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GURUKUL

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Physical Chemistry

Ionic Equilibrium

Lecture No. - 09

By- Dr. Gopal Chaturvedi Sir
(GC Sir)

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Topics to be Covered

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- Topic ✓ Solubility (S)
- Topic ✓ Solubility product (K_{SP})

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Solubility : "Amount of substance dissolved in per L solution"

If represent as "S"

If amount is taken in terms of mole,

Unit of Solubility "M"

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If amount is taken in terms of "g",

Unit of Solubility : "g/L"

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Types of Salt (on the basis of Solubility)

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1. Soluble Salt : $S > 0.1\,M$

2. Partial Soluble Salt : $S = (0.1 \longleftrightarrow 0.01)\,M$

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3. Sparingly Soluble Salt (SSS) : $S < 0.01\,M$

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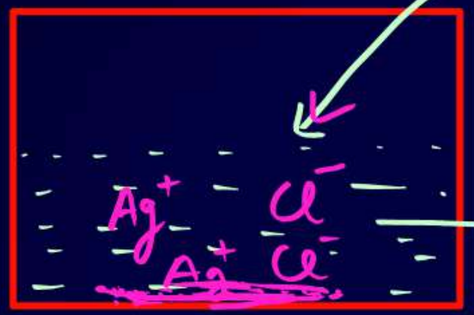
Sparingly Soluble Salt :



$K_{sp} = [Ag^+(aq)][Cl^-(aq)]$

$AgCl(s) \underset{\text{backward}}{\overset{\text{forward}}{\rightleftharpoons}} 1\,Ag^+(aq) + 1\,Cl^-(aq)$

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At equilibrium state

$\Rightarrow$ Rate of forward direction = Rate of backward direction

Precipitate : ppt

formation of ppt

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Q = Reaction Quotient = $[Ag^+(aq)][Cl^-(aq)]$

Equilibrium Constant ← K_{sp} = Solubility product.

(i) If $Q < K_{sp}$, Reaction shift to forward,

Unsaturated Solution

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(ii) If $Q = K_{sp}$, Reaction is in equilibrium state

ppt formation will start.

(iii) If $Q > K_{sp}$, Reaction shift in backward direction.

Appearance of ppt in solution.

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$$A_x B_y (s) \rightleftharpoons (x) A^{y+}_{(aq)} + (y) B^{x-}_{(aq)}$$

$$Q = [A^{y+}_{(aq)}]^{x} [B^{x-}_{(aq)}]^{y}$$

$$K_{sp}\ (A_xB_y) = [A^{y+}_{(aq)}]^{x} [B^{x-}_{(aq)}]^{y} \longrightarrow \text{Eq}^{m}\ \text{state.}$$

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Q. If 0.1 mole of A SSS is dissolved in water.

Only 40% of salt dissolved in the solution (in 1 L)

Calculate: (Provided Cation : Anion = 1 : 2]

Assuming no hydrolysis of cation & ion.

(1) [Cation]

(2) [Anion]

(3) K_{sp} of SSS

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Soln. $S = \frac{0.1 \times 40}{100}$,

Let Solubility = S

$$\textcircled{1}AB_2(s) \rightleftharpoons \textcircled{1}A^{2+}(aq) + \textcircled{2}B^{-}(aq)$$

$$[A^{2+}(aq)] = \frac{0.1 \times 40}{100}, \quad [B^{-}(aq)] = 2 \times \frac{0.1 \times 40}{100},$$

S, 2S

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$$K_{sp}(AB_2) = (A^{+2}_{(aq)})(B^{-}_{(aq)})^2$$

$$= (4\times10^{-2})(8\times10^{-2})^2$$

$$= 64\times4\times10^{-6}$$

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Relationship between Solubility and Solubility Product)

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[Assuming no hydrolysis of ion]

