

ARJUNA

JEE AIR 2024

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Physical Chemistry

Ionic Equilibrium



Lecture No. – 09

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Topics to be Covered

Topic

✓ Solubility (S)

Topic✓ Solubility product (K_{sp})

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

It represent as "S"

If amount is taken in terms of mole,

Unit of Solubility "M"

If amount is taken in terms of "g",

Unit of Solubility : "g/L"

Types of salt (on the basis of Solubility)

1. Soluble Salt :

$$S > 0.1M$$

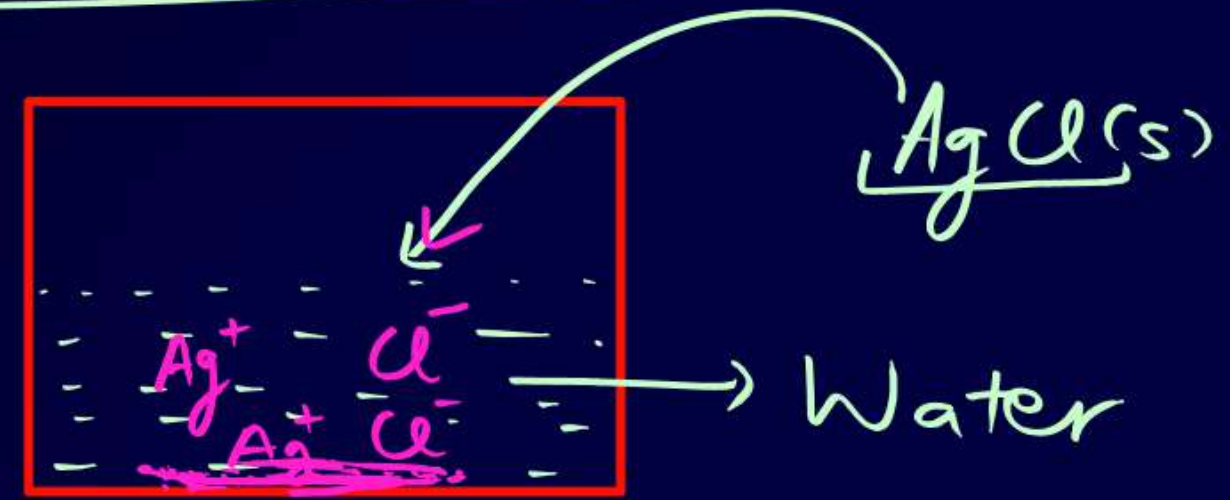
2. Partial Soluble Salt :

$$S = (0.1 \leftrightarrow 0.01)M$$

3. Sparingly Soluble Salt (SSS) :

$$S < 0.01M$$

Sparingly Soluble Salt :



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



At equilibrium state

≡ Rate of forward direction = Rate of backward direction

Precipitate : PPT

formation of ppt



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$$Q = \text{Reaction Quotient} = \underbrace{[Ag^+(aq)] [Cl^-(aq)]}$$

Equilibrium Constant $\leftarrow K_{sp} = \text{Solubility product.}$

(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



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

$$K_{sp} = [A^{y+}(aq)]^x [B^{x-}(aq)]^y \xrightarrow{\text{Eqm state.}} \\ (A_x B_y)$$



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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]

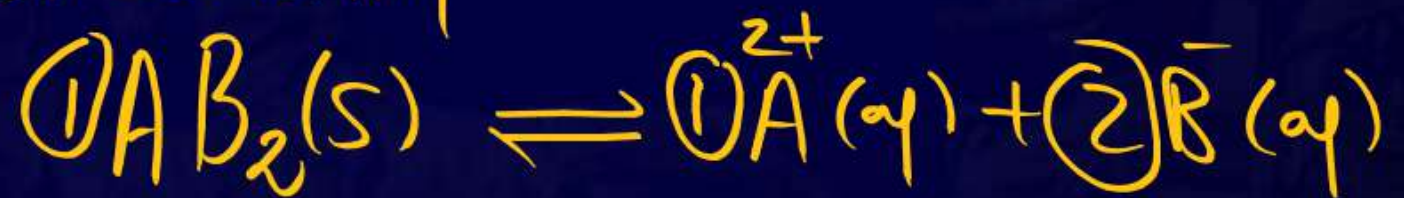
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(2) [Anion]

