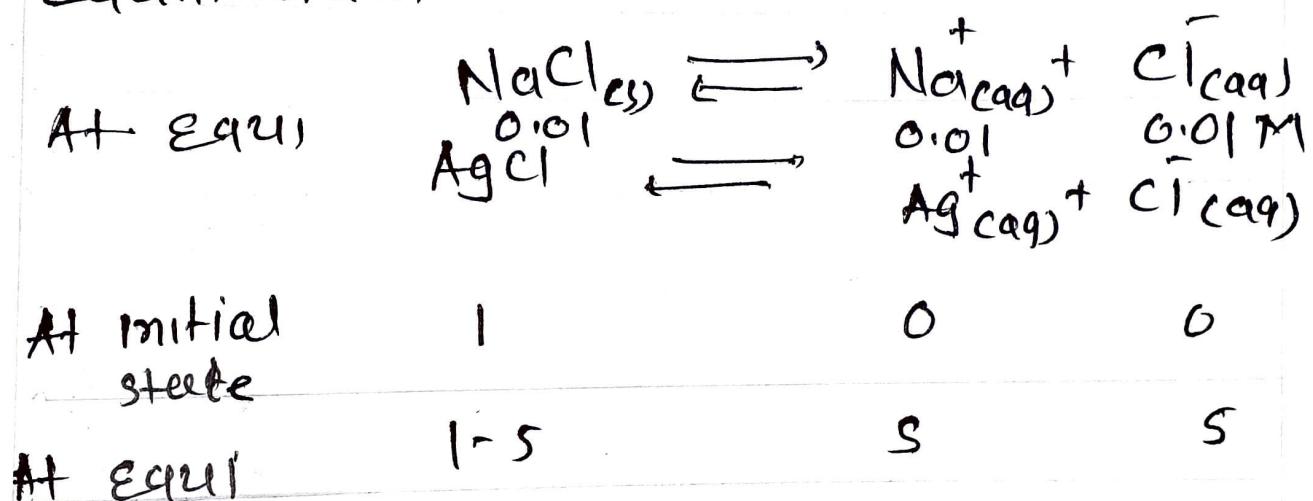
$$s = (2.8 \times 10^{-10})^{1/2} = 1.7 \times 10^{-5} \text{ M} \quad (\text{Ans})$$

- * Thus solubility of AgCl in pure water is 1.07×10^{-5} M

- * Solubility of AgCl in 0.1 M NaCl.

We know that NaCl is strong acid-base salt so it is completely ionized and then soluble in dilute solution

- so ~~ed~~ AgCl form a such ionic equilibrium



$$\text{Total} = S + [S \times 0.01]$$

$[S(Cl)]$ is very low so

$$stool \cong 0.01 M$$

we know

$$K_a \cdot [Ag^{(1)}] = K_{SP} = \frac{[Ag^{(1)}][Cl^{-}]}{[S][0.01]}$$

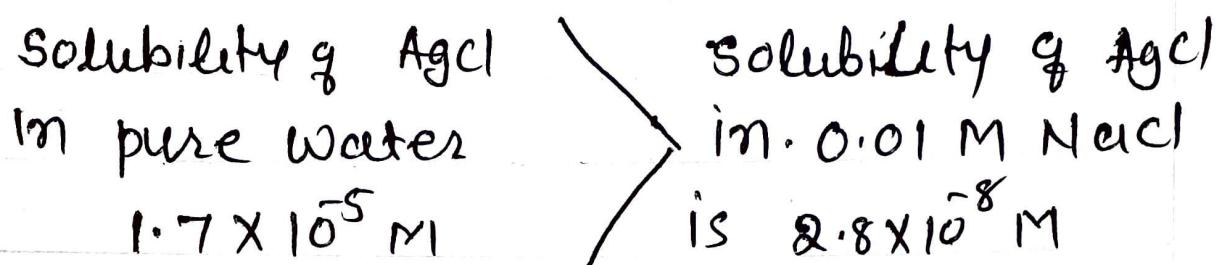
$$\therefore [S] = K_{SP} / 0.01$$

\therefore solubility of AgCl in 0.01M NaCl .
Solution is

$$[S] = \frac{K_{SP}}{0.01} = \frac{2.8 \times 10^{-8}}{0.01}$$

$$= 2.8 \times 10^{-8} \text{ M.}$$

Thus



Thus it is true that due to presence of common ion (Cl^-) the solubility of salt is decrease. This illustration follows ~~justly~~ to justify La-Chatelier's common ions effect.