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

Let Solubility of $A_xB_y = S$

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$$[A^{y+}(aq)] = xS \quad , \quad [B^{x-}(aq)] = yS$$

$$K_{sp} = [A^{y+}]^x [B^{x-}(aq)]^y = (xS)^x (yS)^y = x^x y^y S^{x+y}$$

(A_xB_y)

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$$K_{sp}(A_xB_y) = x^x y^y S^{x+y} \quad M^{x+y}$$

$$S = \left(\frac{K_{sp}(A_xB_y)}{x^x y^y} \right)^{1/(x+y)}$$

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Cation : Anion

(1) 1 : 2

or

2 : 1

$$K_{sp}(AB_2) = 4S^3$$

or

$$K_{sp}(A_2B)$$

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(2) 2 : 3

or

3 : 2

$K_{sp(A_2B_3)} = 108\ S^5\ M^5$

or

$K_{sp}(A_3B_2)$

(3) 3 : 1

or

1 : 3

$K_{sp(A_3B)} = 27\ S^4\ M^4$

or

$K_{sp(AB_3)}$

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Q. $Ag_3(PO_4)_1$

Relation bet^n K_{sp} & S

3 : 1

Ans. $K_{sp} = 27 S^4$

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Q. If 10^{-4} M KCl(aq) solution is mixed with 10^{-6} M $AgNO_3$(aq) in such a way that their volume ratio is 3:1 respectively. Predict whether precipitation of AgCl will occur or not.

Given: $K_{sp}(AgCl) = 10^{-10}\ M^2$

25°C

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Soln.

$$KCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

V_1 : 10^{-4} M ; V_2 : 10^{-6} M

$V_f = V_1 + V_2$ ⟶ $[Ag^+(aq)] = \frac{10^{-6} \times V_2}{V_1 + V_2}$, $[Cl^-(aq)] = \frac{V_1 \times 10^{-4}}{V_1 + V_2}$

$= 10^{-6} \times \frac{1}{4}$ $= \frac{3}{4} \times 10^{-4}$

$\frac{V_1}{V_2} = \frac{3}{1}$

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$AgCl$

1 : 1

$$Q = [Ag^+_{(aq)}][Cl^-_{(aq)}] = \frac{1}{4} \times 10^{-6} \times \frac{3}{4} \times 10^{-4}$$

$$= 10^{-10} \times \frac{3}{16} < 1 \times 10^{-10}$$

ppt will not occur

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Calculation of Solubility in presence of Common ion:

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Q. Calculate solubility of AgCl in 0.1M $AgNO_3(aq)$ solution at 25°C. Given $K_{sp(AgCl)} = 10^{-10}\ M^2$

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Sol^n.

$AgNO_3(aq)$

0.1M

Let Solubility of AgCl in 0.1M $AgNO_3$ = x

$$AgNO_3(aq) \longrightarrow \underset{0.1M}{Ag^+(aq)} + \underset{0.1M}{NO_3^-(aq)}$$

$$AgCl(s) \rightleftharpoons \underset{(0.1+x)}{Ag^+(aq)} + \underset{x}{Cl^-(aq)}$$

Due to pr of C.I of Ag^+, Solubility of AgCl ↓

$$K_{sp(AgCl)} = [Ag^+_{(aq)}]_T [Cl^-_{(aq)}] = (0.1+x)x$$

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$$K_{sp(AgCl)} = 10^{-10} = (0.1+x)x$$

Solubility of AgCl, $K_{sp} = S^2$, $S = 10^{-5}$
in water

10^{-10}

$x < S$ due to C.I. effect.