(3) K_{sp} of SSS

Solⁿ $S = \frac{0.1 \times 40}{100}$

Let Solubility = S



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



$$\begin{aligned}K_{sp}(AB_2) &= (A^{+2})(B^{-1})^2 \\&= (4 \times 10^{-2})(8 \times 10^{-2})^2 \\&= 64 \times 4 \times 10^{-6}\end{aligned}$$

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Relationship between Solubility and Solubility Product)



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[Assuming no hydrolysis of ion]



Let solubility of $A_x B_y = S$

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

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

($A_x B_y$)



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$$\underline{K_{sp}}(A_x B_y) = x^x y^y \underline{= S^{x+y}} M^{x+y}$$

$$S = \left[\frac{K_{sp}(A_x B_y)}{x^x y^y} \right]^{\frac{1}{x+y}}$$

(1) Cation : Anion
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

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

or

$$K_{sp}(A_3B_2)$$

(3) 3 : 1

or

1 : 3

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

or

$$K_{sp}(AB_3)$$



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Relation betⁿ K_{sp} & S

Ans.

3:1

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

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Q. If 10^{-4} M KCl(aq) solution is mixed with 10^{-6} M $\text{AgNO}_3(\text{aq})$ in such a way that their volume ratio is $\boxed{3:1}$ respectively.

Predict whether precipitation of AgCl will occur or not.

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

25°C

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Solⁿ.



$$V_f = V_1 + V_2 \longrightarrow \boxed{[\text{Ag}^+(\text{aq})] = \frac{10^{-6} \times V_2}{V_1 + V_2}, [\text{Cl}^-(\text{aq})] = \frac{V_1 \times 10^{-4}}{V_1 + V_2}} \quad , \quad \frac{V_1}{V_2} = \frac{3}{1}$$

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



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1:1

$$Q = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})] = \frac{1}{4} \times 10^{-6} \times \frac{3}{4} \times 10^{-9} \\ = 10^{-10} \times \frac{3}{16} < 1 \times 10^{-10}$$

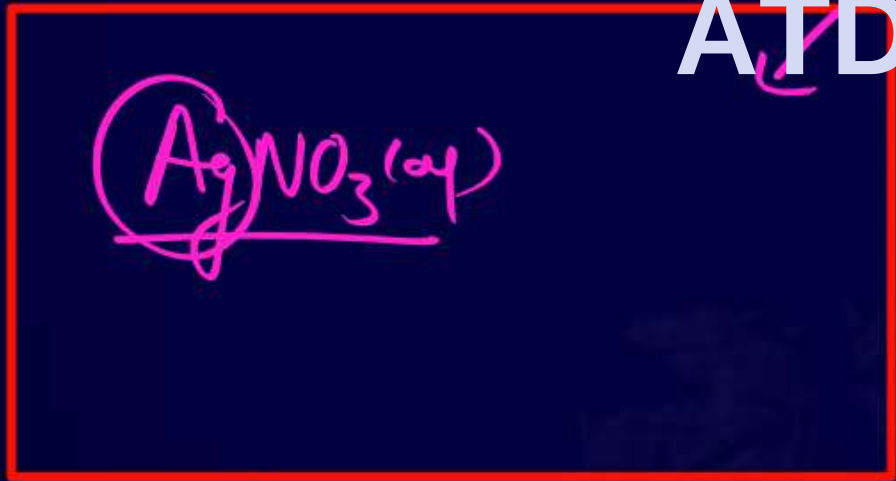
ppt will not occur

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Calculation of Solubility in presence of Common ion: GURUKUL

Q. Calculate solubility of AgCl in ~~0.1M~~ AgNO₃(aq) solution at 25°C. Given $K_{sp}(\text{AgCl}) = 10^{-10} \text{ M}^2$