* EX - 07

Calculate solubility of sparingly soluble salt- PbSO_4 in aqueous solution

(i) in $0.1\text{M } \text{Pb}(\text{NO}_3)_2$ solⁿ

(ii) in $1.0 \times 10^3 \text{M } \text{Na}_2\text{SO}_4$ solⁿ.

$$K_{SP}[\text{PbSO}_4] = 1.8 \times 10^{-8} \text{ mol/lit}$$

Ans-07 :- Consider Saturated solution of PbSO_4 in pure water, it form a ionic equilibrium such as { consider solubility of PbSO_4 is 's' }

$$\text{PbSO}_4(s) + \text{H}_2\text{O} \rightleftharpoons \text{Pb}^{+2} + \text{SO}_4^{-2}$$

At initial	1 mol/lit	0. mol/lit	0. mol/lit
	stege		

At equi $1-s$ s s

$$\therefore K_a = \frac{[\text{Pb}^{+2}][\text{SO}_4^{-2}]}{[\text{PbSO}_4]}$$

$$\therefore K_a [\text{PbSO}_4] = K_{sp} = [\text{Pb}^{+2}][\text{SO}_4^{-2}]$$

$$\therefore 1.8 \times 10^{-8} \text{ M} = [s][s]$$

$$\therefore s = \sqrt{1.8 \times 10^{-8} \text{ M}} = 1.34 \times 10^{-4} \text{ M}$$

Solubility of PbSO_4 in water is $1.34 \times 10^{-4} \text{ M}$.

i) In 0.1 M $\text{Pb}(\text{NO}_3)_2$ soln.

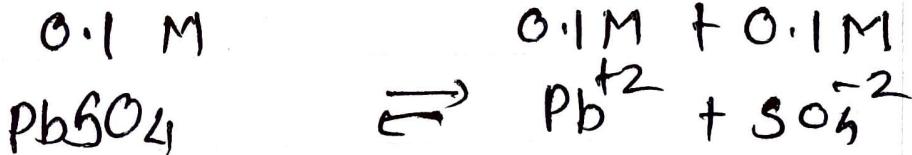
$\text{Pb}(\text{NO}_3)_2$ is a strong-acid-base salt

it is completely soluble in dilute solⁿ via ionization; PbSO_4 add in this solⁿ. Form a Ionic eq.

such as



At eq.



At equi



$$\text{Total conc. of } \text{Pb}^{+2} = 0.1 + s \approx 0.1$$

because 's' of Pb^{+2} is very low.

(15)