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$\therefore 0.1 + x \simeq 0.1$

$10^{-10} = (0.1)x$

$x = 10^{-9}$

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Calculation of Solubility of SSS in presence of other SSS

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Simultaneous Solubility

$AgCl(s) \rightleftharpoons \underset{(x'+y')}{Ag^+(aq)} + \underset{x'}{Cl^-(aq)}$

$AgBr(s) \rightleftharpoons \underset{(x'+y')}{Ag^+(aq)} + \underset{y'}{Br^-(aq)}$

AgCl & AgBr

SSS ← → SSS

$K_{sp(AgCl)}$ $K_{sp(AgBr)}$

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Let Solubility of AgCl in pr. of AgBr = x'

Solubility of AgBr in pr. of AgCl = y'

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$$\frac{K_{sp(AgCl)}}{K_{sp(AgBr)}} = \frac{[Ag^+(aq)]_T [Cl^-(aq)]}{[Ag^+(aq)]_T [Br^-(aq)]} ;$$

$$\frac{K_{sp(AgCl)}}{K_{sp(AgBr)}} = \frac{[Cl^-(aq)]}{[Br^-(aq)]} = \frac{x'}{y'} \quad \text{—— (1)}$$

$$K_{sp(AgCl)} = [Ag^+(aq)]_T [Cl^-(aq)] = (x'+y')\,x' \quad \text{—— (2)}$$

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$$K_{sp(AgBr)} = [Ag^+(aq)]_T [Br^-(aq)] = (x'+y')\,y' \quad \text{—— (3)}$$

Eqn (2) + Eqn (3), we get $K_{sp(AgCl)} + K_{AgBr} = (x'+y')^2$ —— (4)

$$x'+y' = \sqrt{K_{sp(AgCl)} + K_{sp(AgBr)}}$$

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Calculation of Solubility of SSS in presence of hydrolysis:

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e.g. Solubility of AgCN at 25°C

Given: $K_{sp(AgCN)}$, $P^H > 7$ (Basic)

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$$AgCN(s) \rightleftharpoons \underset{x}{Ag^+(aq)} + \underset{(x-y)}{CN^-(aq)}$$

(K_{HCN})

$$\underset{(x-y)}{CN^-(aq)} + H_2O(l) \rightleftharpoons HCN(aq) + \underset{y}{OH^-(aq)}, \quad K_h = \frac{K_w}{K_{HCN}}$$

$\therefore$ Solubility of AgCN $\uparrow$ y y

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Let solubility of AgCN in basic medium

$= x$

$$K_{sp(AgCN)} = x(x-y) \quad \text{——①}$$

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$$\frac{K_w}{K_{HCN}} = \frac{[HCN)(OH^-)}{[CN^-)} = \frac{y \times y}{x-y} \quad \text{——②}$$

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In presence of Acidic medium

$p^H < 7$

$$AgCN(s) \rightleftharpoons \underset{x'}{Ag^+(aq)} + \underset{x'-y'}{CN^-(aq)}, \quad K_{sp} = (x'-y')x' \quad -①$$

$$\underset{(x'-y')}{①\,CN^-(aq)} + \underset{y'}{H^+(aq)} \rightleftharpoons \underset{y'}{HCN(aq)}, \quad \frac{1}{K_{HCN}} = \frac{[HCN]}{[CN^-][H^+]} = \frac{y'}{(x'-y')[H^+]} \quad -②$$

$$\therefore \frac{1}{K_{HCN}} >>> K_{sp},$$

$$AgCN(s) + H^+(aq) \rightleftharpoons \underset{x'}{Ag^+(aq)} + \underset{y'}{HCN(aq)}, \quad \frac{K_{sp}}{K_{HCN}} = \frac{[Ag^+][HCN]}{[H^+]}$$

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Solubility of SSS in Complex formation :-

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e.g. Solubility of AgCl in 0.1 M NH_3

Given:

$K_{f\,[Ag(NH_3)_2]^+}$ = Complex formation Constant or Stability Constant

K_{sp}

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$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$K_{eq} \uparrow$, $\downarrow \Delta G^\circ = -RT \ln K$, Stability $\uparrow$

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K_d or $K_{inst.}$ = Complex dissociation Constant or Instability Constant.