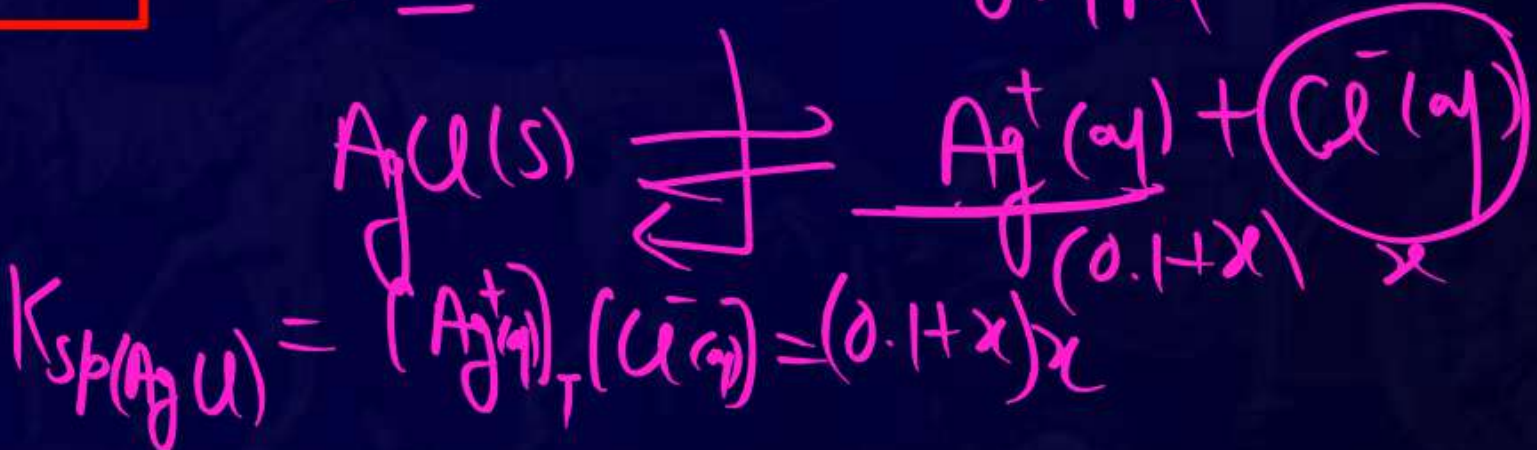
Solⁿ.



Let solubility of AgCl in 0.1M AgNO₃ = x



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





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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
 $\downarrow$
 10^{-10}

$$x < S$$

due to C.I. effect.

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$$0.1+x \simeq 0.1$$

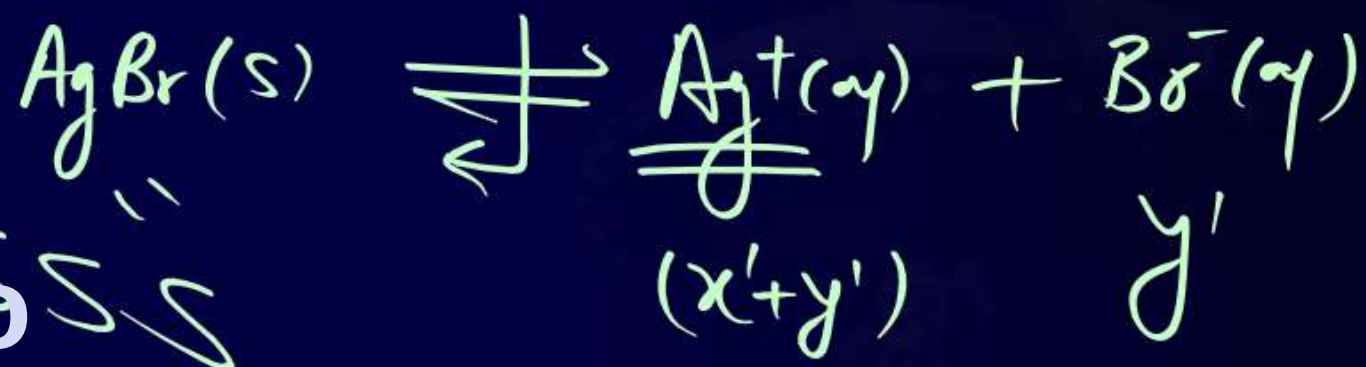
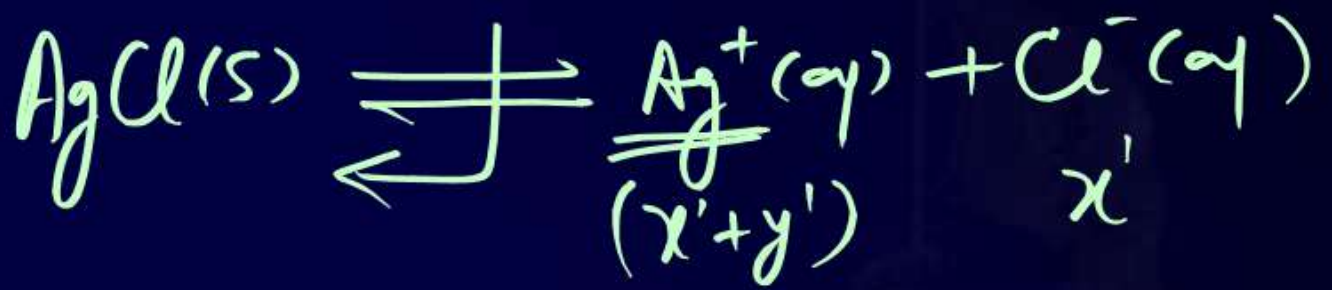
$$10^{-10} = (0.1)x$$