$$K_a = \frac{[Pb^{+2}][S^{2-}]}{[PbSO_4]}$$

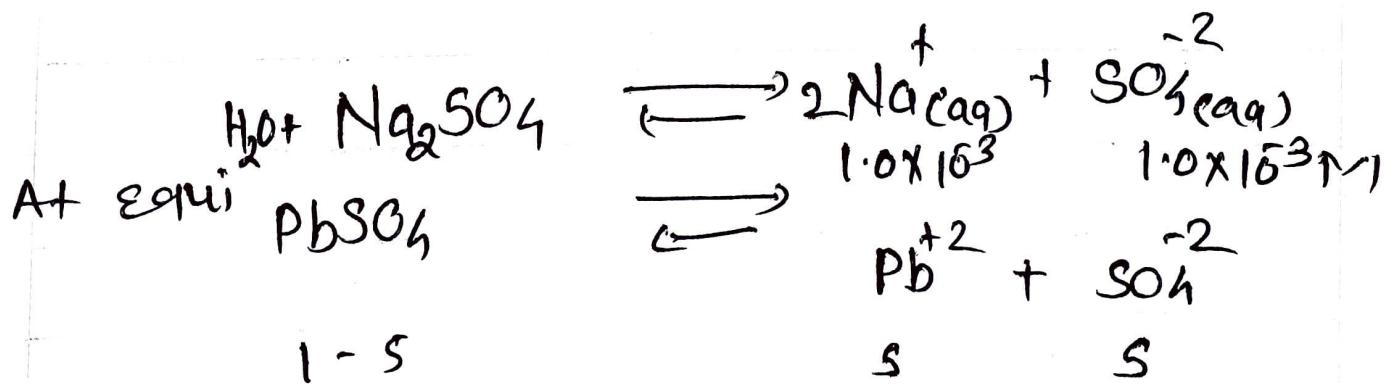
$$\therefore K_a[PbSO_4] = K_{sp} = [Pb^{+2}][S^{2-}] \\ = [0.1 M][S]$$

$$\therefore S = \frac{K_{sp}}{0.1} = \frac{1.8 \times 10^{-8} M}{0.1} \\ = 1.8 \times 10^{-7} M$$

III) in 1.0×10^{-3} Na_2SO_4 solⁿ

Na_2SO_4 is strong acid-base salt. It is completely ionized and soluble in a dilute SO_4^{2-} ($\approx 1.0 \times 10^{-3} M$)

When ~~PbSO~~ PbSO_4 dissolve in it
They form a following Ionic Eqn



$$\text{Total conc.g } [\text{SO}_4^{2-}] \text{ is } = [S + 1.0 \times 10^{-3} M] \\ \cong [1.0 \times 10^{-3} M]$$

$$\therefore g = K_a = \frac{[\text{Pb}^{+2}][\text{SO}_4^{2-}]}{[\text{PbSO}_4]}$$

(1c)

$$K_{sp} = [Pb^{+2}] [SO_4^{2-}]$$

$$= [S] [1.0 \times 10^3 M]$$

$$\therefore S = K_{sp} / 1.0 \times 10^3 M$$

$$= \frac{1.8 \times 10^{-8}}{1.0 \times 10^3}$$

$$S = 1.8 \times 10^{-5} \text{ mol/lit}$$

\therefore Thus solubility of $PbSO_4$ in 0.01M Na_2SO_4 is 1.8×10^{-5} mol/lit that is less than pure water means it is justify le Chatelier & common ions effect principle.

ExA-08 : Calculate soluble solubility of sparingly soluble salt CaF_2 in

(i) Pure water (ii) in 0.1M $CaCl_2$,

(iii) 0.1M NaF soln and justify le Chatelier principle.

Ans-08 : Consider, saturated aqueous solution of CaF_2 form a following ionic equilibrium.



At initial	1. mol/lit	0. M	0.0 M,
Stage		S	25

At equilibrium 1-S

Stage (where as 'S' is solubility of CaF_2)

(20)

(19)

$$\therefore K_a = \frac{[\text{Ca}^{+2}][\text{F}^-]^2}{[\text{CaF}_2]}$$

$$\therefore K_a[\text{CaF}_2] = K_{\text{sp}} = [\text{Ca}^{+2}][\text{F}^-]^2 \\ = [S][2S]^2$$