$$= \left(\frac{1}{K_f}\right)$$

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, $K_{sp(AgCl)}$

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$Ag^+(aq) + NH_3 \rightleftharpoons Ag(NH_3)^+$, K_1

$(Ag(NH_3)^+) + NH_3 \rightleftharpoons (Ag(NH_3)_2^+)$, K_2

→ Net reaction

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

$K_f = K_1 \times K_2$

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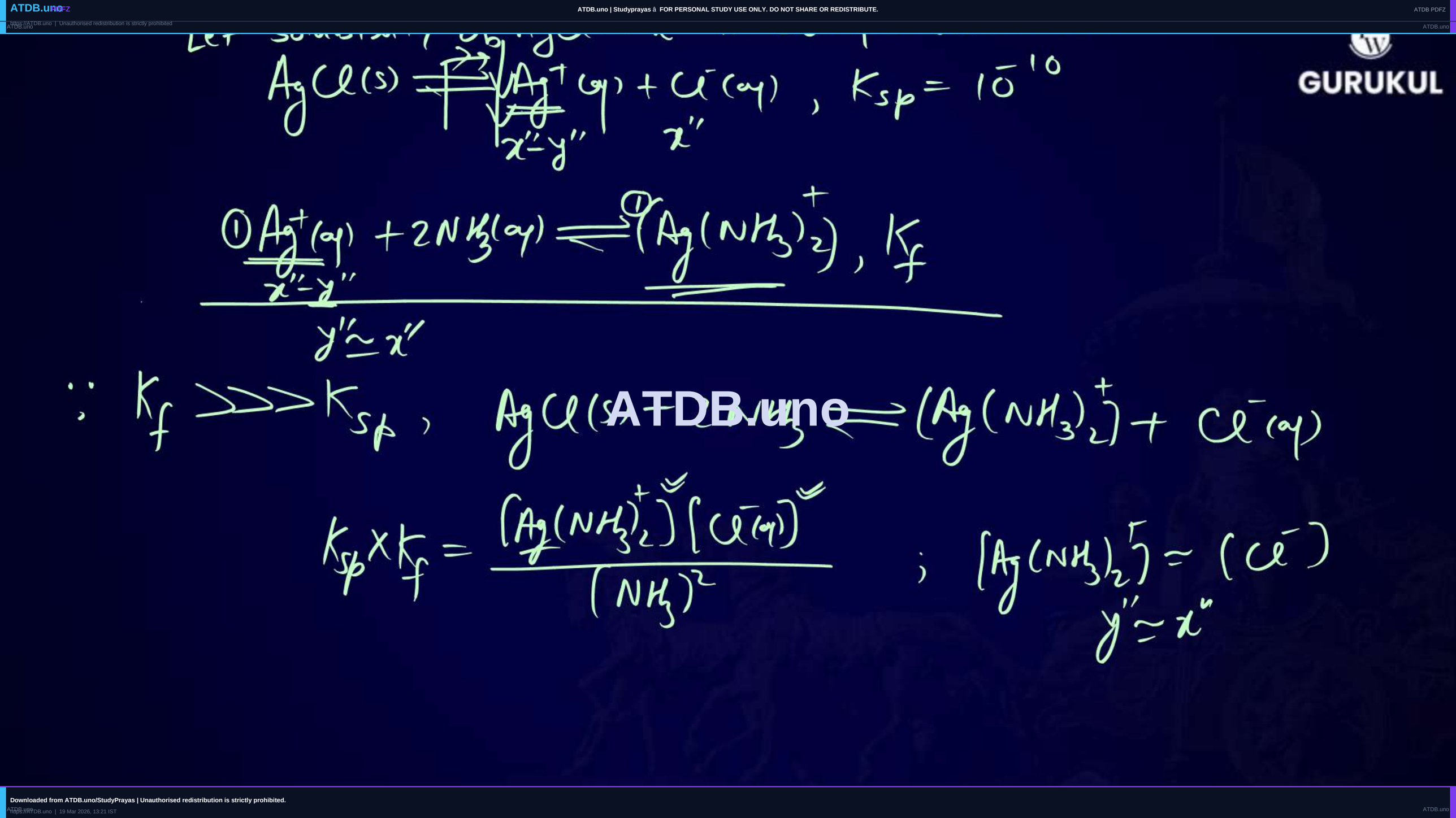