$$x = 10^{-9}$$

Calculation of Solubility of SSS in presence of other SSS



Simultaneous Solubility



SSS

$K_{sp}(\text{AgCl})$

$K_{sp}(\text{AgBr})$

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

Solubility of AgBr in pr. of AgCl = y'



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

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

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

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

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

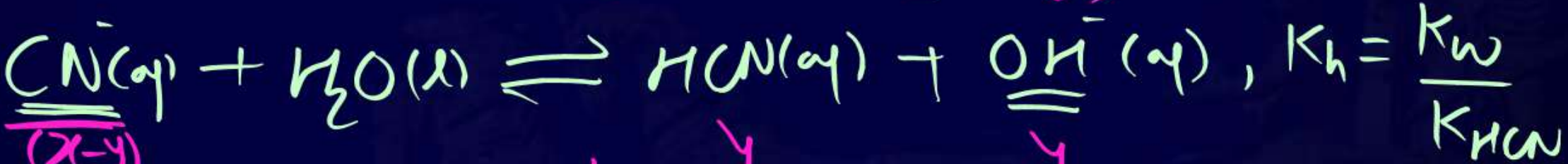
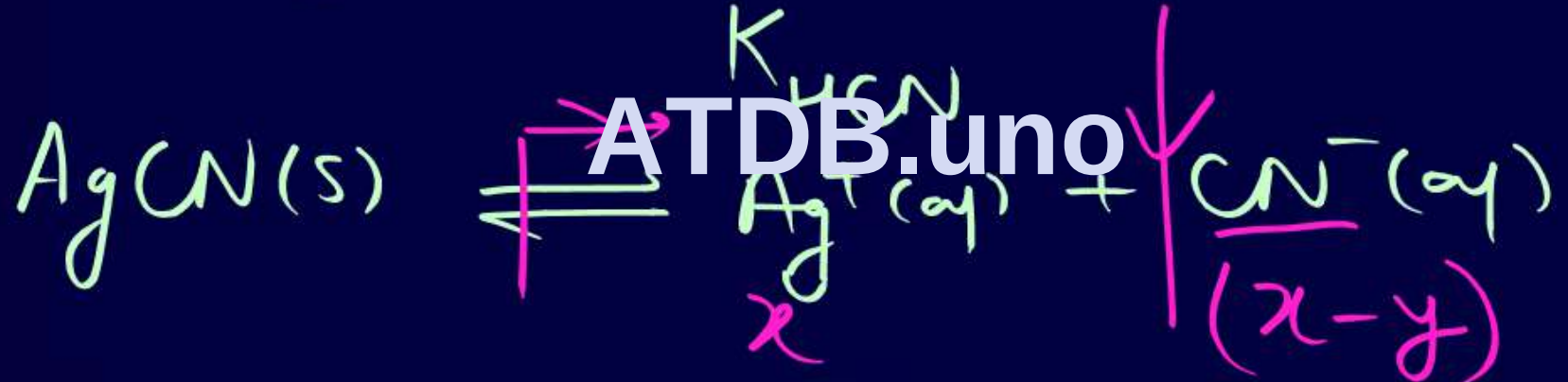
$$x' + y' = \sqrt{K_{sp}(AgCl) + K_{sp}(AgBr)}$$

Calculation of solubility of SSS in presence of hydrolysis: GURUKUL

e.g. Solubility of AgCN at 25°C

Given:

$K_{sp}(\text{AgCN})$, $p^H > 7$ (Basic)