$$\therefore 4S^3 = K_{\text{sp}} = 1.7 \times 10^{-10} \text{ M}$$

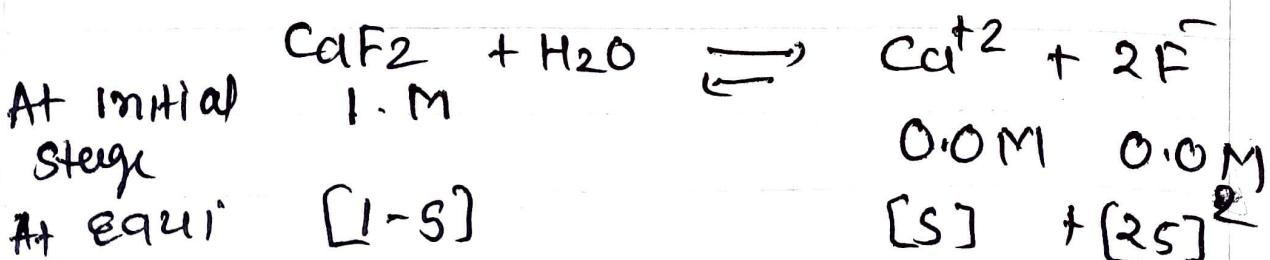
$$= (0.425 \times 10^{-10})^{1/3} \quad \therefore S^3 = \frac{1.7 \times 10^{-10}}{4} = 0.425 \times 10^{-10} \text{ M}$$

$$\therefore S = 3.5 \times 10^{-4} \text{ mol/lit}$$

Thus solubility of CaF_2 in pure water is
 3.5×10^{-4} mol/lit

* (ii) Solubility of CaF_2 in 0.1 M $\text{Ca}(\text{NO}_3)_2$ sol.
 we know that $\text{Ca}(\text{NO}_3)_2$ is strong salt so it is completely ionized and dissolve in dilute aqueous soln.

CaF_2 Saturated CaF_2 solution in 0.1 M $\text{Ca}(\text{NO}_3)_2$ forming following Ionic Eqn



(20)

$$K_a = \text{Conc. of } Ca^{+2} = 0.1 \text{ M} + s$$

$\approx 0.1 \text{ M} \because s \text{ is very small}$

$$\therefore K_a = \frac{[Ca^{+2}][2F^-]}{[CaF_2]}$$

$$\therefore K_a [CaF_2] = K_{sp} = [Ca^{+2}] [2F^-]$$

$$= [0.1] [2s]^2$$

$$\therefore 4s^2 = \frac{1.7 \times 10^{-10}}{0.1}$$

$$\therefore s^2 = \frac{1.7 \times 10^{-10}}{4 \times 0.1} = 0.425 \times 10^{-10}$$

$$\therefore s = 2.05 \times 10^{-5} \text{ M.}$$

The solubility of CaF_2 is $2.05 \times 10^{-5} \text{ M}$ in 0.1 M $Ca(CNCO)_2$ solution that is lower than pure water $[3.5 \times 10^{-4} \text{ Mol/lit}]$

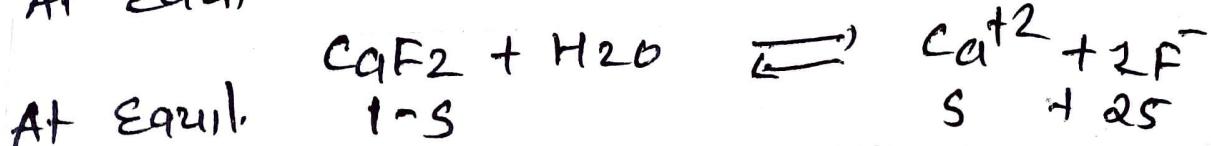
III) In 0.1 M NaF sol .

NaF is strong salt it is completely ionized and dissolved in dilute 0.1 M NaF sol.

Consider CaF_2 in Saturated solution of CaF_2 in 0.1 M NaF forming following ionic equilibrium.



At Equil.