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Selective precipitation :-

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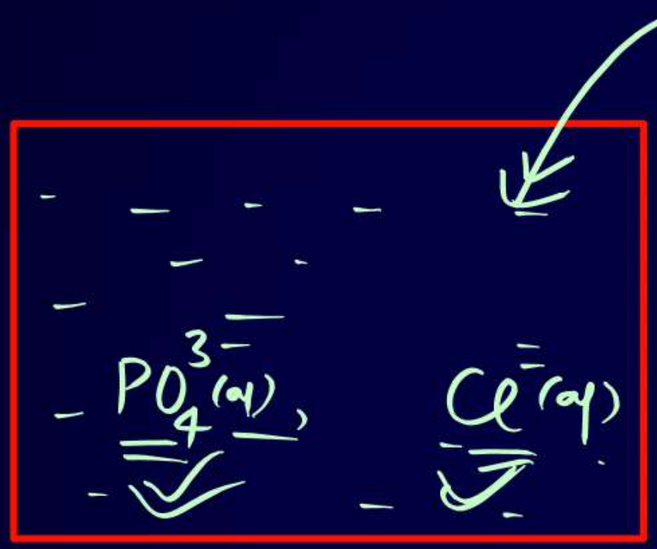

$AgNO_3(aq)$

$K_{sp(Ag_3PO_4)} = [Ag^+(aq)]^3_{req} [PO_4^{3-}(aq)]$

$K_{sp(AgCl)} = [Ag^+(aq)]_{req} [Cl^-(aq)]$

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$$(Ag^+(aq))_{req\ for\ Ag_3PO_4} = \left[\frac{K_{sp(Ag_3PO_4)}}{(PO_4^{3-}(aq))}\right]^{1/3}$$

$$(Ag^+(aq))_{req\ for\ AgCl} = \frac{K_{sp(AgCl)}}{[Cl^-(aq)]}$$

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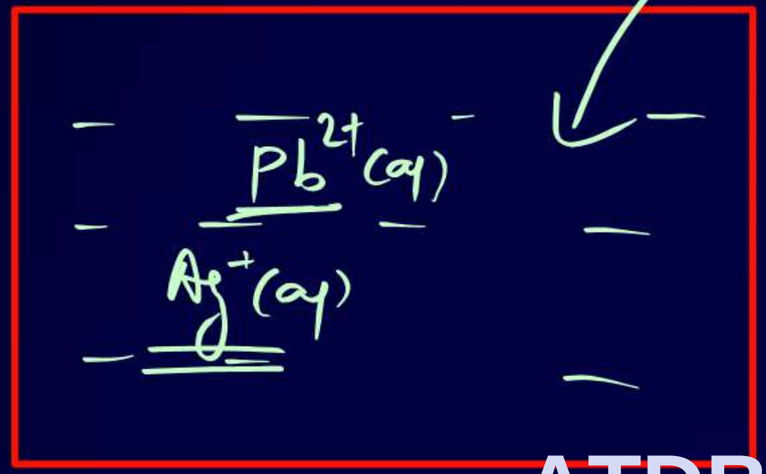

CrO_4^{2-}

$K_{sp}(Ag_2CrO_4) = [Ag^+]^2[CrO_4^{2-}]$

$K_{sp}(PbCrO_4) = [Pb^{2+}][CrO_4^{2-}]$

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$$[CrO_4^{2-}]_{req.\ Ag_2CrO_4} = \frac{K_{sp}(Ag_2CrO_4)}{[Ag^+]^2}$$

$$[CrO_4^{2-}]_{req.\ for\ PbCrO_4} = \frac{K_{sp}(PbCrO_4)}{[Pb^{2+}]}$$

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Question

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#Q. The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18}. Which salt is more soluble? Explain your answer fully.