∴ Solubility of AgCN ↑

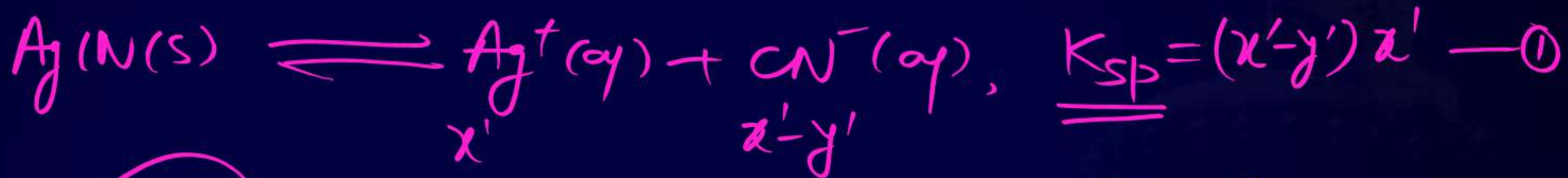
Let solubility of AgCN in basic medium
 $= x$

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

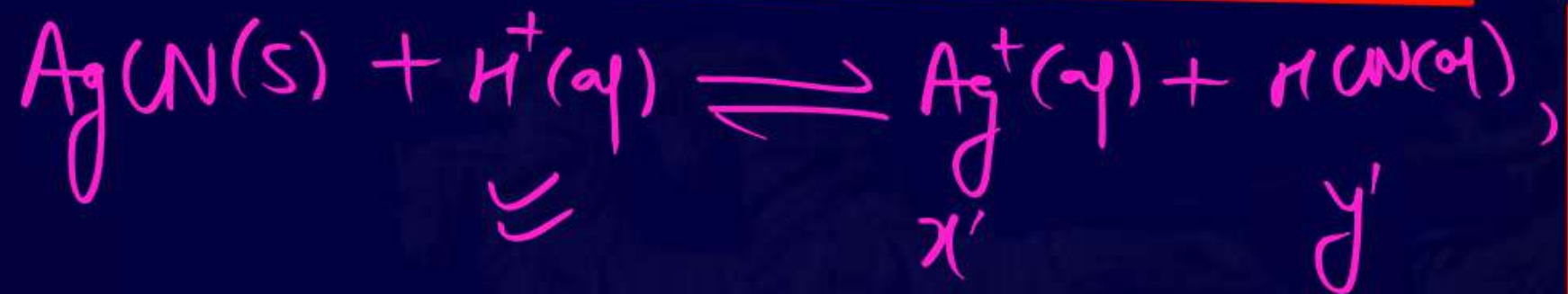
$$\frac{K_w}{K_{\text{HCN}}} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{y \times y}{x-y} \quad \text{--- ②}$$



In presence of Acidic medium
 $p^H < 7$



$\therefore \frac{1}{K_{HCN}} \gg K_{sp}$



$$\frac{K_{sp}}{K_{HCN}} = \frac{[Ag^+][HCN]}{[H^+]}$$



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Solubility of SSS in Complex formation :-

e.g. Solubility of AgCl in 0.1M NH₃

Given:

$K_f [Ag(NH_3)_2]^+$ = Complex formation Constant
or
Stability Constant

K_{sp}

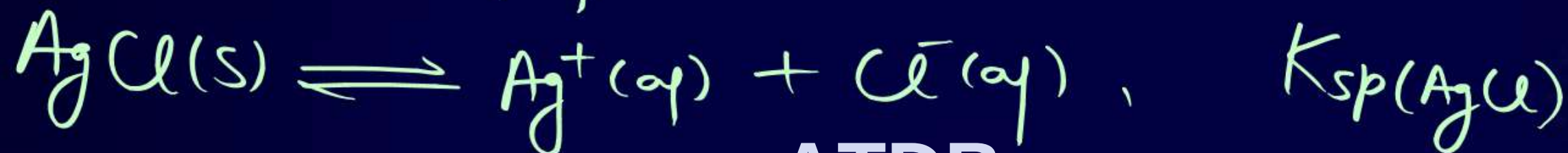


$K_{eq} \uparrow, \Delta G^\circ = -RT \ln K, \text{ Stability } \uparrow$

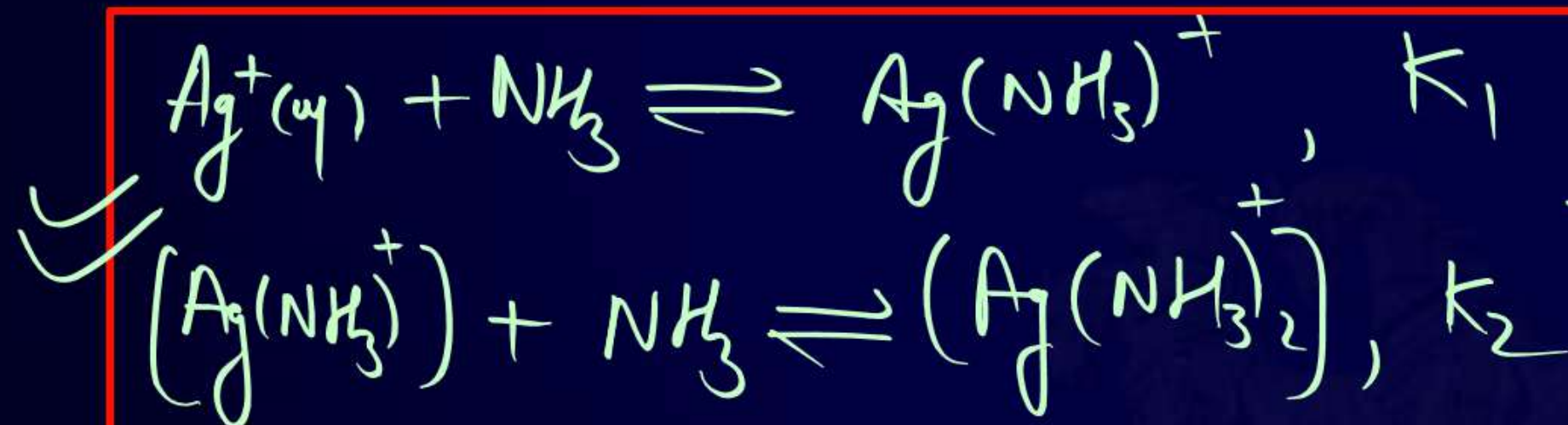


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$\downarrow K_d$
 or
 $K_{inst.}$ = Complex dissociation Constant or Instability Constant.
 $= \left(\frac{1}{K_f} \right)$



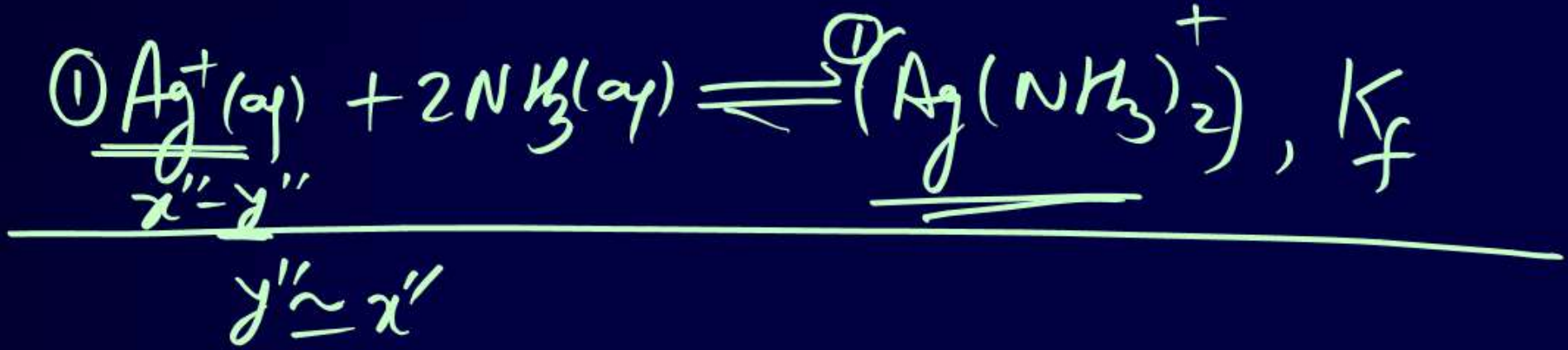
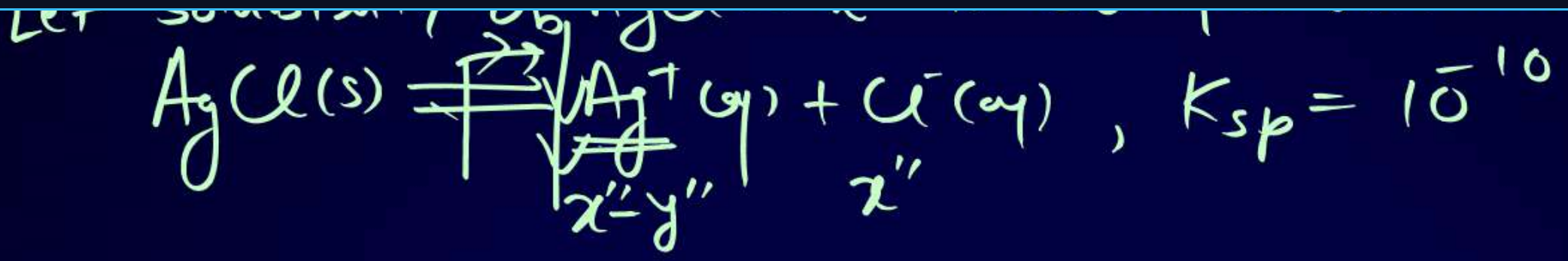
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→ Net
reaction