Total conc. of $\bar{F}^- = 2S + 0.1 \approx 0.1 \text{ M}$
 [Because 'S' is very little]

$$\therefore K_a = \frac{[Ca^{+2}][2\bar{F}^-]}{[CaF_2]} = K_a[CaF_2] = Ca^{+2}$$

$$\therefore K_a[CaF_2] = K_{SP} = [Ca^{+2}]^2 [2\bar{F}^-]^2 \\ = [S] [0.1 \text{ M}]^2$$

$$\therefore S = K_{SP} / [0.1]^2 \\ = \frac{1.7 \times 10^{-8}}{(0.1)^2}$$

Solubility

$$S = 1.7 \times 10^{-8} \text{ mol/lit}$$

Thus. solubility of CaF_2 in 0.1 M NaF solution is $\underline{1.7 \times 10^{-8} \text{ M}}$ that is very lower than pure water $\underline{2.05 \times 10^{-5} \text{ M}}$. It is true that the solubility of salt decreases with presence of common ions.

Ex - 09 :- Calculate solubility of sparingly soluble salt Ag_2CrO_4 in

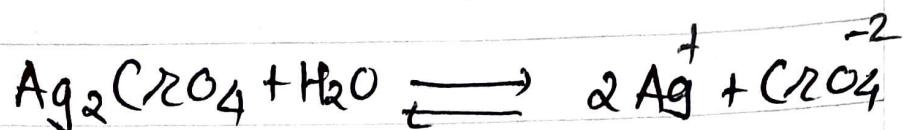
(I) Pure water

(II) 0.05 M $AgNO_3$ soln

(III) 0.05 M K_2CrO_4 soln.

$$K_{SP}[Ag_2CrO_4] = 1.99 \times 10^{-12} \text{ M}$$

Ans-10 → Consider saturated solution of Ag_2CrO_4 in pure water forming a following Ionic Equilibrium



At initial	1.	0	0.	0
Steige.				
At Equi	1 - s		s	+ s

$$\therefore K_a = \frac{[\text{Ag}^+]^2 [\text{CrO}_4^{2-}]}{[\text{Ag}_2\text{CrO}_4]}$$

$$\therefore K_a [\text{Ag}_2\text{CrO}_4] = K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ = 45^3$$

$$45^3 = 1.99 \times 10^{-12}$$

$$s^3 = 0.50 \times 10^{-12}$$

$$s = [0.50 \times 10^{-12}]^{1/3}$$

$$= 7.0 \times 10^{-5} \text{ mol/l}_1$$

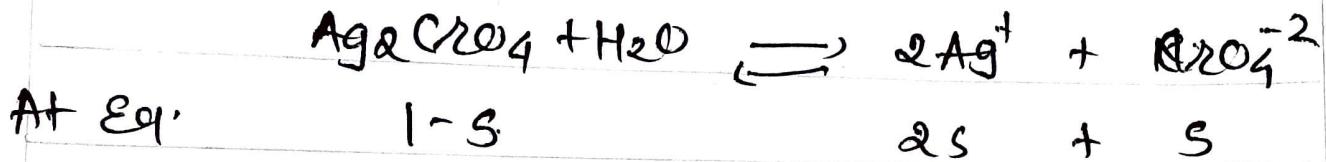
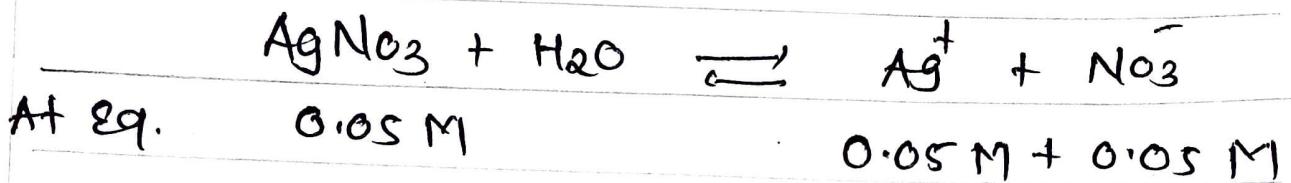
(ii) In 0.05 M AgNO_3 solution

We know that AgNO_3 is a strong salt, it is completely ionized and dissolve in dilute aqueous solⁿ.