HW

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Ans. (QX_2 is more soluble)

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Question

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#Q. The solubility of $PbSO_4$ water is 0.038 g/L. Calculate the solubility product constant of $PbSO_4$.

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Ans. 1.6×10^{-8}

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Question

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#Q. Calculate the solubility of $Mg(OH)_2$ in water. $K_{sp} = 1.2 \times 10^{-11}$.

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Ans. 1.4×10^{-4}

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Question

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#Q. How many mol CuI ($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution?

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Ans. $[Cu^+] = 5 \times 10^{-11}\,M$

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Question

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#Q. A solution of saturated CaF_2 is found to contain 4.1×10^{-4} M fluoride ion. Calculate the K_{sp} of CaF_2. Neglect hydrolysis.

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Ans. 3.4×10^{-11}

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Question

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#Q. The solubility of ML_2 (formula weight, 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate the solubility product constant for ML_2.

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Ans. 2.6×10^{-16}

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Question

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#Q. What is the solubility (in mol/L) of $Fe(OH)_3$ in a solution of pH = 8.0? [K_{sp} for $Fe(OH)_3 = 1.0 \times 10^{-36}$]

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Ans. 1.0×10^{-18} M

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Question

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#Q. Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3, $[K_{sp} = 1.1 \times 10^{-23}]$

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Ans. 1.0×10^{-5} mol/lit

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Question

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#Q. Determine the solubility of AgCl in 0.1 M $BaCl_2$. [K_{sp} for AgCl = 1×10^{-10}]

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Ans. 5×10^{-10} M

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Question

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#Q. A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is [$K_{sp} = 1.2 \times 10^{-11}$]

(a) 10^{-5} mol/L

(b) 10^{-3} mol/L ?

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Ans. (a) no precipitation will occur,
(b) a precipitate will form

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Question

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#Q. Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25°, which is 90% dissociated.

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Ans. 1.6×10^{-3}

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Question

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#Q. Calculate solubility of AgCN ($K_{sp} = 4 \times 10^{-16}$) in a buffer solution of PH = 3.
$[K_{a(HCN)} = 4 \times 10^{-10}]$

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Ans. 3.16×10^{-5}

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Question

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#Q. Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 1.1×10^{-12}, K_{sp}(AgBr) = 5×10^{-13}

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Ans. 4×10^{-7} mol/L AgBr, 9×10^{-7} mol/L AgSCN

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Question

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#Q. Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2

$K_{sp}(MgF_2) = 9.5 \times 10^{-9}$, $K_{sp}(SrF_2) = 4 \times 10^{-9}$

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Ans. $[F^-] = 3 \times 10^{-3}M$

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Question

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#Q. Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mol AgC in 100 L solution.
$[K_f(AgCl_2^-) = 3 \times 10^5, K_{sp} = (AgCl) = 1\times10^{-10}]$

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Ans. 19.5 kg

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Question

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#Q. A recent investigation of the complexation of SCN^- with Fe^{3+} represented by constant K_1, K_2 and K_3 as 130, 16 and 1.0 respectively. What is the overall formation constant of $Fe(SCN)_3$ from its component ions, and what is the dissociation constant of $Fe(SCN)_3$ into its simplest ions on the basis of these data?

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Ans. $K_d = 1/K_f = 4.8 \times 10^{-4}$

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Question

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#Q. How much AgBr could dissolve in 1.0 L of 0.40 M NH_3? Assume that $Ag(NH_3)_2^+$ is the only complex formed.
$[K_f(Ag(NH_3)_2^+) = 1 \times 10^8 ; K_{sp}\ (AgBr) = 5 \times 10^{-13}]$

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Ans. 2.8×10^{-3} M

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