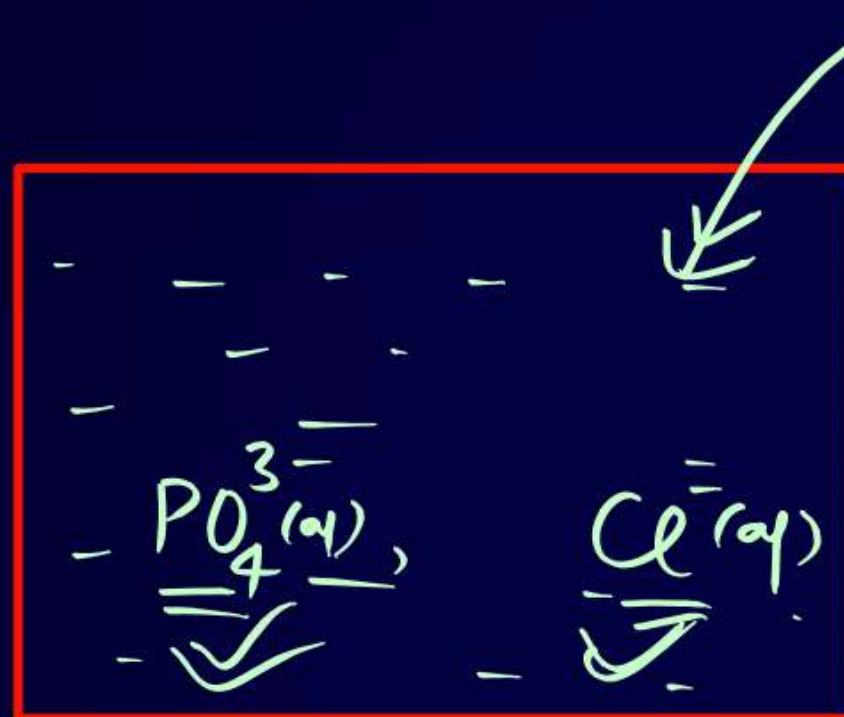
$$K_f = K_1 \times K_2$$



$$K_{sp} \times K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{(\text{NH}_3)^2}; [\text{Ag}(\text{NH}_3)_2^+] \approx (\text{Cl}^-)$$

$y'' \approx x''$

Selective precipitation :-



$$K_{sp}(\text{Ag}_3\text{PO}_4) = [\text{Ag}^+(\text{aq})]_{\text{req}}^3 [\text{PO}_4^{3-}(\text{aq})]$$