~~Ag+~~ saturated solution of ~~AgN~~

Ag_2CrO_4 in 0.05 M AgNO_3 solⁿ, form a

such as



$$\text{Total conc. of } \text{Ag}^+ = (0.05 + 2S) \text{ M}$$

$$\approx 0.05 \text{ M}$$

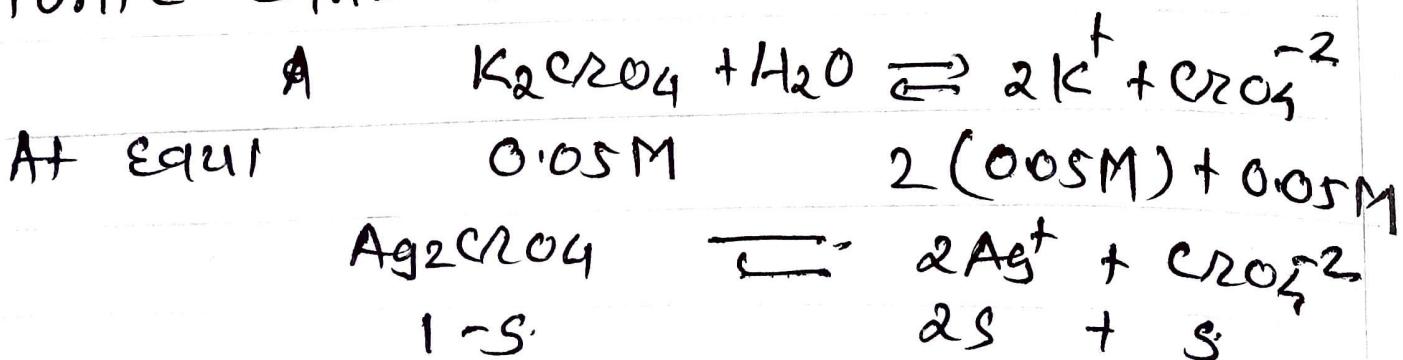
$$\therefore K_a = \frac{(2\text{Ag}^+)^2 [\text{CrO}_4^{2-}]}{[\text{Ag}_2\text{CrO}_4]}$$

$$\therefore K_a [\text{Ag}_2\text{CrO}_4] = K_{\text{sp}} = [2 \cdot 0.05] [S]$$

$$\therefore S = \frac{1.99 \times 10^{-12}}{(0.05)^2} = 0.8 \times 10^9 \text{ mole/lit}$$

(III) in 0.05 M K_2CrO_4 solⁿ.

K_2CrO_4 is strong salt. It is completely ionized and dissolve in dilute aqueous solⁿ. Consider saturated solⁿ of Ag_2CrO_4 in 0.05 M K_2CrO_4 forming following ionic equilibrium.



$$\text{Total conc. of } \text{CrO}_4^{2-} = s + 0.05 \\ = 0.05 \text{ mole/lit}$$

$$\therefore K_a = \frac{[2\text{Ag}^+]^2 [\text{CrO}_4^{2-}]}{[\text{Ag}_2\text{CrO}_4]}$$

$$\therefore K_a [\text{Ag}_2\text{CrO}_4] = K_{sp} = [2\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$\therefore K_{sp} = [2s]^2 [0.05]$$

$$\therefore 4s^2 = \frac{1.99 \times 10^{-10}}{[0.05] \times 4} = 9.95 \times 10^{-10}$$

$$s = \left[\frac{1.99 \times 10^{-10}}{4 \times 0.05} \right]^{1/2} \quad \left| \begin{array}{l} s^2 = \frac{1.99 \times 10^{-10}}{0.2} \\ \qquad \qquad \qquad = 9.95 \times 10^{-10} \end{array} \right. \\ = 1.0 \times 10^{-6}$$

Thus solubility of Ag_2CrO_4 in 0.05 M K_2CrO_4 aqueous solution is $\frac{1.0 \times 10^{-6}}{1.0 \times 10^{-6} \text{ mol/lit}}$,
that is lower than pure water