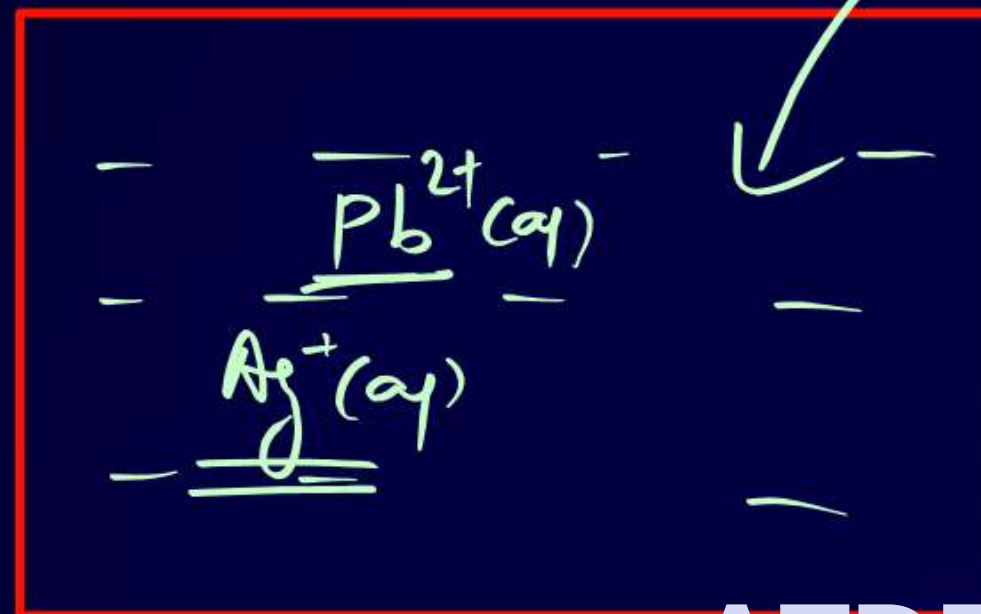
$$K_{sp}(\text{AgCl}) = [\text{Ag}^+(\text{aq})]_{\text{req}} [\text{Cl}^-(\text{aq})]$$

$$[\text{Ag}^+(\text{aq})]_{\text{req}} = \left[\frac{K_{sp}(\text{Ag}_3\text{PO}_4)}{[\text{PO}_4^{3-}(\text{aq})]} \right]^{1/3}$$

for Ag_3PO_4

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

for AgCl



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

$$K_{sp}(\text{PbCrO}_4) = [\text{Pb}^{2+}] [\text{CrO}_4^{2-}]$$

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$$[\text{CrO}_4^{2-}]_{\text{req.}} = \frac{K_{sp}(\text{Ag}_2\text{CrO}_4)}{[\text{Ag}^+]^2}$$

Ag_2CrO_4

$$[\text{CrO}_4^{2-}]_{\text{req.}} = \frac{K_{sp}(\text{PbCrO}_4)}{[\text{Pb}^{2+}]}$$

for PbCrO_4

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. (QX₂ is more soluble)



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Question



GURUKUL

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

HW

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Ans. 1.6×10^{-8}



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Question



GURUKUL

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

HW

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Ans. 1.4×10^{-4}



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Question



GURUKUL

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

HW

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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.

HW

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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 .

HW

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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 $\text{Fe}(\text{OH})_3$ in a solution of $\text{pH} = 8.0$? [K_{sp} for $\text{Fe}(\text{OH})_3 = 1.0 \times 10^{-36}$]

HW

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Ans. $1.0 \times 10^{-18} \text{ M}$



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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 , $[K_{sp} = 1.1 \times 10^{-23}]$

HW

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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 BaCl₂. [K_{sp} for AgCl = 1×10^{-10}]

HW

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Ans. 5×10^{-10} M



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Question

**GURUKUL**

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

- (a) 10^{-5} mol/L
- (b) $10^{-3} \text{ mol/L} ?$

HW

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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 ($K_{\text{sp}} = 1.4 \times 10^{-8}$) in water at 25° , which is 90% dissociated.

HW

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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.
[$K_{a(\text{HCN})} = 4 \times 10^{-10}$]

HW

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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}

HW

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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

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

HW

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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 AgCl in 100 L solution.

$$[K_f(\text{AgCl}_2^-) = 3 \times 10^5, K_{sp}(\text{AgCl}) = 1 \times 10^{-10}]$$

HW

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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 $\text{Fe}(\text{SCN})_3$ from its component ions, and what is the dissociation constant of $\text{Fe}(\text{SCN})_3$ into its simplest ions on the basis of these data?

HW

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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 $\text{Ag}(\text{NH}_3)_2^+$ is the only complex formed.
[$K_f(\text{Ag}(\text{NH}_3)_2^+) = 1 \times 10^8$; $K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$]

HW

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Ans. $2.8 \times 10^{-3} \text{ M}$



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Thank *You* ATDB.uno